Protonation of the Trimethylated Pyrichrominium Ion

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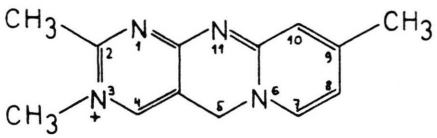
Spectroscopic manifestations of protonation of the trimethylated pyrichrominium ion studied previously experimentally [1] are investigated using a semiempirical INDO/S CI method. Singlet and triplet energy levels of the free ion and several protonated species are calculated, and transition energies and oscillator strengths are compared with experimental spectra. Calculated charge densities on nitrogen atoms are correlated with experimental pK_a values for the ground and lowest excited singlet and triplet states. The possibility of the proton transfer reaction (phototautomerization) in the lowest excited singlet state of monoprotonated species is discussed on the basis of INDO/S CI calculations, fluorescence and absorption spectroscopy.

Introduction

The photophysical properties and the acid-base equilibria in the ground and lowest excited singlet and triplet states of the 2,3,9-trimethyl-5H-pyrido-[1,2-a]pyrimido[4,5-d]pyrimidinium ion (the trimethylated pyrichrominium ion):



have been investigated experimentally [1]. The radiative and radiationless processes have been characterized by means of a lifetime-quantum yield analysis. The pK_a values for the ground and lowest excited singlet and triplet states have been determined using the Förster cycle.

In this paper we discuss results of theoretical calculations concerning protonation of the trimethylated pyrichrominium ion. The properties of the free ion and several protonated species are investigated using a semiempirical INDO/S CI method. Within this model we have tried to correlate the observed absorption and emission spectra and changes in the pK_a values with the theoretical results, and then to distinguish between the different protonation sites in the trimethylated pyrichrominium ion. Therefore we have calculated the singlet and triplet energy levels, the atomic charge densities in the ground and excited states, the transition energies, and the oscillator strengths for the free ion and its assumed protonated forms. Finally, on the basis of above mentioned calculations, and absorption and emission spectroscopy the possibility of the phototautomerization in the lowest excited singlet state of monoprotonated form is discussed.

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Experimental and Computational Details

2,3,9-trimethyl-5h-pyrido[1,2-a]pyrimido[4,5-d]pyrimidinium perchlorate and its conjugated acid form have been synthesized by Zoltewicz et al. [2]. The purification of solvents and preparation of samples have been performed as in [1]. UV-visible absorption spectra were recorded using Specord UV-VIS spectrophotometer (Zeiss, GDR). The absorption spectra have been resolved into separate individual band using procedure described earlier [3].

Electronic properties have been calculated using the spectroscopically parameterized semiempirical INDO/S CI method [4]. Bond lengths and valence angles for the free ion have been taken from the crystallographic study [5]. The calculations for the various protonated species have been performed with a proton placed at the assumed site of protonation (on the CNC angle bisector, with the NH bond length assumed to be 1.04 Å [6]). Excited state wavefunctions have been constructed from the ground state orbitals with about 80 and 200 singly excited configurations included in each configuration interaction calculation for the singlet and triplet

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states, respectively. Electronic dipole transition integrals have been calculated in the dipole length formalism. The atomic charge densities in the excited states have been calculated taking into account all configuration interaction terms.

Results and Discussion

Acid-base equilibria, atomic charge densities

The trimethylated pyrichrominium ion (A^+) subject to a sulfuric acid-water mixture undergoes the proton transfer reactions

$$A^+ + H_3O^+ \rightleftharpoons HA^{+2} + H_2O \qquad (1)$$

and

$$HA^{+2} + H_3O^+ \rightleftharpoons H_2A^{+3} + H_2O\,, \qquad (2)$$

which are characterized by values of the equilibrium constants K_a^I and K_a^{II}, respectively. The pK_a values for the ground and lowest excited singlet and triplet states have been determined in the previous study [1].

The use of atomic charge densities as a static index for a proton transfer reaction has been well established [7, 8] and, therefore, to distinguish between the different protonation sites in the free ion we have calculated the atomic charge densities in the ground and lowest excited singlet and triplet states. The results are shown in Figure 1. It is apparent from this figure that among the four heteroatoms of the free ion only two nitrogen atoms, designated N-1 and N-11, are the most probable sites of protonation. Although all three nitrogen atoms, which can be considered as protonation sites, have a net basic character in the ground and excited states, an excess of negative charge on the nitrogen atom N-6 is small, comparable to that on the carbon atoms. The N-11 atom is predicted to be the most basic heteroatom in the ground state. It is not possible to distinguish with confidence between the N-1 and N-11 atoms solely on the basis of the atomic charge densities. These data, however, along with changes in the absorption spectrum upon protonation (see below), the values of the pK_a constants for the ground and excited states obtained previously [1] as well as results of NMR study [2] strongly indicate that the N-11 atom is the site of protonation in the ground state of the free ion. The N-11 atom is predicted to loose negative charge in the lowest excited singlet and triplet states because of the large changes in the charge densities with excitation. This change in a net atomic charge on the N-11 atom is in a qualitative agreement with changes in the pK_a values with excitation, ΔpK_a^I(singlet) = − 8.3 and ΔpK_a^I(triplet) = − 6.2 [1]. As a result, the N-1 atom is predicted to be the most basic heteroatom and, therefore, the most probable site of protonation in both the lowest excited states of the free ion. This together with the observed dual, strongly temperature dependent fluorescence of the protonoated species [1] suggests that the proton transfer reaction (phototautomerization) can occur in the lowest excited singlet state.

