

NH TAUTOMERISM AND VISIBLE ABSORPTION SPECTRA OF PORPHYRINS WITH ASYMMETRICAL SUBSTITUTION: OSCILLATOR MODEL AND MO CALCULATIONS

E.I. ZENKEVICH, A.M. SHULGA, I.V. FILATOV,
A.V. CHERNOOK and G.P. GURINOVICH

Institute of Physics, BSSR Academy of Sciences, Minsk 220602, USSR

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On the basis of experiments the oscillator model has been established for individual NH tautomers of porphyrins with asymmetrical substitution. CNDO/2 calculations explain the inversion of $Q_x(0,0)$ and $Q_y(0,0)$ electronic transition intensities in NH tautomers as a consequence of the inversion of LUMO coefficients c_1 and c_2 for fixed x and y molecular oscillators.

1. Introduction

It is well documented that the two inner hydrogens (so-called NH protons) in free-base porphyrins show tautomerism, due to protons jumping from one pair of nitrogens to another [1]. But in symmetrical porphyrins NH tautomers are not distinguished by structure and have identical electronic spectra. It has been shown by us recently that for a whole class of isocycle-containing porphyrins spectral and energetic characteristics of individual NH tautomers differ greatly because of non-symmetrical substitution due to the isocyclic ring. Therefore they may easily be measured using normal electronic spectra in a wide temperature range (77–500 K) [2,3]. Comparison of the fluorescence and absorption spectra of two tautomers of one compound has revealed a spectral separation between their S_0-S_1 transitions of as much as 380 cm^{-1} , while that for S_0-S_2 transitions can amount to $\approx 800\text{ cm}^{-1}$. Moreover, it should be emphasized that the visible absorption spectra of tautomers show noticeable inversion of $Q_x(0,0)$ and $Q_y(0,0)$ band intensities in every compound in going from one tautomer to another. Finally, when methyl [4] or ethyl groups are attached to the opposed pyrrole rings of porphyrin molecules, similar peculiarities in the electronic spectra of the two tautomeric forms are observed in isotropic solutions at different temperatures (77–400 K).

So far the four-orbital model of porphyrin absorption electronic spectra [5] has not taken into account the influence of NH tautomerism in non-symmetrical porphyrins on the frequencies and intensities of electronic transitions in the visible region. The theoretical consideration of this problem involves solving the fundamental question of the absolute orientation of the electronic transition oscillators for each tautomer. First, the correspondence between the direction of the lowest absorption oscillator and that of the H–H axis connecting the NH protons must be found in the individual tautomeric forms.

In this paper, we present straightforward experimental arguments which permit us to relate the real position of the H–H axis to the molecular oscillator axes determined by the substituents of different types (isocycle or alkyl groups) in the two NH tautomers. We use this structural information as a basis for analysing the inversion of electronic $Q_x(0,0)$ and $Q_y(0,0)$ band intensities using the four-orbital model.

2. Experimental

Synthesis, purification and identification of the investigated compounds have been carried out in our laboratory (refs. [2,3], and references therein). The results of the spectroscopic measurements as well as

structural peculiarities of these compounds have also been reported [2]. We consider the results obtained using as an example two compounds: 2,3,12,13-tetraethylporphyrin (TEP) and 3¹,5¹-cyclo-5¹-ethyl-10,15,20-tripropylporphyrin (TPPC), containing an isocyclic ring. The optical experiments were carried out in an EPIP mixture (diethyl ether, petroleum ether, isopropanol 5:5:2) with a porphyrin concentration of 4×10^{-6} to 4×10^{-5} M. In NMA investigations we used higher concentrations ($\approx 5 \times 10^{-3}$ M) and dried solvents (CDCl₃, CS₂ and toluene-*d*₈).

