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Abstract

Full Text

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ANISOTROPY OF OPTICAL TRANSITIONS

IN MOLECULES OF METALLOCHLORINS AND CHLOROPHYLL

The hydrogenation of one of the pyrrole rings in the porphyrin macrocycle, leading to the structure of dihydroporphyrin (chlorin), is accompanied by sharp changes in the electronic spectra (see the review ([1])), the most important of which is the appearance of an intense long-wavelength absorption band in the red region of the spectrum. Despite considerable progress in the understanding of the electronic spectra of porphyrins, the spectra of chlorins and metallochlorins, including that of the most important photosynthetic pigment—chlorophyll—still cannot be regarded as interpreted with sufficient reliability. If in the spectra of chlorins the "porphyrin" structure is preserved in the blue-green region of the spectrum, then upon introduction of a metal it disappears, and it is difficult to compare the visible spectra of metallochlorins and metalloporphyrins (at the boundary between the visible and ultraviolet regions, in all the cases indicated there is an intense Soret band characteristic of the porphyrin ring).

Fig. 1. Polarization spectrum (*a*) and absorption spectrum (*b*) of Zn-tetraphenylchlorin at 77°K

Valuable information on the nature of electronic bands is provided by Vavilov's method of polarization spectra ([2,3]), which reflects the vector properties of electronic transitions. A polarization spectrum, as is known, is the dependence of the degree of polarization of fluorescence on the wavelength of the exciting light; the degree of polarization of fluorescence is different upon excitation in different absorption bands because of the presence of a certain angle α between the

Fig. 2

Figure 2: Fig. 2

emission oscillator and the corresponding absorption oscillator. The quantity P is related to α by the relation

$$P = \frac{3\cos^2\alpha - 1}{\cos^2\alpha + 3},$$

called the Levshin–Perrin formula (^{4}). Fine details of the polarization spectrum appear at low temperatures (for porphin and chlorin such measurements were carried out in (^{5})).

In the present communication we give the results of polarization measurements for metallochlorins. The measurements were carried out at liquid-nitrogen temperature on an apparatus with two monochromators, analogous to that described in (^{5}). The spectral width of the slits was usually 2-5 mµ. As solvent we used a mixture of isopropyl alcohol, diethyl ether, and petroleum ether $(2:5:5)$.

Figure 1 presents the polarization spectrum of Zn-tetraphenylchlorin. It is seen from the figure that, upon moving from the long-wavelength band toward shorter wavelengths, the degree of polarization of fluorescence decreases sharply and almost reaches the theoretically limiting value $P = -1/3$ for $\alpha = 90°$ (upon excitation at the maximum of the 2nd absorption band). In the fluorescence spectrum there is no band mirror-symmetric to the 2nd absorption band. In addition, electron-vibrational transitions with frequencies up to 1000 cm^{-1} in molecules of porphyrin derivatives are usually polarized pa-

parallel to the purely electronic one (^{5}), while the distance between the 1st and 2nd absorption bands of Zn-tetraphenylchlorin is only 700 cm^{-1}. The experimental data thus lead us to the conclusion that the 2nd absorption band of Zn-tetraphenylchlorin belongs to an independent (second) electronic transition. This interpretation was proposed earlier by Gouterman, who proceeded from the similarity in position of the 2nd band of metal derivatives of tetraphenylchlorin and the long-wavelength absorption band of Me-tetraphenylporphyrins (^{6}). In the region of the Soret band, polarization data convincingly indicate the presence of two electronic transitions.

Fig. 2. Polarization spectrum (a) and absorption spectrum (b) of chlorophyll a at 77°K

The polarization spectrum of Zn-chlorin (unsubstituted), unfortunately, does not make it possible to establish the localization of the 2nd transition, which is apparently connected with its low intensity. In turn, this may be connected with the low intensity of the corresponding 0—0 transition in metal-free chlorin (^{1},^{5}).

In the metalloporphyrin molecule there are 2 electronically excited levels that give transitions in the visible region of the spectrum (including the Soret-band region), and these levels are doubly degenerate. In metallochlorin, as follows from the experimental data presented, the number of excited levels is doubled, which is natural to associate with the lowered symmetry of the system (C_{2v}), in which degeneracy is impossible. In this respect there is an analogy between metallochlorins and metal derivatives of asymmetrically substituted aza-benzoporphyrins investigated in ([7]).