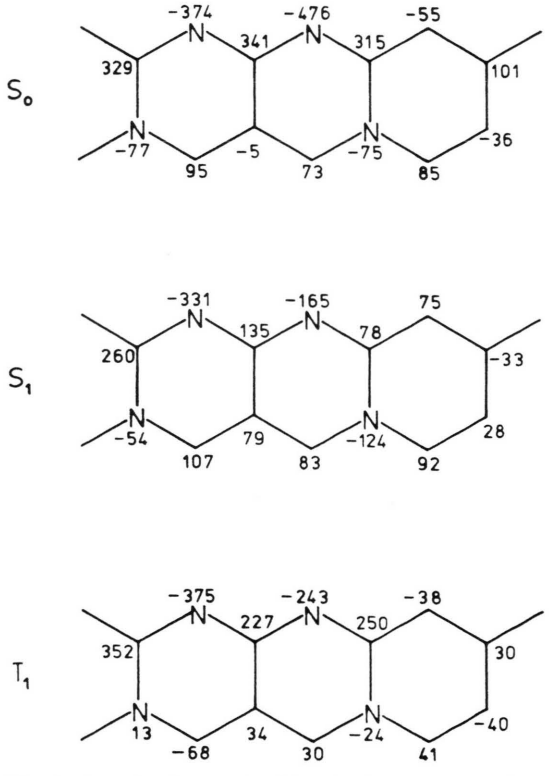

Fig. 1. Atomic charge densities in the ground and lowest excited singlet and triplet states of the trimethylated pyrichrominium ion (in 0.001 e units).

Figure 2 shows the atomic charge densities for the N-11 monoprotonated ion. It is evident from this figure that the N-1 atom is the site of protonation in the ground and lowest excited singlet and triplet states of the N-11 monoprotonated ion.

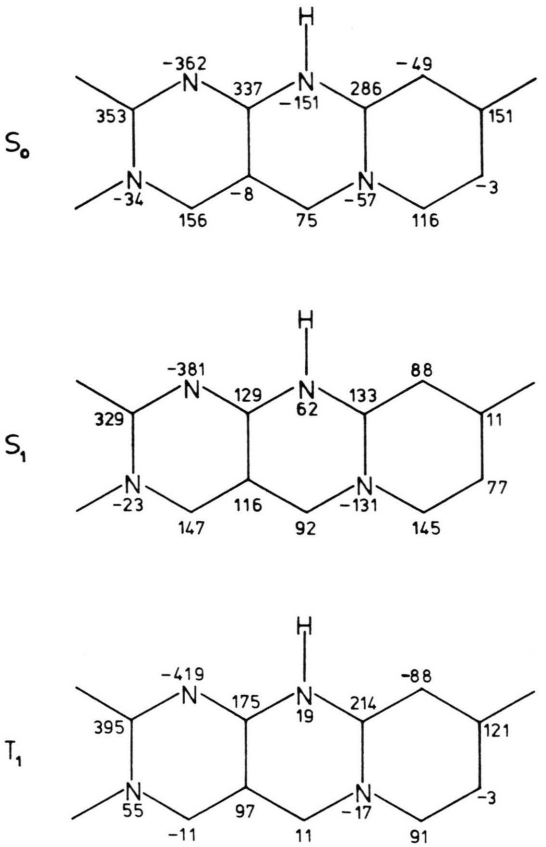

Fig. 2. Atomic charge densities in the ground and lowest excited singlet and triplet states of the N-11 monoprotonated ion (in 0.001 e units).

Absorption and luminescence spectra, transition energies and oscillator strengths

The absorption, fluorescence, and phosporescence spectra of the trimethylated pyrichrominium ion and its protonated forms have been investigated previously [1]. The absorption and fluorescence spectra of the free ion originate at about 420 nm, and the 0–0 phosphorescence band is observed at 471 nm. In 0.025–12 M sulfuric acid, spectra of the monoprotonated species are observed. Protonation of the free ion leads to both a hypsochromic shift and a decrease in the intensity of the long wavelength band in the absorption spectrum. Dual, strongly temperature dependent fluorescence of the monoprotonated species is observed, short wavelength fluorescence with the intensity maximum at about 370 nm and long wavelength one with the intensity maximum at about 450 nm. The latter can be explained as fluorescence of the monoprotonated tautomer or fluorescence of the diprotonated form (see below). In concentrated (18 M) sulfuric acid the measured spectra can be assigned to the diprotonated form [1].

Table 1. Observed and calculated transition energies and oscillator strengths for the trimethylated pyrichrominium ion.

