LOW-TEMPERATURE POLARIZATION SPECTRA OF ASYMMETRIC AZA-BENZOPORPHYRINS AND THEIR METAL DERIVATIVES

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Abstract

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LOW-TEMPERATURE POLARIZATION SPECTRA OF ASYMMETRIC AZA-BENZOPORPHYRINS AND THEIR METAL DERIVATIVES

The structure of the porphyrin ring, which is the chromophore of the most important natural pigments, permits a number of structural variants realized in synthetic compounds of the tetrazoporphin, tetrabenzoporphin, and phthalocyanine types. A spectroscopic study of compounds of this type makes it possible to establish correlations among porphyrins, azaporphyrins, benzoporphyrins, and aza-benzoporphyrins, which is essential for understanding the electronic structure of the porphyrin ring.

The electronic absorption spectra of asymmetric aza derivatives of tetrabenzoporphin described in the literature indicate the inhomogeneity of the compounds studied ([1]-[3]). In our laboratory these compounds were apparently isolated in pure form for the first time. The present communication gives the results of a study of the low-temperature polarization spectra of the indicated aza-benzoporphyrins and their magnesium complexes. As is known, Vavilov' s method of polarization spectra ([4], [5]) substantially supplements the information obtained from absorption and emission spectra, providing data on the relative orientation of molecular oscillators.* The effectiveness of the low-temperature method for measuring polarization spectra in the case of porphyrin derivatives was shown in work ([6]). According to the presently accepted interpretation of the electronic spectra of porphyrins ([7]-[11]), 4 electronic transitions appear in the electronic absorption spectra of porphyrin derivatives, 2 of which are responsible for the intense Soret band, and 2 for the weak visible bands (aza and benzo substitution removes the quasi-forbidden character of the first two transitions and the corresponding 0-0 bands become stronger). In the case of metalloporphyrins (symmetry D_{4h}), the excited electronic states are doubly degenerate, which leads to a decrease in the number of bands in the spectrum (the bands merge as the symmetry increases). Some puzzlement in this connection was caused by the absence of signs of splitting of the long-wavelength band into two components in "obviously" asymmetric (judging from the set of peripheral substituents) metalloporphyrins ([12]).

Figure 1

Figure 1: Figure 1

In the case of metal derivatives of aza-benzoporphyrins, the perturbation introduced by aza substitution is sufficiently large, and even at room temperature, in the spectra of compounds not possessing fourth-order symmetry, 2 bands are observed instead of one in the highly symmetric compound. For example, in Mg-TBP one intense 0–0 band is observed in the absorption spectrum at 636 mμ, whereas in Mg-MATBP there are 2 intense bands at 650 and 633 mμ. The symmetry of the molecules studied is as follows: 1) for metal derivatives: monoaza C_{2v}, trans-diaza D_{2h}, cis-diaza C_{2v}, triaza C_{2v}; 2) for free bases: monoaza C_s, trans-diaza C_i, cis-diaza C_{2v}, triaza C_s.

The polarization spectra of the magnesium complexes of monoazatetrabenzoporphine and triaza-tetrabenzoporphine are shown in Fig. 1. For diaza compounds, qualitatively analogous results were obtained (isomeric diaza compounds cannot be separated, and when working with a mixture it is impossible to obtain quantitative data on the degree of polarization). It is clear from the figure that the 2nd absorption band (adjacent to the long-wavelength band) corresponds to large (in absolute value) negative values of the degree of polarization of fluorescence, close to the theoretically limiting value −1/3 for mutually perpendicular absorption and emission oscillators. Since the oscillator of the 1st absorption band coincides in direction with the emission oscillator, we come to the conclusion that the 1st and 2nd absorption bands are caused by different electronic transitions having close frequency values but polarized mutually perpendicularly. This corresponds exactly to the theoretically expected picture for the lifting of degeneracy in the transition from symmetry D_{4h} to symmetry C_{2v} or D_{2h}. We add that in the fluorescence spectra of aza-benzoporphines there is only one intense band; mirror symmetry of the spectra is absent, which confirms the assignment of the 2nd intense absorption band to the 2nd electronic transition.

Fig. 1. *a*—Mg-monoaza-tetrabenzoporphine; *b*—Mg-triaza-tetrabenzoporphine. *I*—absorption spectra; *II*—polarization spectra

These data make it possible to assert that, in the above-mentioned metalloporphines with an asymmetric system of lateral substituents, splitting of the visible bands is not observed because the effect is small. We note that in azoloporphines without benzene rings, splitting of the long-wavelength band is not detected at room temperature (^{13}).

In the region of the Soret band of Me-aza-benzoporphines, the polarization

* By a polarization spectrum we mean, as is customary (^{5}), the dependence of the degree of polarization of fluorescence on the wavelength of the exciting light.