A special feature of metallo-tetraphenylchlorins is that removal of the degeneracy is accompanied by removal of the quasi-forbidden character of the 1st electronic transition, while the frequency and intensity of the 2nd electronic transition are preserved. Similar properties are possessed by the second electronic transition in metal-free compounds: bands III and IV, belonging to the second transition in the porphyrin molecule, are practically not shifted upon hydrogenation, and the course of the polarization spectrum in this region is preserved ([1],[5]). Thus, in all free porphyrin bases and in metalloporphyrins substituted at the methine bridges,* hydrogenation of one of the pyrrole rings does not affect the frequency of the 2nd electronic transition. It seems tempting to generalize this conclusion to all metallochlorins.

For the most important of the tetrapyrrole pigments—chlorophyll a, which is a complex metallochlorin—reasoning by analogy, one may expect that the second electronic transition has a frequency close to that of the 0—0 transition of protochlorophyll (λ about 625 mμ). Indeed, in some solvents, for example in pyridine, between the 0—0 band and the vibrational band of the 1st electronic transition, a distinct absorption band appears (in this case the absorption bands in the yellow-green region of the spectrum, the characteristic "staircase" of bands decreasing in intensity with decreasing λ, disappear—see Fig. 2b). We found a similar type of spectrum, apparently belonging to disolvates, in frozen alcohol-in glass and investigated the polarization spectrum (Fig. 2). The data obtained are analogous to the results obtained for Zn-tetraphenylchlorin, with the difference that large (in absolute value) negative values of P are not reached. In the fluorescence spectrum the corresponding mirror-symmetric band is likewise absent. Consequently, the band in the solvate spectrum does indeed belong to the 2nd electronic transition.

The question arises: where is the 2nd transition located in the "ordinary" spectrum of chlorophyll, where the band described is absent and there is a "staircase" of bands decreasing in intensity? In this case the polarization measurements indicate localization of the 2nd electronic transition in the region of the 3rd absorption band ([1]). However, it is not excluded that in the present case the 2nd transition is still localized between the 1st and 2nd absorption bands, but

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* The spectroscopic effect of phenyl groups is close to the effect of alkyl groups ([8]); the Zn-tetraphenylchlorin studied by us is a typical representative of meso-substituted metallochlorins.

has a reduced intensity and is masked by the vibrational structure of the 1st transition. In such a case the 3rd band (580 mμ) is a vibrational satellite of this masked band. The question requires further experimental study. We add that the disappearance of the "staircase" upon solvation is more likely evidence of a shift of the band from 580 to 635 mμ, but at the same time the magnitude of the shift itself (55 mμ, i.e., about 1500 cm^{-1}) seems too large for a shift of an electronic level upon solvation at the magnesium atom.

It should be noted that at room temperature (in castor oil) the polarization spectrum of chlorophyll a has near 630 mμ a small "dip," which becomes more noticeable at −110° (in an ethanol—ethylene glycol mixture). With a further lowering of the temperature to 77°K, the value of P at the minimum almost reaches zero. It is interesting that in chlorophyll a', which differs only slightly from chlorophyll a in the structure of the iso-cycle, this effect is expressed somewhat more clearly, which apparently is connected with inclusion of the cyclopentanone ring in the conjugated system.

In the region of the Soret band of chlorophyll, the polarization data indicate the presence of two electronic transitions, as in other metallochlorins. The course of the polarization spectrum in this region may be interpreted as follows. Apparently, each of the two components of the Soret band has intense vibrational satellites, so that the polarization minimum corresponds to the O—O-transition of the first component (absorption maximum 450 mμ). The 1st polarization maximum corresponds to the superposition of the O—O-transition of the 2nd component and the vibrational structure of the 1st component (absorption maximum 430 mμ), while the region of high polarization near 380 mμ corresponds to the vibrational structure predominantly of the 2nd component.

In the polarization spectrum of chlorophyll there are no regions of negative polarization. Apparently, this is due not only to some broadening of the bands (in comparison with other chlorins and metallochlorins), but also to a real difference of the angles a from 90°, which is associated with the strong asymmetry of the molecule. Similar facts were noted by us for asymmetric aza-benzoporphyrins (^{7}).

Thus, the polarization data indicate a relationship between the excited electronic states of metallochlorins and metalloporphyrins, with the 2nd electronic transition tending to retain its frequency upon hydrogenation of one of the pyrrole rings.

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Note: Figure translations are in progress. See original paper for figures.