Observed		Calculated		
Energy (cm^{-1})	Oscillator strength	Symmetry	Energy (cm^{-1})	Oscillator strength
Singlet states[a]				
25 600	0.328	A′	27 200	0.580
		A″	30 400	0.0
		A″	36 200	0.007
		A′	36 300	0.061
35 100	0.148	A′	37 400	0.313
39 600	0.025	A″	38 300	0.013
43 700	0.348	A′	41 900	0.228
		A″	42 700	0.001
		A′	43 400	0.044
		A′	47 500	0.040
		A″	48 300	0.003
49 200	0.525	A′	48 300	0.444
Triplet states[b]				
21 300	0.32×10^{-8}[c]	A′	24 200	0.25×10^{-10}
		A′	27 650	0.29×10^{-8}

[a] From absorption spectra in water at room temperature.
[b] From phosphorescence spectra in ethanol at 77 K.
[c] Calculated from the radiative lifetime $\tau_p^0 \sim 3$ s [1].

Table 2. Observed and calculated transitions energies and oscillator strengths for the N-11 monoprotonated ion.

Observed		Calculated		
Energy (cm^{-1})	Oscillator strength	Symmetry	Energy (cm^{-1})	Oscillator strength
Singlet states[a]				
29 500	0.274	A′	32 100	0.391
		A″	35 600	0.001
37 700	0.128	A′	38 200	0.195
		A″	40 800	0.011
		A′	41 500	0.019
41 800	0.117	A′	43 200	0.271
43 900	0.136	A′	45 300	0.188
		A′	47 600	0.220
49 500	0.933	A′	50 700	0.789
Triplet states[b]				
27 400	0.29×10^{-8}[c]	A′	28 900	0.12×10^{-9}
		A′	31 700	0.12×10^{-9}

[a] From absorption spectra in 0.025 M sulfuric acid at room temperature.
[b] From phosphorescence spectra in H_2SO_4:n-C_3H_7OH:C_2H_5OH (1:5:2) at 77 K.
[c] Calculated from the radiative lifetime $\tau_p^0 \sim 2$ s [1].

The calculations have been performed for the following four species: the free ion, the N-11 and N-1 monoprotonated ions, and the N-1, N-11 diprotonated ion. The observed and calculated spectra, given in Tables 1–4, are in good qualitative agreement. Comparying the spectra one must bear in mind that the calculated spectra refer to ions in vacuo while the observed spectra have been taken in highly polar solvents (water-sulfuric acid). Despite of this limitation there is a good correlation between the observed and calculated changes in the transition energy and oscillator strength of the long wavelength absorption band upon protonation. The results presented here provide firm evidence that the absorption spectrum of the monoprotonated form observed in 0.025–12 M sulfuric acid is due to the N-11 monoprotonated ion. The N-11 atom is the only protonation site for which both the observed hypsochromatic shift and decrease in the intensity of the long wavelength band upon protonation are confirmed by the calculations. The observed dual fluorescence can be identified as a fluorescence of both the N-11 and N-1 monoprotonated ions. The long wavelength fluorescence can be attributed to the N-1 monoprotonated form while the short wavelength one to the N-11 monoprotonated form. Changes in both the fluorescence spectrum pattern and quantum yield with temperature suggest that the N-1 monoprotonated tautomer is probably formed by the proton transfer reaction (via solvent) in the excited state [1]. However, in more concentrated sulfuric acid solutions the observed effects may also be explained by the influence of the second acid-base equilibrium. In this case, the long wavelength fluorescence may be attributed to the diprotonated form (see Tables 3 and 4). The static fluorescence spectroscopy and theoretical calculations performed do not give explicit solution which species are responsible for the long wavelength fluorescence in more concentrated sulphuric acid solutions.

The lowest singlet and triplet states of the free ion are calculated to be of the $\pi\,\pi^*$ type. This is consistent with the spectral characteristic of these states: strong fluorescence with the lifetime of about 6 ns and weak phosphorescence with the lifetime of 3 s [1]. The lowest excited states of the protonated forms are also predicted to be of the $\pi\,\pi^*$ type.

Table 3. Calculated transition energies and oscillator strengths for the N-1 monoprotonated ion.

Symmetry	Energy (cm^{-1})	Oscillator strength
Singlet states		
A′	27 600	0.357
A′	28 500	0.352
A″	30 500	0.002
A′	38 100	0.143
A′	40 400	0.089
A′	42 700	0.180
A″	43 000	0.0
A′	43 800	0.302

Table 4. Observed and calculated transition energies and oscillator strengths for the N-1, N-11 diprotonated ion.

Observed		Calculated		
Energy (cm^{-1})	Oscillator strength	Symmetry	Energy (cm^{-1})	Oscillator strength
Singlet states[a]				
29 300	0.303	A′	27 800	0.432
		A′	35 000	0.006
		A′	35 700	0.064
38 200	0.097	A′	38 300	0.084
41 800	0.251	A′	40 300	0.390
		A′	42 800	0.157
44 600	0.146	A′	44 500	0.098

[a] From absorption spectra in 18 M sulfuric acid at room temperature.

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