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Intramolecular heavy-atom effect in the photophysics of organic molecules

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Contents

Abstract. **This review systematizes the data on the effect of intramolecular spin – orbit perturbations on the photophysics of organic molecules introduced by heavy atoms (the intramolecular, or 'internal', heavy-atom effect). The focus is on two classes of compounds: (1) halogenated derivatives of aromatic and heteroaromatic compounds and (2) porphin derivatives (halogenated porphyrins and metalloporphyrins). The enhancement of radiative and nonradiative intercombination transitions under the heavy-atom effect is responsible for fluorescence quenching and the shortening of phosphorescence duration. Photophysical investigations show that the transition probabilities in different channels of deactivation of excited electronic states exhibit specific dependence on the structure of heavy-atom bearing molecules. This allows one to acquire information on the spin – orbit interaction in molecules and their electronic structure, and to control the parameters of chromophores and luminophors in optical systems.**

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1. Introduction

The spin – orbit perturbations of electronic states play an important part in the photophysics of molecules. The incorporation of heavy atoms into molecular systems leads to changes in photophysical parameters due to the enhancement of intercombination transitions, which have come to be known as the heavy-atom effect. This effect is said to be intramolecular, or 'internal', when the heavy atoms are chemically parts of the molecules and 'external' when they belong to the environment.

The enhancement of radiative and nonradiative intercombination transitions under the heavy-atom effect is responsible for fluorescence quenching and the shortening of the phosphorescence duration. Photophysical investigations show that the corresponding transition probabilities in different channels of excited-state deactivation exhibit specific dependence on the molecular structure. It is significant that the fluorescence quenching is directly related to the population of the lowest triplet electronic state.

Although the range of effects resulting from the intramolecular spin – orbit perturbations introduced by heavy atoms is not among those that are being intensively studied in the world literature, interest in it persists. With the perfection of experimental techniques and the theory of electronic transitions, the level of investigations and the value of the information gained increase. In principle, with a sufficiently elaborated theory, the internal heavy-atom effect may be employed for experimentally 'probing' the electronic structure of molecules. From the practical stand-

point, it is possible to take on the task of producing materials with predetermined properties. In the investigations of the relation between the luminescence properties and the molecular structure, the factor of heavy atoms is also of paramount importance.

More than 30 years have passed since the publication of monograph Ref. [1], in which much consideration was given to the heavy-atom effect, and there is good reason to review the literature concerned specially with the internal heavy-atom effect and embracing all new results. At the same time, we endeavored to systematize the material beginning with the earliest works. Two classes of objects are considered: (1) halogenated derivatives of aromatic and heteroaromatic compounds and (2) porphyrins and metalloporphyrins — analogues of biologically significant pigments.

2. Brief characterization of the photophysics of molecules

2.1 Photophysics and photochemistry

Relatively recently, the notion of 'molecular photophysics' was formed, which embraces the totality of the processes of the transformation of absorbed light energy in molecular systems and transitions with the absorption of a photon. Previously, these effects were included in the notion 'molecular luminescence'. The term 'photophysics' contrasts with the term 'photochemistry', which embraces light-induced transformations of substances. It is pertinent to note that the cases of rapid reversible photoprocesses (for instance, electron or proton transfer) turn out to be as if they are at the photophysics – photochemistry borderline.

In his basic monograph [2], Academician A N Terenin introduced the term 'photonics of molecules', which unites all the above cases. However, this term has not come into wide use because in engineering, the word 'photonics' applies to instruments and devices reliant on the action of optical radiation.

A significant part in the works on molecular photophysics is occupied by the investigation of organic compounds, i.e., carbon compounds whose molecules contain hydrogen atoms and may also contain the so-called heteroatoms: nitrogen (N), oxygen (O), fluorine (F), etc. From the very name of these compounds, it is clear that many of them are medically and biologically significant. Moreover, they enjoy a wide variety of technical applications — for example, this broad class comprises dyes and high-molecular compounds (polymers).