Fig. 2

Figure 2: Fig. 2

data also indicate the presence of two components of the split initial degenerate level of Me-tetrabenzoporphine. The same distinct splitting is observed in the Soret band of metal-free tetrabenzoporphine (symmetry D_{2h}) (14). However, in the latter case, compared with the metalloporphines studied in the present work, the course of the polarization spectrum is different: the long-wavelength component corresponds to high values of the degree of polarization, and the short-wavelength component to low values. In contrast to this, the perturbation of the conjugated metalloporphine system introduced by asymmetric aza substitution leads to a course of the polarization spectrum in the Soret-band region opposite to that observed in the visible region. In Platt' s notation* (7), for Me-aza-benzoporphines the sequence Q_x, Q_y, B_y, B_x is obtained. Naturally, it should be considered—one may consider that the x axis, along which the transition to the Q_x state is polarized, runs, in the case of the monoaza compound, along the symmetry axis C_2, i.e., through the nitrogen bridge, and in the case of the triaza compound —perpendicular to it, i.e., through two nitrogen bridges, since successive aza substitution leads to a gradual shift of the first band to the long-wavelength side from tetrabenzoporphin to phthalocyanine (an oscillator passing through a nitrogen bridge "feels" the aza substitution more strongly, as it were, and corresponds to the long-wavelength band). It is therefore clear why the B_x band, polarized in the same way, is shifted more strongly to the short-wavelength side: aza substitution is always accompanied by a shift of the Soret band into the ultraviolet region.

Fig. 2. *a*—monoaza-tetrabenzoporphin; *b*—triaza-tetrabenzoporphin. *I*—absorption spectra; *II*—polarization spectra

In the absorption spectrum of Mg-triaza-tetrabenzoporphin there is a weak but distinct band near 450 mμ, which becomes stronger as the temperature is lowered (apparently owing to narrowing). This band, as shown by investigation of the fluorescence spectrum upon excitation in this band and of the fluorescence excitation spectrum, does not belong to an impurity. It corresponds to sharply negative polarization, which indicates a perpendicular orientation of the corresponding oscillator relative to the oscillator of the first band. We suppose that this band belongs to an $n \to \pi^*$ transition, which, as is known, should be polarized perpendicular to the plane of the molecule. If this band belonged to a $g \to g$ transition, forbidden for D_{4h} symmetry but becoming allowed in the

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* In these designations, the letter Q corresponds to weak bands in the visible region, the letter B to the Soret band, and the subscripts indicate the polarization of the transition. When the quasi-forbiddenness is lifted, this system of notation retains limited applicability.

absence of a center of symmetry, then one would expect the same band in Mg-monoaza-tetrabenzoporphin, which is not observed. Transitions of the $n \to \pi^*$ type in metal complexes of aza-porphyrins are possible owing to the presence of tertiary nitrogens having two unshared $2s$-electrons.

For the free bases, the polarization spectra (Fig. 2) are in general analogous to the polarization spectra of tetrabenzoporphin ([14]) and phthalocyanine ([15]) and confirm the general picture of four-electron transitions responsible for the visible bands and the Soret band. The complication of the Soret band is accompanied by a corresponding complication of the polarization spectrum, which at present is still difficult to interpret, despite the use of the low-temperature measurement technique.

In the visible region, for monoaza-tetrabenzoporphin the following circumstance attracts attention: the degree of polarization reaches high positive values, close to 1/2 (the limiting value for

set of linear oscillators) in the region of the 1st electronic transition, whereas in the region of the 2nd transition it is close to zero.

The first fact leaves no doubt as to the applicability of the linear-oscillator model in the present case; the second, in combination with the data described above for the metal derivatives, apparently indicates that the angle between the 1st and 2nd oscillators is not close to 90°, as is the case in systems with second-order symmetry. In the region of the Soret band the values of the angles between the oscillators are different, which makes interpretation difficult.

Often, especially in the foreign literature, the polarization spectra of conjugated systems are interpreted in terms of a set of electronic oscillators oriented along two mutually perpendicular directions in the plane of the molecule. The observed deviations from +1/2 and −1/3 are explained by the presence of depolarizing factors and by overlap of the regions of different electronic transitions. In other words, deviations of the angles between oscillators, determined from the Levshin-Perrin formula (16)

$$P = (3\cos^2\alpha - 1)/(\cos^2\alpha + 3),$$

from the values $\alpha = 0$ and $\alpha = 90^\circ$ are not regarded as significant. Our data show that for asymmetric molecules such an approach is not always justified, and that any values of the angles between oscillators determined from the classical Levshin-Perrin formula may have a real physical meaning.

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