3. Results and discussion

3.1. Electronic spectra

Using the corrected fluorescence visible excitation spectra for low concentrations ($C \leq 10^{-5}$ M) and low optical density ($D \leq 0.10$) solutions, which were monitored in fluorescence bands of the individual tautomers, we managed to obtain and analyse NH-tautomer

absorption spectra for each porphyrin. The data summarized in table 1 reveal that each NH tautomer exhibits four visible bands which are generally characteristic of free-base porphyrins. But the observed intensity pattern changes dramatically when passing from one tautomer to another for each compound: while $I(Q_x) < I(Q_y)$ is observed for one tautomer, $I(Q_x) > I(Q_y)$ occurs for the second and vice versa. In addition to the redistribution in the electronic Q_x(0,0) and Q_y(0,0) band intensities, the relative intensities of S₀-S₁ transitions of different tautomers of the same compound show significant dependence on the temperature. This temperature effect is caused by changing equilibrium tautomer concentrations due to the existence of a potential barrier to proton migration in the ground state. For example, the experimental value for the activation enthalpy of NH tautomerism is 510 cm⁻¹ for TPPC. It has been found that in all cases at 77 K the predominant component in solution (90%) was as a rule a tautomer with a short wave S₀-S₁ transition (tautomer 1).

Table 1

Maxima of absorption and fluorescence spectra (λ , in nm) and relative band intensities (in parentheses) in NH tautomers of non-symmetrical porphyrins (EPIP, 77 K)

Compound a)	Tautomer	Absorption				Fluorescence	
		Q _y (1,0)	Q _y (0,0)	Q _x (1,0)	Q _x (0,0)	f ⁰⁻⁰	f ^{vib}
OEPC	1	499(1.0)	532(0.26)	561(0.74)	612(0.80)	614(1.0)	679(0.48)
	2	496(1.0)	529(0.67)	569(0.74)	622(0.23)	624(1.0)	692(0.90)
OEPC=CH ₂	1	507(1.0)	544(0.88)	568(0.67)	621(0.19)	622(0.94)	689(1.0)
	2	504(0.94)	535(0.36)	580(1.0)	636(0.72)	637(1.0)	707(0.28)
TPPC	1	520(0.85)	552(1.0)	582(0.32)	638(0.38)	639(1.0)	709(0.49)
	2	513(0.81)	543(0.48)	594(0.28)	653(1.0)	654(1.0)	728(0.17)
10-EFE b)	1	514(0.70)	557(1.0)	571(0.71)	623(0.06)	624(0.33)	692(1.0)
	2	507(0.78)	533(0.2)	581(1.0)	638(0.9)	639(1.0)	709(0.18)
4-VPF b)	1	530(0.69)	570(1.0)	588(0.76)	643(0.17)	644(0.25)	714(1.0)
	2	515(0.83)	549(0.4)	605(1.0)	653(0.60)	654(1.0)	730(0.21)
TEP	1	494(1.0)	529(0.68)	559(0.42)	610(0.03)	611(0.1)	677(1.0)
	2	490(1.0)	514(0.22)	564(0.95)	618(0.67)	619(1.0)	687(0.3)
7-Br-TEP	1	500(0.85)	535(1.0)	559(0.75)	612(0.04)	613(0.09)	678(1.0)
	2	479(1.0)	516(0.25)	568(0.93)	622(0.68)	623(1.0)	691(0.18)

a) Abbreviations: OEPC, 3¹,5¹-cyclo-3¹-methyl-2,7,8,12,13,17,18-heptaethylporphyrin; OEPC=CH₂, 3¹,5¹-cyclo-3¹-exomethyl-ene-2,7,8,12,13,17,18-heptaethyl-22H, 24H-porphine; 10-EFE, 10-ethoxyphylloerythrin methyl ester; 4-VPF, 4-vinylprotopheophytin.

b) 10-EFE and 4-VPF were dissolved in a mixture of tetrahydrofuran and diethyl ether (1:1).

