Physics

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1965

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Abstract

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Quasi-Line Electronic Spectra of Tetrabenzoporphin

The study of the influence of benzo substitution on the spectroscopic properties of the porphin ring is of great importance for elucidating the electronic structure of porphyrins and chlorophyll. Spectroscopic study is also of interest in connection with the semiconducting properties discovered in phthalocyanines. In the present work the quasi-line absorption and fluorescence spectra of tetrabenzoporphin—the progenitor of the benzoporphyrin series—have been studied.

Tetrabenzoporphin was obtained by us by a method analogous to that of Linstead and Weiss (^{1}), by fusing cadmium acetate with 3-carboxymethylphthalimidine at a temperature of 340°. The product (Cd-tetrabenzoporphin) was first purified by precipitating impurities from a pyridine solution upon addition of a fourfold amount of ether and was chromatographed on an alumina column, developing with a pyridine–ether mixture (1 : 4). Dissolution of the purified cadmium complex in concentrated sulfuric acid, followed by neutralization with ammonia, gave tetrabenzoporphin of a high degree of purity.*

In view of the poor solubility of tetrabenzoporphin in normal hydrocarbons, the substance was first dissolved in chlorobenzene and introduced into the hydrocarbon as a small addition of solution. The quasi-line spectra were photographed on an ISP-51 glass spectrograph with a UF-84 long-focus camera.

The absorption spectrum of tetrabenzoporphin at room temperature, the long-wavelength part of which is shown in Fig. 1a, differs markedly from the spectra of porphyrins, although in the region bordering on the ultraviolet in both cases there is an intense band ("Soret band"), split in the case of tetrabenzoporphin into two components. Instead of the four weak bands in the visible region characteristic of porphyrins, tetrabenzoporphin exhibits two intense bands, the second band moreover having an unusual structure (three maxima). However, as polarization measurements have shown (^{2}), there is a deep analogy between the spectra of porphyrins and tetrabenzoporphin: in both cases, in the visible region, including the region of the Soret band, four electronic transitions appear, each with its own vibrational structure. The changes in the level scheme reduce to small changes in the distances between levels, but the transition probabilities

Fig. 1

Figure 1: Fig. 1

change more substantially (the quasi-forbidden character is removed from the first and second electronic transitions). As in porphyrins, the second transition is polarized perpendicular to the first; it was shown that the third electronic transition (the first component of the Soret band) is polarized in the same way as the first, and the fourth transition in the same way as the second (^{2}). The fluorescence spectrum of tetrabenzoporphin at room temperature has one intense band with vibrational structure (Fig. 1a).

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* As studies of the quasi-line spectra have shown, the product obtained by the Linstead and Weiss method, i.e., using zinc acetate, contains a small amount of impurity which could not be completely separated either by vacuum sublimation or by chromatography. At room temperature this impurity is almost unnoticeable, and the spectra of preparations obtained by the different methods are practically identical.

Under the conditions of the Shpolskii effect, for all four electronic transitions one observes splitting of the spectral bands into individual quasi-lines, which is shown schematically in Fig. 1. As can be seen from the figure, the quasi-line absorption and fluorescence spectra correspond well to the spectra at room temperature, which indicates the monomolecular nature of the absorbing and emitting centers that give quasi-line spectra.* A second, still more convincing argument in favor of this assertion is the considerable change in the quasi-line spectrum on going from *n*-octane to *n*-decane (analogous reasoning was used in work (^{4}) for coronene).

Fig. 1. *a*—absorption and fluorescence spectrum of tetrabenzoporphin in pyridine at room temperature; *b*—schematic representation of the main components of the splitting of the fluorescence spectrum in *n*-octane; *v*—the same for the absorption spectrum, first electronic transition; *g*—the same for the absorption spectrum, second electronic transition (wavelengths in nanometers)

The quasi-line fluorescence spectrum of tetrabenzoporphin in *n*-octane at 77° K is presented in Fig. 2a. The spectrum begins with a group of lines, among which the most intense are the lines forming the doublet 657.98/659.38 nm. This doublet structure is then repeated throughout the entire spectrum with unchanged spacings between components, i.e., two series are obtained, displaced relative to one another by $\Delta\nu = 32$ cm^{-1}.

The quasi-line absorption spectrum was studied in all four electronic transitions observed in the visible region of the spectrum. The absorption spectrum in the region of the first transition (Fig. 2b), analogous to the fluorescence spectrum, consists of doublets and begins with two very intense lines, which coincide reso-

Fig. 2

Figure 2: Fig. 2

nantly with the head multiplet of the luminescence spectrum; this permits the given group of lines to be assigned to a purely electronic transition.

