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

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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$800 cm$^{-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 locate 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.

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 3\textsuperscript{1},5\textsuperscript{1}-cyclo-5\textsuperscript{1}-ethyl-10,15,20-triethylporphyrin (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 $4 \times 10^{-6}$ to $4 \times 10^{-5}$ M. In NMA investigations we used higher concentrations ($\approx 5 \times 10^{-3}$ M) and dried solvents (CDCl\textsubscript{3}, CS\textsubscript{2} and toluene-	extsubscript{$d8$}).

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 $S_0 - S_1$ 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\textsuperscript{-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 $S_0 - S_1$ transition (tautomer 1).

Table 1

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

| Compound a) | Tautomer | Absorption | Fluorescence |
|------------|----------|------------|--------------|
|            |          | $Q_x(1,0)$ | $Q_y(0,0)$   | $Q_x(1,0)$ | $Q_y(0,0)$ | $I^{\text{0-vib}}$ |
| 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\textsubscript{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(0.22)    | 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, 3\textsuperscript{1},5\textsuperscript{1}-cyclo-3\textsuperscript{1}-methyl-2,7,8,12,13,17,18-heptaethylporphyrin; OEPC=CH\textsubscript{2}, 3\textsuperscript{1},5\textsuperscript{1}-cyclo-3\textsuperscript{1}-exomethyl-ene-2,7,8,12,13,17,18-heptaethyl-22H, 24H-porphine; 10-EFE, 10-ethoxyphyloerythrin methyl ester; 4-VPF, 4-vinylprotoephin.

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 $^1$H NMR method ($J = 1.8$ Hz). Based on the complete assignment of signals in the $^1$H 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 $^1$H 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 $90^\circ$ 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 situation 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 $90^\circ$, i.e. when transition from tautomer 1 to tautomer 2 takes place, we investigated the dichroism $d = (D_{\perp} - D_{\parallel})/(D_{\parallel} + D_{\perp})$ 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, by radiating 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 (I) or perpendicular (L) to the excited beam, the following basic differences were observed: $D_{1L} < D_{1I}$ whereas $D_{2L} > D_{2I}$ 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 $90^\circ$ 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
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 Gutermann [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:

$$Q_X = Q_X^0 + \lambda_X B_X^0$$

$$\lambda_X = \frac{[e(c_2) - e(b_1)] - [e(c_1) - e(b_2)]}{2\Delta}$$

$$Q_Y = Q_Y^0 + \lambda_Y B_Y^0$$

$$\lambda_Y = \frac{[e(c_1) - e(b_1)] - [e(c_2) - e(b_2)]}{2\Delta}$$

(1)

where $\Delta$ is an initial energy gap between $B_0^0$ and $Q_0^0$ bands, $e(b_i)$ and $e(c_j)$ are orbital energies. The intensities of the $Q_X$ and $Q_Y$ states are proportional to $\lambda_X^2$ and $\lambda_Y^2$. 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 mole-
cule [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 essen-
tial 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 tauto-
mer to another) the orbital combinations \((b_ic_j)\) determin-
ing \(X\)- and \(Y\)-polarized excitations must change. For
example, this change for \(X\)-polarized excitations is as
follows: \((b_1c_2), (b_2c_1) \rightarrow (b_1c_1)(b_2c_2)\). As a result,
the CI energies of the \(X\)- and \(Y\)-polarized excitations
do not change from one tautomer to another and con-
sequently, the absorption spectra are indistinguishable.
However, for non-symmetrical porphyrins with fixed
\(X\) and \(Y\) axes, the orbital combinations \((b_ic_j)\) corre-
sponding 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 \(\rightarrow\) tauto-
tomer 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-tetra-
methylporphyrin (TMP) tautomers 1 and 2. And our
results, in fact, are in agreement with the theoretical

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Structures, visible absorption spectra and four-orbital MO diagram for NH tautomers of non-symmetrical porphyrins.}
\end{figure}
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 iso-
cycle.

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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