3.2. The NH-tautomer structure

Determination of the location of internal protons in each tautomer of the investigated porphyrins with non-symmetrical substitution will result in definite correlations between tautomer spectra and their structures. Here we present such information for TPPC. This compound has no alkyl substituents on the pyrrole rings and therefore, one is able to measure the constant of the spin-spin interaction of pyrrole ring protons with NH protons using a ^1H NMR method ($J = 1.8$ Hz). Based on the complete assignment of signals in the ^1H NMR spectrum of TPPC and using double resonance and the Overhauser nuclear effect it has been found that in tautomer 1 the NH protons are located on the opposed pyrrole rings which are not bonded with the isocycle [6]. The experimental data obtained enable us to conclude that this is true for most isocycle-containing porphyrins.

In the case of TEP, using low-temperature ^1H NMR spectra it has been found that in the short-wave tautomer 1 the NH protons are fixed on the opposed pyrrole rings having alkyl substituents. Thus, we have now direct information as to which types of absorption spectra of individual tautomers correspond to a real distribution of NH protons in these forms.

3.3. Absolute orientation of long-wave absorption oscillators in NH tautomers

It is known [5,7] that in free-base porphyrins, due to the D_{2h} symmetry, the electric transition dipoles in the X and Y directions are not equivalent and Q_x and Q_y absorption electronic bands are modelled by mutually perpendicular linear oscillators X and Y passing through the pyrrole rings. Moreover, for both symmetrical [7,8] and non-symmetrical [5,9] porphyrins the oscillator of the long-wave absorption Q_x band is believed to be oriented along the H-H axis, and to rotate through 90° following the migration of the inner protons. The cyclic polyene model [10] also predicts band polarizations relative to the H-H axis. The only experimental work available to us [8] presents evidence for correspondence of the long-wave absorption oscillator X to the H-H axis for the case of the symmetrical crystal tetraphenylporphine. Nevertheless up to now there has been no straightforward independent information confirming the same situa-

tion for porphyrins with non-symmetrical substitution. Furthermore, the theoretical consideration of this problem for porphyrins with external substituents (namely, 2,3,12,13-tetramethylporphine [5]) did not take into account the existence of the two spectrally different NH tautomers which we have discovered for such compounds (see table 1).

In order to specify the behaviour of a system of molecular oscillators X and Y in non-symmetrical porphyrins as NH protons move through 90° , i.e. when transition from tautomer 1 to tautomer 2 takes place, we investigated the dichroism $d = (D_{\parallel} - D_{\perp}) / (D_{\parallel} + D_{\perp})$ of photoinduced changes in TPPC absorption spectra at 77 K caused by polarized light irradiation of glassy solutions. It is well known that at 77 K the above tautomerism may be induced only by selective irradiation of solutions into absorption bands of one of the NH tautomers (refs. [2,3,11], and references therein). As can be seen from table 1, the significant difference between the S_0-S_1 transitions of the two tautomers of TPPC permits us to investigate separately changes in their long-wave Q bands after irradiation. In our experiments, initially the concentration of tautomer 2 was extremely low relative to that of tautomer 1 (see spectrum A, fig. 1). Then irradiating the solution (for about 30 min) with linearly polarized light into the absorption band Q_x of tautomer 1 (638 nm, optical density D_1), we could measure the rising Q band of tautomer 2 (654 nm, optical density D_2) (see spectra B and C, fig. 1).

