

SPECTRAL PECULIARITIES OF NH-TAUTOMERISM IN ISOCYCLE-CONTAINING PORPHYRINS AND THEIR COVALENTLY LINKED DIMERS

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Received 8 May 1984

It has been found experimentally that a whole class of isocycle-containing porphyrins, including synthetic and natural objects and their covalently linked dimers, shows NH-tautomerism which manifests itself in isotropic solutions in normal electronic spectra both at 77 K and higher temperatures (up to 500 K).

1. Introduction

The investigation of isocycle-containing porphyrins and their dimers has aroused interest for several reasons. First, the isocycle is a structure element of chlorophyll and its natural analogues, and, even more so, it participates in the formation of pigment aggregates [1]. Second, it has been shown recently that the reaction center in photosynthetic systems contains a pair of strongly interacting chlorophyll molecules, the so-called "special pair", which is involved in the initial photophysical processes of the reaction center (see, for example, ref. [2]). So, a synthetic porphyrin dimer in which isocycles are covalently linked may be a good model system for studying natural chlorophyll aggregated forms and photophysical processes in pigment aggregates.

The investigation of such systems requires taking into account the possibility of the appearance of some specific effects characteristic of porphyrin molecules. First of all, it is known that in porphyrins two inner hydrogens which, in their stable conformation, are bound to opposite nitrogens, may jump from one pair of nitrogens to another [3]. At room temperature these hydrogens migrate relatively quickly [4]. But at 77 K the above tautomerism ceases when the porphyrin molecule is in the ground electronic state [5]. The migration of the center protons may still be induced even at liquid-helium temperature by photoexcitation of the porphyrin molecule. Such phototransformation

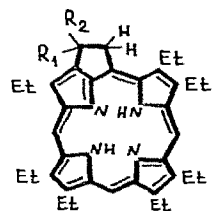
between two tautomers at low temperatures has been observed in two types of experiments: (i) photoinduced reversible conversion of admixture centers into one another for porphyrin-free bases incorporated in an *n*-octane Shpol'skii matrix [6,7], (ii) variations in the emission intensity and fluorescence depolarization of glassy solutions of porphyrins at 77 K during excitation by constant polarized monochromatic light [5].

In most cases the spectral separation between the individual tautomers (ΔE) does not exceed 100 cm^{-1} [6,7]. Therefore NH-tautomerism can be effectively detected at 77 and 4.2 K in the Shpol'skii matrix only. Accordingly, the fluorescence depolarization due to photoinduced proton migration may be observed only with selective monochromatic excitation [5]. In chlorins, the spectral separation between the two tautomers is large: $\Delta E \approx 800\text{--}1500 \text{ cm}^{-1}$ [8-10]. But the second tautomer which can be produced by photoexcitation can be stable only at 4.2 K due to the fast reverse photochemical relaxation [10].

Subsequent to a preliminary study of cyclopentanoporphyrin NH-tautomerism [11], we present in this paper a more detailed consideration of some new experimental results which show that a whole class of porphyrins — with the isocyclic ring — including natural objects, their derivatives and covalently linked dimers, exhibit NH-tautomerism in isotropic solutions both at 77 K and at higher temperatures (500 K), which can be detectable in normal absorption and fluorescence spectra.

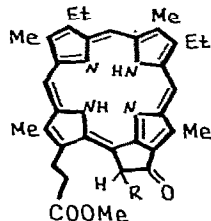
2. Experimental

Synthesis and identification of cyclopentanoporphyrins and their chemical dimers covalently linked via isocycles have been described in previous papers [12,13]. The porphyrins with the cyclopentanone ring have been prepared and purified by familiar methods [14–16]. Our experimental results were obtained when investigating the following compounds: 3',5'-cyclo-3'-methyl-2,7,8,12,13,17,18-heptaethylporphyrin (1); 3',5'-cyclo-3'-exomethylen-2,7,8,12,13,17,18-heptaethyl-22H,24H-porphin (2); phylloerythrin methyl ester (3); deoxyphylloerythrin methyl ester (4); 10-ethoxyphylloerythrin methyl ester (5); pheoporphyrin-a₅ dimethyl ester (6); 2-vinylpheoporphyrin-a₅ dimethyl ester (7); 4-vinylprotopheophytin a (8); meso-tripropylcyclopentanoporphyrin (9) and 5',5'-cyclodimer (10) which consists of two molecules 1 and 2:



(1), $R_1 = H$, $R_2 = CH_3$

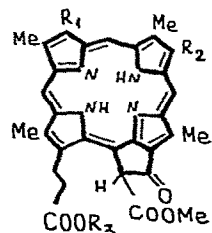
(2), $R_1, R_2 = =CH_2$



(3), $R = H$

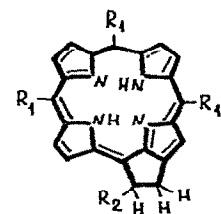
(5), $R = OC_2H_5$

(6), $R = COOCH_3$



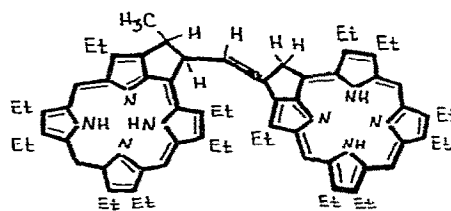
(7), $R_1 = CH=CH_2$, $R_2 = C_2H_5$, $R_3 = CH_3$

(8), $R_1 = CH=CH_2$, $R_2 = CH=CH_2$



(9), $R_1 = CH_2CH_2CH_3$,

$R_2 = CH_2CH_3$



(10)

Compounds 1, 2, 4, 9, 10 were dissolved in EPIP (diethyl ester, petroleum ester, isopropanol 5 : 5 : 2) at concentrations $\leq 10^{-5}$ mol l^{-1} whereas compounds 3, 5, 6, 7, 8 were dissolved in THF–DE (tetrahydrofuran, diethyl ester 1 : 1) at the same concentrations. These solvent mixtures can be frozen as glassy samples at 77 K. The absorption spectra were recorded on a standard SF-10 spectrophotometer or a Beckman-5270. The measurements of fluorescence excitation and emission spectra were made with the aid of an SLM-4800 spectrofluorometer with automatic correction of spectral response.

3. Results and discussion

When analyzing in detail the spectroscopic observations of the investigated compounds and symmetrical porphyrins [3], some spectral peculiarities should be emphasized, which are characteristic only of isocycle-containing porphyrins. Figs. 1–4 give some experimental results obtained for porphyrins with different side and isocycle substituents.

(a) *Absorption spectra* (fig. 1). In most cases, along with the four-band spectrum in the visible region, which is normal for porphyrin free bases [3], an additional real band or shoulder can be observed on the long-wave side of the main 0–0 absorption band at 293 K. The relative intensity of this new band becomes greater on heating the solutions to 500 K. In contrast, the intensity of the additional band decreases as the solutions are cooled to 77 K but this band becomes sharper and narrower (fig. 1b).

(b) *Fluorescence spectra* (fig. 2). At 77 K the spectra exhibit features common to all objects: besides the two bands of the main product, there is a new system of bands which corresponds to the additional absorbing center. The relative intensity of these new bands

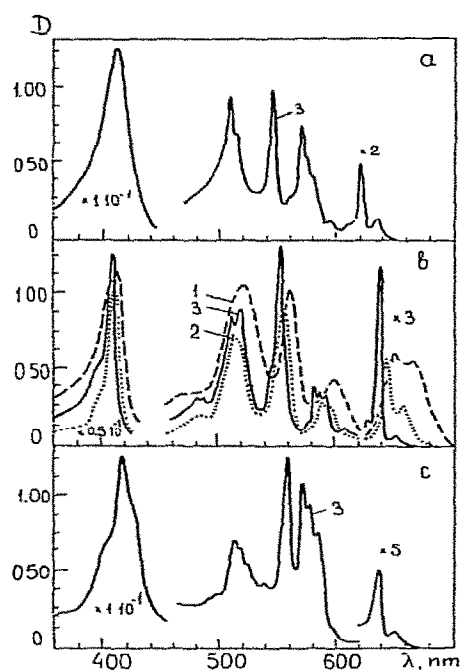


Fig. 1. Absorption spectra of compounds 2 (a) and 9 (b) in EPIP and 5 (c) in THF-DE. (1) 500 K (in methylnaphthalene), (2) 293 K, (3) 77 K.

