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Excited state intramolecular proton transfer in free base hemiporphyrazine

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Received 5 December 2001; in final form 16 January 2002

Abstract

The photophysics of free base hemiporphyrazine has been studied by steady-state fluorescence and theoretical computations. The fluorescence spectrum shows two bands peaked at 420 and 675 nm, which, with the aid of theoretical computations, have been assigned to the emissions of two tautomers, differing for the position of the two central protons. © 2002 Published by Elsevier Science B.V.

1. Introduction

Hemiporphyrazine is the phthalocyanine analogue where two opposite faced isoindoles are replaced by two pyridine rings [1,2]. Because of that substitution, the four inner nitrogens of the macrocycle are not chemically equivalent, so that free-base hemiporphyrazine (HpH_2) has three tautomeric forms, which are shown in Scheme 1.

In the ground state, HpH_2 is expected to be prevalently in the tautomeric form with the two central hydrogens linked to the isoindoles rings, tautomer A, because for this form 2^4 resonance

structures can be drawn, whereas tautomers B and C, cf. Scheme 1, possess only 2^2 and 2^3 resonance structures, respectively.

Unlike the majority of macrocycles of the porphyrin and phthalocyanine family, for HpH_2 in the form A no resonance structures spanning the whole macrocycle can be written: tautomer A is only cross conjugated, with isolated conjugation paths involving the two benzene rings of isoindoles and the pyridine rings. The low degree of π delocalization is also a feature of some Hp metal complexes, as shown by NMR and infrared studies of germanium and tin Hp complexes [3,4]. On the contrary, for tautomer B, that with the two central protons linked to the pyridine nitrogens, a fully conjugated ring with $4n$ π electrons, $n = 5$, can be drawn. Thus, tautomer B should absorb at much
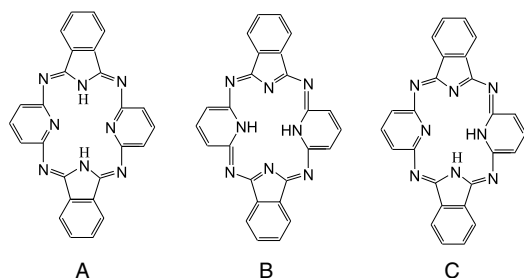
Scheme 1.

longer wavelengths than A, so that, if the energy difference between the ground states of the two forms is not too large, the first excited singlet of B could occur at lower energy than that of A and therefore play an important role in the photophysical behavior of HpH_2 [5].

Tautomer C is also cross-conjugated and therefore its first excited singlet is expected to lie at higher energy than that of A. However, it could also play a role in the photophysics of the lowest energy states of HpH_2, especially in nonradiative decay paths, because its low lying triplet states could fall in the same energy region of the lowest excited singlets of A, so that excited state intramolecular proton transfer (ESIPT) could promote intersystem crossing [6].

Thus the photophysics of HpH_2 appears to be very interesting, since it could exhibit many interesting and different facets, with several radiationless decay paths in competition between them, involving three different tautomeric forms. Despite that, it has not received until now the attention that it deserves; in this Letter we try to partially fill the gap, starting from the analysis of the fluorescence spectrum of HpH_2, recorded by a high power Laser source and interpreted with the aid of theoretical computations.

2. Experimental and computational details

HpH_2 has been prepared following the procedure of Esposito et al. [4]. The crystalline solid was recrystallized from nitrobenzene and obtained as red needles.

The fluorescence spectrum has been recorded at room temperature from a N,N-dimethylforma-mide solution, using as excitation source the second harmonic of a femtosecond Titanium–Sapphire laser operating at 1 kHz repetition rate, with pulse duration of 130 fs and pulse energy up to 20 μJ. The center wavelength and the bandwidth of the excitation source are 380 and 25 nm, respectively. The solution contained into a quartz cell has been irradiated with a collimated, 4 mm diameter beam. The small amount of light diffused by a beam dumper was collected by a photodiode (PD), whose signal was employed both as a trigger for the acquisition electronics and as a reference signal. The light from the cell was analyzed at 90° by a monochromator, whose output slit was equipped with a photomultiplier tube (PMT). The signals from the PD and the PMT were fed into a digital oscilloscope (500 MHz bandwidth), which allowed averaging over a variable number of signals (typically 100).