When absorption spectra were recorded using a photometric beam polarized either parallel (\parallel) or perpendicular (\perp) to the excited beam, the following basic differences were observed: $D_1^{\parallel} < D_1^{\perp}$ whereas $D_2^{\parallel} > D_2^{\perp}$ i.e. the dichroism of long-wave Q bands of the two tautomers is opposite in sign ($d_1 = -9\%$, $d_2 = +6\%$). This remarkable result, as seen from fig. 1, seems to have the following explanation: the oscillator of the long-wave absorption band of tautomer 2 induced by polarized irradiation into the Q band of tautomer 1 must be parallel to the exciting light vector E , and, correspondingly, to the oscillator of the long-wave Q_x band of tautomer 1. Hence, under central proton displacement the H-H axis rotates through 90° whereas the long-wave transition oscillator X presumably remains fixed at the same pyrrole rings of both tautomers. Insofar as the electron distribution is not identical for each tautomer of the same compound, it is not

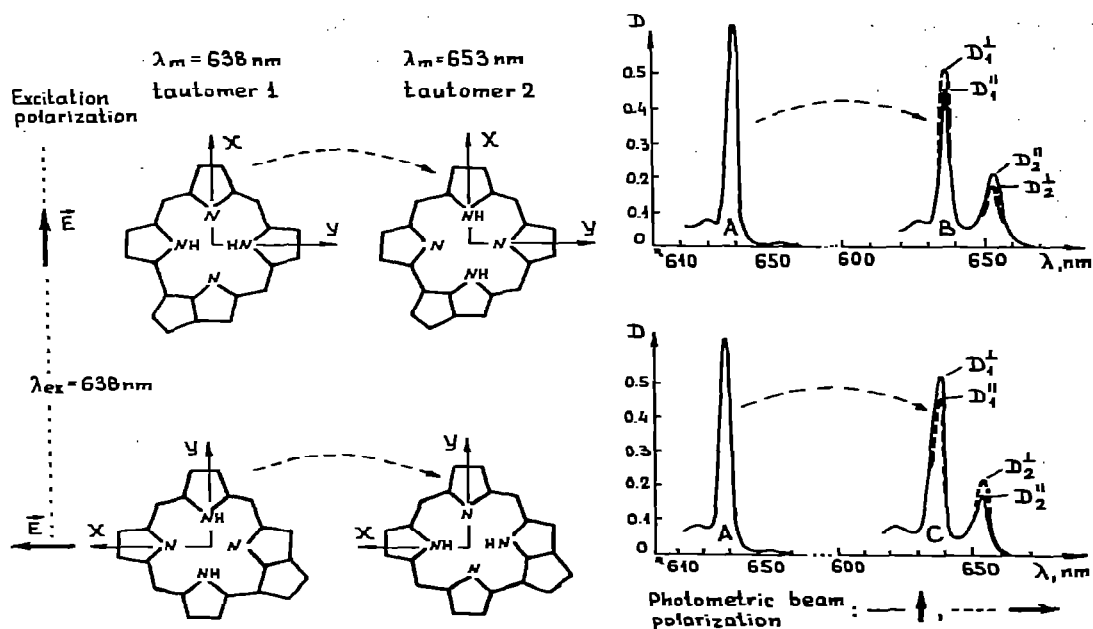


Fig. 1. Absorption onset experiments for photoinduced conversion of TPPC NH tautomers in EPIP at 77 K: (A) Initial spectrum; (B,C) monitored spectra after irradiation ($\Delta t \approx 30$ min) by polarized light ($\lambda_{ex} = 638$ nm). Conditions for polarized excitation and polarized monitoring are shown by arrows. The displacement of the inner protons in tautomers conforms to experimental data. The direction of the X-axis is chosen for tautomer 1 to be parallel to the vector E of the exciting light.

excluded that the mutual displacement of oscillators X and Y may be slightly different. But as a whole the system of oscillators X and Y does not rotate through 90° in going from tautomer 1 to tautomer 2 in the compounds considered.