is strongly dependent on the exciting light wavelength. It should be noted that the fluorescence lifetimes of the 0-0 bands for the two luminescent centers, measured at 77 K, are rather close (for example, in solution of compound 2 $\tau_1 = 21.9$ ns at $\lambda_{\text{reg}} = 622$ nm and $\tau_2 = 20.3$ ns at $\lambda_{\text{reg}} = 637$ nm). At room temperature the spectral pattern is not so clear due to the temperature broadening and shift of the fluorescence bands. Nevertheless, in some cases additional bands can be observed even at 293 K (fig. 2b).

(c) *Excitation spectra of fluorescence (fig. 3).* The analysis of fluorescence excitation spectra recorded at different emission wavelengths shows that the system of fluorescence bands may be assigned only to two fluorescent centers. Comparison between different excitation spectra of fluorescence (fig. 3) and absorption spectra of the same compounds (fig. 1) permits us to conclude that in all the cases the two absorption centers are non-interacting. Clearly, at 77 K the existence of two centers which have their own fluorescence and absorption spectra can be revealed for all

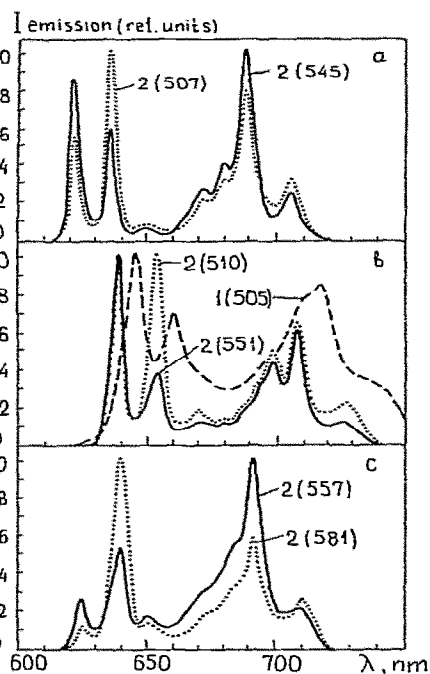


Fig. 2. Fluorescence emission spectra of compounds 2 (a) and 9 (b) in EPIP and 5 (c) in THF-DE at 293 K (1) and 77 K (2). $\Delta\lambda_{\text{excit}} = 4$ nm, $\Delta\lambda_{\text{monit}} = 2$ nm. Excitation wavelengths are shown in parentheses.

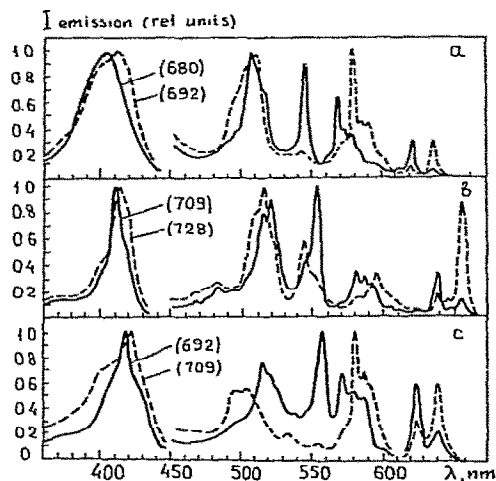


Fig. 3. Fluorescence excitation spectra of compounds 2 (a) and 9 (b) in EPIP and 5 (c) in THF-DE at 77 K. The recording wavelengths are shown in parentheses. $\Delta\lambda_{\text{excit}} = 2$ nm, $\Delta\lambda_{\text{monit}} = 4$ nm. Correction of exciting light spectral distribution has been done up to 600 nm.