At 600 nm there is observed a very strong and somewhat less sharp single line, which has no counterpart in the luminescence spectrum. In accordance with what was said above about the nature of the band near 600 nm, it is natural to assign this line to a purely electronic transition to the second excited state. Transitions to vibrational sublevels of the second excited state also correspond to singlet lines in the quasi-line absorption spectrum (Fig. 1g).

* We note this circumstance in connection with the poor solubility of tetrabenzoporphin in *n*-octane and the need to use artificial methods for preparing solid solutions (see text). For other substances the molecular nature of the quasi-lines has been established (see ([3])).

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Fig. 2. Quasilinear spectra of tetrabenzoporphin in *n*-octane at 77° K: fluorescence spectrum (*a*), absorption spectrum in the region of the first electronic transition (*b*), absorption spectrum in the region of the third and fourth electronic transitions (*c*) (wavelengths in nanometers)

Figure 2b presents the quasi-line spectra in the region of the third and fourth transitions. The structure of the multiplet splitting in them repeats the pattern observed for the first and second transitions. The lines belonging to the third electronic transition form doublets, and the distance between the components of the doublets also turns out to be equal to 32 cm^{-1}, while the fourth transition is represented by single lines.

Table 1

Fluorescence, cm^{-1}	Fluorescence, int.	Absorption, electronic transition 1, cm^{-1}	Absorption, electronic transition 1, int.	Absorption, electronic transition 2, cm^{-1}	Absorption, electronic transition 2, int.	Absorption, electronic transition 3, cm^{-1}	Absorption, electronic transition 3, int.	Absorption, electronic transition 4, cm^{-1}	Absorption, electronic transition 4, int.
118	med.			113	int.				
127	med.	126	very weak	124	med.	121	weak		
218	int.	218	int.	211 226	med. int.	215	med.	220	med.

Fluorescence, cm^{-1}	Fluorescence, int.	Absorption, electronic transition 1, cm^{-1}	Absorption, electronic transition 1, int.	Absorption, electronic transition 2, cm^{-1}	Absorption, electronic transition 2, int.	Absorption, electronic transition 3, cm^{-1}	Absorption, electronic transition 3, int.	Absorption, electronic transition 4, cm^{-1}	Absorption, electronic transition 4, int.
351	very weak			356	weak	338	very weak	334	very weak
449	very weak			450	very weak	435	very weak		
480	v. weak	479	v. weak	478	weak	474	v. weak		
510	very weak					527	v. weak		
566	v. weak	565	v. weak	554	v. weak	553	v. weak	538	v. weak
629	very weak			623	very weak	587	very weak	582	very weak
		673	very weak			664	weak	639	very weak
698	int.	692	med.	702	med.	700	weak	689	very weak
723	med.			721	med.			718	very weak
801	med.	798	weak	804	weak			780	very weak
874	very weak	871	very weak	865	very weak	865	very weak	857	very weak
914	very weak	902	v. weak			901	v. weak	885	very weak
1018	very weak			1002	very weak			1003	very weak
1049	very weak					1024	weak		
1125	weak	1066	med.	1070	very weak				
1156	weak	1116	weak	1116	very weak	1112	v. weak	1117	v. weak
1223	med.	1185	int.	1179	int.			1180	v. weak
1250	med.	1253	very weak	1223	very weak	1244	v. weak	1225	very weak

Fluorescence, cm^{-1}	Fluorescence, int.	Absorption, electronic transition 1, cm^{-1}	Absorption, electronic transition 1, int.	Absorption, electronic transition 2, cm^{-1}	Absorption, electronic transition 2, int.	Absorption, electronic transition 3, cm^{-1}	Absorption, electronic transition 3, int.	Absorption, electronic transition 4, cm^{-1}	Absorption, electronic transition 4, int.
1331	med.	1305	int.	1270	int.	1326	v. weak	1328	v. weak
1344	med.	1343	very weak	1353	very weak			1357	very weak
1418	very weak	1418	very weak	1418	very weak	1407	very weak	1396	very weak
1451	very weak	1448	very weak	1457	very weak				
1492	very weak	1478	very weak	1474	very weak				
1526	very weak	1520	very weak	1513	very weak			1506	very weak
1596	med.	1595	weak			1582	v. weak	1554	v. weak
1624	med.	1620	med.	1609	weak	1613	very weak	1610	v. weak

Designations: very weak —extremely weak, v. weak —very weak, weak —weak, med. —medium intensity, int. —intense.