2.2 Electronic structure and electronic spectra of organic molecules

The commonly studied visible and near-UV spectra of polyatomic molecules are, as a rule, due to the existence of a conjugated bond system in the molecule, i.e., of a 'cloud' of delocalized π-electrons. The number of electronic transitions that manifest themselves in the above spectral ranges is moderate, and therefore the absorption spectra of polyatomic molecules in room-temperature solutions consist of bands or groups of bands belonging to separate electronic transitions. When a group of bands belongs to a common electronic transition and corresponds to vibrational-electronic (vibronic) transitions to the vibrational sublevels of some electronic state, this electronic transition is said to have a vibrational structure.

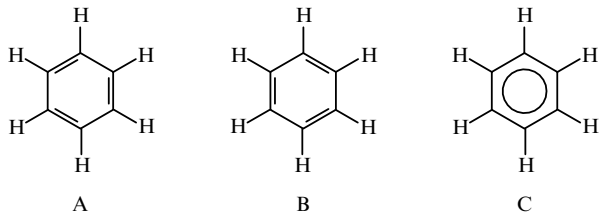

Figure 1. Structural formulas of benzene: A and B — Kekule structures, C — conventional representation of the benzene molecule with the conjugation effect taken into account.

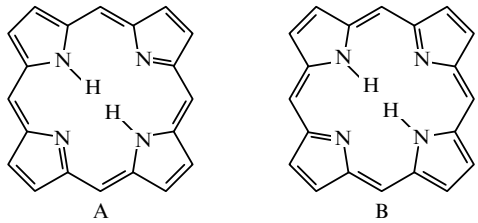

Figure 2. Structure of the porphin molecule: A and B — Kekule structures.

The conjugation effect is normally observed in molecules with alternating single and double bonds and is due to the overlap of atomic orbitals (AOs) of the p_z type, which emerge in double-bond formation, for atoms formally bound by a single bond. As a result, for instance, in the benzene molecule (a six-member cycle), the classical structural formula A with three single and three double bonds is completely equivalent to the structure B in which the bond types are mutually transposed (Fig. 1). (Suchlike structures are referred to as the Kekule structures.) Owing to the conjugation effect, the properties of the bonds C–C and C=C equalize, the π-electrons become delocalized, and the molecule has the D_{6h} symmetry. It is conventional to symbolically represent a complete or partial conjugation by circles, as shown in the structure C. In chemistry, the benzene derivatives are termed aromatic compounds. As indicated in the Introduction, their halogenated derivatives are one of the subjects of this review.

The second class of molecular systems under consideration is the derivatives of porphin, whose molecule can also be represented with the aid of two Kekule structures (Fig. 2).

Porphin has a macrocyclic structure — its molecule consists of four five-member pyrrole rings connected by methine bridges. The porphin derivatives are termed porphyrins or metalloporphyrins when two central hydrogen atoms are replaced with a metal atom. Among metalloporphyrins are the biologically very significant pigments chlorophyll and heme (a constituent of hemoglobin). Typical absorption spectra of porphin and its metal complex are shown in Fig. 3.

The properties of electronic molecular states are the subject under consideration in the quantum theory of molecules, which has received the name quantum chemistry (which may not be quite adequate a term). The reader is referred to monograph Refs [3 – 5].

Quantum-chemical problems are, as a rule, solved in the adiabatic approximation and usually for the equilibrium configuration of a molecule in the ground electronic state. The best way of solution is to find one-electron wave functions — molecular orbitals (MOs). These are then used