Table 1

Maxima of absorption and fluorescence spectra (λ , nm), molar decimal extinction coefficients ($\epsilon \times 10^{-3}$, $\text{l mol}^{-1} \text{cm}^{-1}$, in parentheses) and energy separation ΔE between S_0-S_1 transitions of tautomers in porphyrins with isocycle and their dimer

Compound	T (K)	Absorption					Luminescence		ΔE (cm^{-1})	
		B(0, 0)	$Q_2(1, 0)$	$Q_2(0, 0)$	$Q_X(1, 0)$	$Q_X(0, 0)$	λ_{0-0}	λ_{vib}		
1	293	399(185)	494(15.5)	531(4.0)	566(6.7)	620(7.8)	622	628	230	
	* a)	77	399	499	532	560	612	614		
	**	77	403	496	529	569	622	624		692
2	293	407(199)	508(14.1)	545(13.1)	572(8.6)	627(4.2)	629	696	300	
	*	77	407	507	544	568	621	622		
	**	77	413	504	535	580	636	637		707
5	293	416(200)	519(9.5)	560(15.0)	577(12.5)	628(0.6)	632	696	380	
	*	77	418	514	557	571	623	624		
	**	77	420	507	533	581	638	639		709
7	293	419	524	566	586	639	641	710	320	
	*	77	422	523	568	590	637	638		
	**	77	426	513	546	592	651	652		726
8	293	425	526	568	590	644	649	716	260	
	*	77	429	530	570	588	643	644		
	**	77	431	516	549	606	653	654		730
9	293	414(345)	516(13.0)	554(15.8)	587(5.1)	645(3.4)	646	718	360	
	*	77	412	520	552	582	638	639		
	**	77	413	513	543	594	653	654		728
10	293	397(306)	500(24.0)	534(9.1)	566(11.0)	621(8.6)	623	690	230	
		293	410(291)	506(26.1)	548(18.3)	574(13.6)	628(4.7)	630		700
	*	77	400	500	534	561	613	—		—
	*	77	412	509	549	569	622	624	692	380
**	77	423	501	534	580	637	638	709		

a) * I tautomer; ** II tautomer.

isocycle-containing porphyrins (table 1). The spectral separation between the S_0-S_1 transitions of these centers is different as can be seen from table 1. Therefore, it is difficult for some compounds to find the second center at 293 K, but for compounds 2 and 9, for example, this center can easily be detected even at higher temperatures (413 and 500 K) (fig. 1b).

It should be noted that the existence of different centers is also found in the covalently linked dimer 10. Moreover, the analysis of all data obtained for dimers points clearly towards the efficient transfer of the excited singlet state energy from two centers of compound 1 to two acceptor centers of compound 2

in dimers (these results will be published elsewhere). Increase in the porphyrin concentration by 300–700 times (say, for compounds 1 and 2) does not cause additional changes in electronic spectra as against diluted solutions. If the results obtained from temperature experiments (fig. 1b) and measurements of fluorescence lifetimes in different bands are taken into account, one may conclude that the additional centers observed in solutions of the investigated compounds are not due to porphyrin molecule aggregation. Below we present experimental results which clearly show that the two absorbing and fluorescing centers are due to NH-tautomerism.

(d) *Photoinduced reversible conversion of the centers* (fig. 4). Because of the intrinsic asymmetry caused by the isocyclic ring, the tautomers in the investigated compounds are chemically inequivalent and can absorb at rather different frequencies (see table 1). Therefore, it is possible to realize transformation between the two tautomers, which can be achieved by irradiating either of them in the region of the priority absorption. As can be seen from fig. 4, the fluorescence intensity of the first tautomer decreases in time upon excitation into its absorption band by constant (polarized or non-polarized) light. At the same time, the band of the first tautomer in the fluorescence excitation spectra decreases while that of the other increases. The reverse transformation can be realized by exciting the solution into the absorption band of the second tautomer. It is essential that we could observe in such experiments not only a decrease in the fluorescence intensity of the first tautomer, but an increase in the fluorescence intensity of the other, too (fig. 4a, curve 3). Consequently, this photoprocess is exactly phototransformation and not photodestruction.