3.4. Interpretation of NH-tautomer visible absorption spectra

In the four-orbital model [5], low-lying $\pi\pi^*$ states of free-base porphyrins (D_{2h} symmetry) are considered as resulting from single electron excitations from a pair of non-degenerate HOMOs (b_1, b_2) to a pair of non-degenerate LUMOs (c_1, c_2). In the case of D_{2h} symmetry, mutually perpendicular electric transition dipoles X and Y are not equivalent and, therefore, in the visible absorption spectra of free-base porphyrins two different electronic bands $Q_x(0,0)$ and $Q_y(0,0)$ are observed (table 1 and fig. 2). The question of relative intensities of the Q_x and Q_y transitions, which is important in the present part of the paper, has been

solved by Gouterman [12] using perturbation theory. If it is assumed that states of different polarization (Q_x^0 and Q_y^0) are not mixed, the Q states of arbitrary free-base porphyrin are constructed as follows:

$$Q_x = Q_x^0 + \lambda_x B_x^0,$$

$$\lambda_x = \{[\epsilon(c_2) - \epsilon(b_1)] - [\epsilon(c_1) - \epsilon(b_2)]\}/2\Delta,$$

$$Q_y = Q_y^0 + \lambda_y B_y^0,$$

$$\lambda_y = \{[\epsilon(c_1) - \epsilon(b_1)] - [\epsilon(c_2) - \epsilon(b_2)]\}/2\Delta, \quad (1)$$

where Δ is an initial energy gap between B^0 and Q^0 bands, $\epsilon(b_i)$ and $\epsilon(c_j)$ are orbital energies. The intensities of the Q_x and Q_y states are proportional to λ_x^2 and λ_y^2 . Hence, the amounts of absorption intensity, gained in the initially forbidden Q_x^0 and Q_y^0 transitions of arbitrary free-base porphyrin by borrowing from appropriate B_x^0 and B_y^0 Soret states by configuration interaction, are related to differences in orbital energies of states created by x - or y -polarized single elec-

tron excitations. That is, for each polarization, as the equality of the transition energies breaks down (or CI becomes weaker), the corresponding visible band becomes allowed.

In order to consider the inversion of the $Q_x(0,0)$ and $Q_y(0,0)$ electronic transition intensities in NH tautomers of non-symmetrical free-base porphyrins, we calculated the ground-state orbital energies of the investigated molecules by a CNDO/2 method using the symmetrized crystal geometry of the porphyrin molecule [13,14]. On the basis of the above experimental results, we introduce a system of molecular X and Y axes, identically fixed in both tautomers. Then using theoretical MO calculations and the analysis of their symmetry properties, the ordering of orbitals b_1 , b_2 , c_1 and c_2 is determined. Fig. 2 illustrates that, as with symmetrical porphyrins [5], the ordering of c_1 and c_2 orbitals changes as NH protons displace. It is essential that in symmetrical porphyrins the X axis always keeps the H-H axis direction [5,9]. Therefore, as the H-H axis rotates through 90° (going from one tautomer to another) the orbital combinations ($b_i c_j$) determining X - and Y -polarized excitations must change. For

example, this change for X -polarized excitations is as follows: $(b_1 c_2), (b_2 c_1) \rightarrow (b_1 c_1), (b_2 c_2)$. As a result, the CI energies of the X - and Y -polarized excitations do not change from one tautomer to another and consequently, the absorption spectra are indistinguishable. However, for non-symmetrical porphyrins with fixed X and Y axes, the orbital combinations ($b_i c_j$) corresponding to X - and Y -polarized excitations remain unchanged under the NH-proton migration. Then, as seen in fig. 2, the differences in orbital energies of the states reached by X and Y excitations differ for each polarization when the tautomer 1 \rightarrow tautomer 2 transition occurs. Such variation of the CI energies for each polarization must result in principal changes in relative intensities of the $Q_x(0,0)$ and $Q_y(0,0)$ absorption bands in two tautomers of the same molecule.