The ground state relative energies of the three tautomers have been computed at ab initio HF/MP2 level of theory, using standard polarization functions on all the heavy nuclei and the GAMESS package [7]. The structures of the three tautomers have been fully optimized at the HF level of the theory, using a standard 6-31g basis set. For tautomers A and B, D_{2h} symmetry has been imposed. In view of the encouraging results obtained in studies of the dynamics of important photochemical processes, [8–10] electronic excitations have been estimated by the semiempirical MNDO method [11], using PM3 parameterization [12], and the MOPAC package [13]. The active space in the CI computations included the three highest occupied and the six lowest unoccupied molecular orbitals; only single and double excitations have been considered.

3. Results

The absorption spectrum of HpH_2 is shown in Fig. 1. It consists of a large band peaked around 350 nm, with a shoulder at 420 nm and the onset at ca. 500 nm [2,14].

The computed ground state relative energies of the three tautomers are reported in Table 1, together with the vertical transitions predicted by
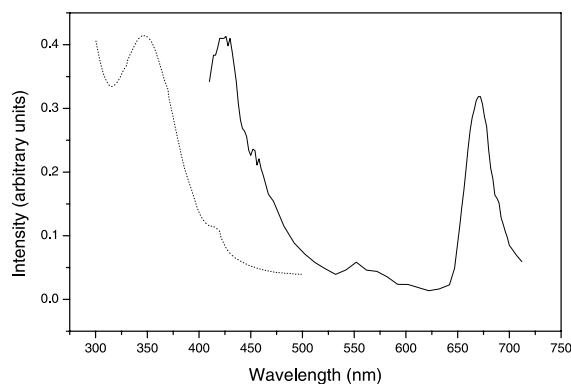
Fig. 1. Absorption (dotted line) and emission (full line) spectra of free-base hemiporphyrazine in N, N-dimethylformamide solution.

PM3/CI computations for the two lowest lying singlet excited states. Both ab initio and semiempirical computations indicate that the tautomer A is the most stable form of HpH_2 in the ground state; the energy differences are significant: 0.7 eV for both the forms B and C, at MP2 level of the theory.

For the tautomer A the lowest transition is predicted to occur at 2.97 eV (417 nm), with relatively weak transition dipole, whereas the second one has a strong transition moment and falls at 3.67 eV (338 nm). For the tautomer B, PM3/CI computations predict a weak transition at 1.96 eV (633 nm), in line with the fact that for a fully conjugated ring extending over 20 centers with 20 π electrons, the absorption band is expected to be peaked in the region between 500 and 700 nm, where porphyrins and phthalocyanines absorb [15]. Thus, the fact that in this spectral region the absorbance of HpH_2

drops rapidly to zero, together with the computed relative energies of Table 1, clearly indicates that in the ground state the B form is not present. For the tautomer C, the vertical transitions from the ground state to the two lowest singlet states are estimated to occur at 2.56 eV (484 nm) and 3.30 eV (375 nm). Both transitions are allowed, with the latter stronger than the former. Thus, according to PM3/CI computations, the absorption spectrum of C partially overlaps with that of A, but the possible contribution of C to the absorption spectrum is ruled out both by the very low absorbance in the region around 500 nm and by the computed relative energies of Table 1.

In conclusion, both the shape of the absorption spectrum and the results of theoretical computations indicate that in the ground state the tautomer A is the predominant form. That conclusion is further supported by the fact that in the X-ray crystal structures of some Hp metal complexes the distances of the meso nitrogens from the isoindole carbons are much shorter than those from the pyridine α carbons, e.g. 1.29 versus 1.41 Å in Hp–Ge, [16,17]. Therefore, according to the data reported in Table 1, the weak shoulder observed in the absorption spectrum at 420 nm can be ascribed to the comparatively weak $S_0 \rightarrow S_1$ transition of A, whereas the strong band peaked at 350 is due to the more intense $S_0 \rightarrow S_2$ transition.

The emission spectrum is also reported in Fig. 1. It consists of two well separated, weak bands, peaked at 420 and 675 nm. For both bands the PMT signal drops to zero within a few nanoseconds after its maximum, so that we can exclude contribution due to phosphorescence.

Table 1
Computed relative energies (eV) and vertical transition energies (eV) from the optimized nuclear configurations of the ground state for the three tautomers of free-base hemiporphyrazine

Tautomer	S_0			PM3/CI	
	HF/6-31g	HF/MP2/6-31g*	PM3/CI	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$
A	0.00	0.00	0.00	2.97	3.67
B	1.00	0.68	1.07	1.96	3.01
C	0.94	0.68	0.83	2.57	3.31