On the basis of a study of the quasi-line spectra of fluorescence and absorption corresponding to the four electronic transitions, the frequencies of the normal vibrations of tetrabenzoporphin were determined (Table 1). A distinctive feature of the quasi-line spectra of tetrabenzoporphin, in comparison with other porphyrins studied by us, is the less strict fulfillment of the Levshin mirror-symmetry rule. Deviations from mirror symmetry occur both in the frequency values and in the intensities of the lines. In a number of cases these deviations are so large that it becomes difficult to correlate the frequencies of normal vibrations in the ground and first excited states. This difficulty was overcome by comparing the spectra of tetrabenzoporphin with the spectra of Zn-tetrabenzoporphin. It turned out that in the presence of metals the mirror-symmetry rule is fulfilled considerably better, and it is possible to carry out a consistent correlation of the four sets of frequencies observed in the absorption and fluorescence spectra of tetrabenzoporphin and its zinc complex. Thus it was possible to establish a correspondence between the vibrational frequencies 1125; 1223; 1331 cm^{-1} (of the ground state) and the frequencies 1066;

1185 and 1305 cm^{-1} (of the first excited state), and in absorption the corresponding vibronic transitions are considerably more intense. It may be assumed that the enhancement of these lines is connected with the proximity of the second excited electronic level. If this assumption is correct, then the indicated vibrations must be non-totally symmetric (B_{1g}), so that the vibronic wave function has the same symmetry type as the purely electronic wave function of the second excited level, owing to which interaction of the levels is possible. It should be noted that the conclusion that non-totally symmetric vibrations are active in the electronic spectra of tetrabenzoporphin was made by us earlier on the basis of polarization measurements (2). For other vibrations the frequencies in the ground and excited states are approximately the same. The vibrations 127; 218; 698 cm^{-1} in the fluorescence spectrum and the corresponding 126; 218; 692 cm^{-1} in the absorption spectrum, as the most intense and giving combination frequencies, may be assigned to totally symmetric vibrations. On going to higher excited levels the vibrational frequencies are approximately preserved (changes no greater than 30 cm^{-1}).

The data obtained make it possible to clarify the reason for the presence of three maxima in the second absorption band of tetrabenzoporphin. The first maximum corresponds to intense vibronic transitions to the first excited state $\nu^{(1)}_{\text{vib}} = 1185$ and 1305 cm^{-1}. The second maximum corresponds to a purely electronic transition to the second excited state; the third maximum corresponds to a series of vibronic transitions to both excited states ($\nu^{(1)}_{\text{vib}} = 1595$ and 1620, $\nu^{(2)}_{\text{vib}} = 113, 211, 226$ cm^{-1}). On the basis of the spectra obtained, the separations between the electronic levels of the tetrabenzoporphin molecule were determined: $\Delta E_{12} = 1400$ cm^{-1} and $\Delta E_{34} = 850$ cm^{-1}.

The question of the nature of multipletness in quasilinear spectra has been discussed for a long time. On the basis of a comprehensive analysis of experimental data, E. V. Shpol' skii concluded that multiplets correspond to molecules incorporated into the solvent lattice in different ways (3). This conclusion was experimentally confirmed by G. M. Svyashchev (5). This interpretation, however, is contradicted at first glance by the difference in the pattern of multiplet splitting in different electronic transitions, first found for pyrene (6). Our data for tetrabenzoporphin make it possible to express some considerations on this question. As indicated above, the first and third transitions of tetrabenzoporphin are polarized identically, and the second and fourth also identically, but in the perpendicular direction. Comparison of these data with the spectra described indicates that one of the polarizations corresponds to a doublet structure (with $\Delta\nu$ the same), and the other to a singlet structure. In other words, the structure of the multiplet in the case studied by us is determined only by the orientation of the electronic oscillator relative to the molecular axes.

One may imagine different models of incorporation of molecules into a crystalline matrix, when oscillators of one orientation find themselves in similar conditions, while oscillators polarized along the perpendicular molecular axis are in different conditions. Apparently, the interpretation of multipletness as the result of different incorporation of molecules is correct, and the difference between the centers responsible for the separate components of the multiplets is connected with the difference in the orientation of the incorporated molecules.

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Received
3 XII 1964

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