Actually such a situation is experimentally observed for TEP (fig. 2): the ethio-type spectrum of tautomer 1 transforms into the deoxophyllo-type spectrum of tautomer 2. It is particularly relevant to note that the same types of spectra are observed for 2,3,12,13-tetramethylporphyrin (TMP) tautomers 1 and 2. And our results, in fact, are in agreement with the theoretical

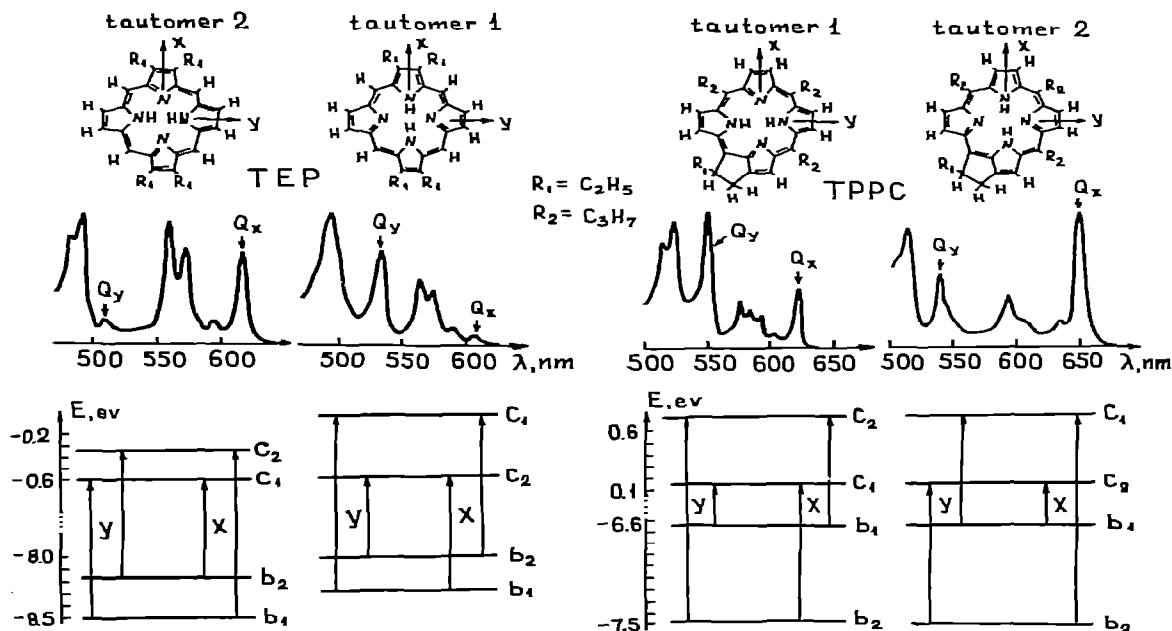


Fig. 2. Structures, visible absorption spectra and four-orbital MO diagram for NH tautomers of non-symmetrical porphyrins.

considerations of Gouterman on parallelism of H-H and methyl axes [5], although that is the case only for tautomer 1. Moreover, the lowest Q band of the TMP absorption spectrum discussed in ref. [5] actually belongs to tautomer 2, as is seen from table 1 and fig. 2. Furthermore, at 293 K TEP or TMP show just an ethio-type spectrum, in contrast to the rhodo-type spectrum used in ref. [5]. Our experimental data (NMR, mass spectrometry and absorption spectra) permit us to confirm that a rhodo spectrum belongs to a Br derivative of TEP (or TMP) which is a byproduct in the synthesis of these compounds. 7-Br-TEP also has two tautomers with different spectra (table 1).

Arguments of this type have been used by us to explain characteristic peculiarities in spectra of TPPC NH tautomers (fig. 2) and were applied to understand the principal changes in the NH-tautomer visible absorption of the investigated porphyrins with an isocycle.

It may be concluded that difficulties in the theoretical treatment of spectral peculiarities of porphyrins with π -acceptor substituents [9] are caused by the absence of detailed absorption and fluorescence excitation spectra of individual tautomers of these compounds.

The results of the present investigation serve as a basis for an up-to-date theoretical interpretation of porphyrin electronic spectra.

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