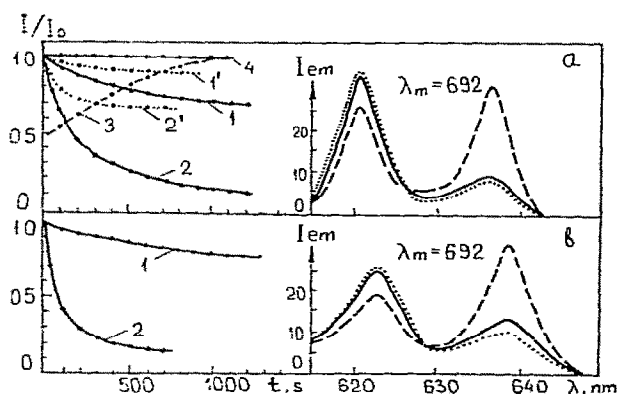


Fig. 4. Changes of fluorescence intensity and fluorescence excitation spectra of compounds 2 in EPIP (a) and 5 in THF-DE (b) with irradiation time at 77 K. $\Delta\lambda_{\text{excit}} = 4$ nm, $\Delta\lambda_{\text{monit}} = 4$ nm. (a) (1), (1'): $\lambda_{\text{ex}} = 621$ nm, $\lambda_{\text{mon}} = 690$ nm; (2), (2'): $\lambda_{\text{ex}} = 636$ nm, $\lambda_{\text{mon}} = 690$ nm (1' and 2' - deuterated compound 2 in THF-DE); (3): $\lambda_{\text{ex}} = 622$ nm, $\lambda_{\text{mon}} = 707$ nm; (4): polyvinylbutyral film as a solvent, $T = 293$ K, $\lambda_{\text{ex}} = 627$ nm, $\lambda_{\text{mon}} = 697$ nm. (b) (1): $\lambda_{\text{ex}} = 623$ nm, $\lambda_{\text{mon}} = 692$ nm; (2): $\lambda_{\text{ex}} = 637$ nm, $\lambda_{\text{mon}} = 692$ nm. Excitation spectra: — initial; - - - after irradiation into the absorption band of the first tautomer; ... after irradiation into the absorption band of the second (long-wavelength) tautomer.

The rate of transformation under the same excitation conditions is greater for long-wave tautomers than for short-wave ones, which is due to the existence of a potential barrier at photoinduced NH-proton jumping at 77 K. From the temperature dependence of the absorption spectra of compound 9 we found that the enthalpy of activation was $\Delta H_{\text{NH}} \approx 530-570$ cm⁻¹ in the ground state.

We have also investigated the effect of deuterium substitution of the inner protons in the molecule center. For example the addition of deuterioethanol to THF-DE solution of compound 2 causes a significant difference between the kinetic curves and, consequently, the quantum efficiency of photoprocesses as compared with a similar case where normal ethanol is added (fig. 4a). This fact can readily be associated with the inhibition of ND-tautomerism as against NH-tautomerism due to the growth of the mass of the jumping particles. Additional evidence of the NH-tautomerism process is the observation of only one absorbing and luminescing form in solutions of the Zn-complex of compound 2 and its diprotonated derivative and the absence of any phototransformation processes under similar conditions. Finally, we have not observed any photoinduced transformations of the two tautomers of compound 2 in rigid films of polyvinylbutyral at 293 K. This latter result is due to the quick thermal migration of inner protons, which inhibits the photoselection of individual tautomers. So, directing our attention to the experimental part of the present work, it should be noted that for isocycle-containing porphyrins and their dimers, the spectral and energy characteristics of individual NH-tautomers can be detected with assurance when using normal electronic spectra. These objects are fairly convenient for the study of the detailed mechanism of tautomer photoinduced transformation. Such experiments are performed in our laboratory.

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