Geometry optimizations of the lowest excited singlets of all the tautomers bring about only small variations in the nuclear configurations and therefore in the relative energies. The energy of the first excited singlet of A goes down by ca. 0.1 eV upon optimization and the vertical radiative transition to S_0 is predicted to occur at 2.80 eV (443 nm). Therefore the first band of the emission spectrum, with the maximum at 420 nm, can be assigned to the radiative decay of the lowest excited singlet of tautomer A, populated via internal conversion from the door state S_2. The latter can also undergo internal conversion via single or double ESIPT to the first excited singlets of both C and B. The former is predicted to be at higher energy than both S_1 of A and B, so that it is expected to rapidly evolve via ESIPT to S_1 of either A or B. According to that expectation, the emission spectrum is quite flat in the region between 550 and 650 nm, where PM3/CI computations predict the vertical radiative transition from the optimized geometry of S_1 of C to the ground state

(2.11 eV, 587 nm), but for a very weak signal at 550 nm, thus confirming that the tautomer C could be only a transient structure, with a short lifetime.

As concerns the band at 675 nm, PM3/CI computations indicate that it can only be ascribed to the radiative decay of the first excited singlet of tautomer B, formed in the excited state via a double intramolecular proton transfer. That assignment is also in line with the fact that ESIPT usually implies a dual emission spectrum, with well separated bands, as it occurs for instances in flavons [18].

All the results of CI computations are schematized in Fig. 2, where the possible radiative and nonradiative decay paths have also been reported. The energy position of the computed lowest lying triplet states are also shown for completeness, even though intersystem crossing has not been considered here, since both bands appearing in the emission spectrum have been assigned to the radiative decay of singlet states.
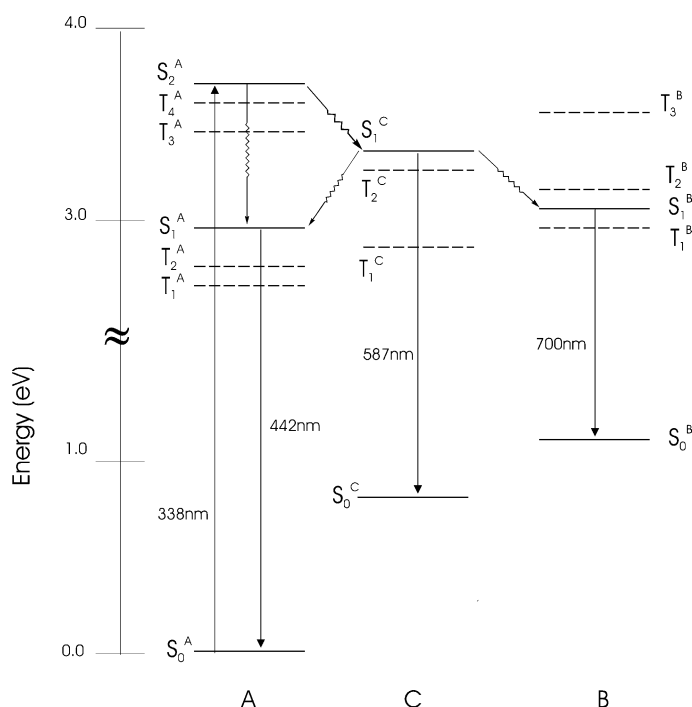

Fig. 2. Sketch of the possible radiative and radiationless decay paths of free-base hemiporphyrazine according to the computed PM3/CI energies of the lowest electronic states of the three tautomers in the gas-phase.

The fluorescence quantum yield of HpH_2 has been determined by comparison with a solution of quinine sulfate in sulfuric acid 0.5 M, which is the most suited reference substance, because it absorbs and emits in the same spectral region of HpH_2. Using the value of 0.546 for the yield of the standard, measured upon excitation at 350 nm [19], we have found for the fluorescence quantum yield of HpH_2 the value of 0.052, slightly higher than that observed in free-base porphyrin: 0.0425 in presence of O_2 [15].

4. Conclusion

The emission spectrum of HpH_2 in N, N-dimethylformamide is characterized by a dual emission, due to the fact that at the excited state HpH_2 undergoes a double intramolecular proton transfer. Thus the tautomeric form with the two central protons linked to pyridine nitrogens plays a part in the photophysics of HpH_2. That finding can also explain the large redshift of the absorption band observed upon substitution of the two inner protons with metal ions [20,21], far longer than that usually observed in porphyrins and phthalocyanines [15]. In fact, in the case of metal complexes, the metal ion occupies approximately the center of the macrocycle, thus allowing for a direct transition between the ground state, with an electronic configuration characteristic of the tautomer A to the lowest excited singlet with the electronic configuration characteristic of B. Such a transition cannot occur in HpH_2 because of the Franck–Condon principle.

Further studies intended to determine the dynamical features of the double ESIPT are in progress.

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