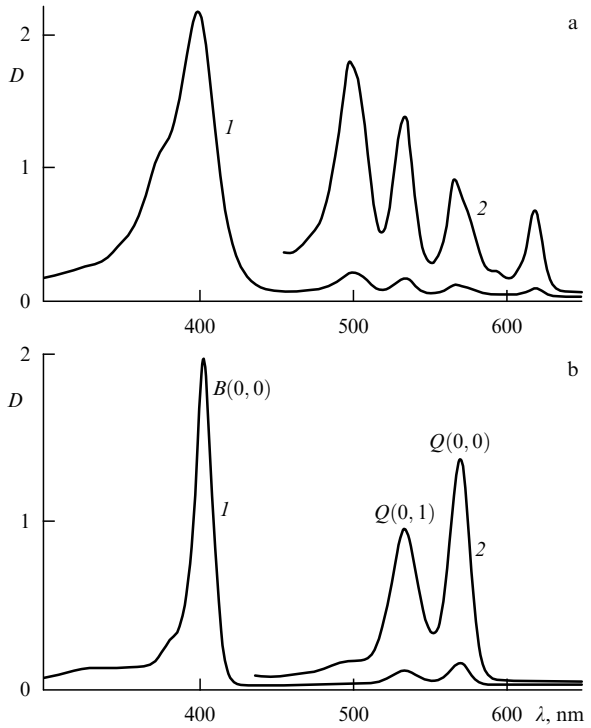

Figure 3. Absorption spectra of octaethylporphin (a) and its zinc complex (b) in chloroform at 293 K. The ordinates of curve *2* are increased ten-fold relative to the ordinates of curve *1*.

to construct the totally antisymmetrized wave function, i.e., the wave function satisfying the generalized Pauli principle, to be used as the initial function for subsequent approximations. In conjugated bond systems, there emerge delocalized MOs, which, like p_z-AOs, are antisymmetric about the molecular plane and are termed π-orbitals. The energy difference between the upper filled (electrons occupying one-electron levels according to the Pauli principle) and the lower unfilled π-MOs, which defines the frequencies of long-wavelength electronic transitions in the zeroth approximation, turns out to be relatively small. This is precisely the reason why absorption is observed in the visible and near-UV spectral ranges, as noted at the beginning of Section 2.2.

In the ground state of a neutral organic molecule containing no atoms with incompletely filled d and f shells, all MOs are filled with pairs of electrons with antiparallel spins, the total spin of the system is zero, and hence the ground state is singlet. It is denoted by S_0.

In the excitation of a molecule, which may be roughly treated as the transition of one electron to an unfilled MO, the spins of 'optical' electrons may be either antiparallel or parallel, which gives either a singlet ($S = 0$) excited state S_i or a triplet ($S = 1$) excited state T_i, respectively. Owing to the exchange interaction, the energy of the T_i state is lower than that of the S_i state (the Hund rule). A more rigorous consideration leads to precisely the same conclusion about the multiplicity of excited states, but the correspondence of the spatial wave functions of the states S_i and T_i is lost. It can only be claimed that there is a set of singlet excited states $S_1, S_2, \ldots$ and a set of triplet excited states $T_1, T_2, \ldots$. A situation is possible where there is an approximate correspondence in the electronic structure of the singlet and triplet states but the order in which the state energies increase is different for the singlet and triplet sets.

2.3 Basic photophysical processes and parameters

It is the practice to describe the molecular luminescence of organic compounds employing the so-called three-level diagram, which is commonly attributed to A Jabłoński [1]. Recently, however, B Nickel in a background review [6, 7] showed that a significant part in the determination of the importance of the three-level diagram was played by the investigations and ideas of F Perrin published in Ref. [8] four years earlier than Jabłoński's famous publication in 1933 [9], and by a still earlier paper by P Pringsheim and S I Vavilov on phosphorescence polarization [10]. Furthermore, it was not until 1943 that the triplet nature of the metastable level was substantiated by A N Terenin [11]; subsequently, it was amply borne out experimentally (see Ref. [1]). To this must be added that a more complete level diagram should include vibrational sublevels and the upper S_i and T_i levels: although they are not the 'working' levels in the emission of light, they may participate in absorption and play a significant part in emission as perturbing levels and as intermediate stages of photoprocesses. This more complete diagram of levels and photoprocesses is shown in Fig. 4 (borrowed from Ref. [12]).

For simplicity, the vibrational structure is limited to one active vibration. Wavy arrows in the diagram indicate nonradiative processes significant for molecular photophysics and straight arrows stand for transitions involving the absorption and emission of light.

The transitions from the ground electronic state S_0 to excited singlet electronic states S_i correspond to the ordinary stationary absorption. The downward transitions from the S_1 state to the S_0 state give fluorescence. In contrast to the case of atoms and simple molecules in the gas phase, the excitation of high electronic levels in a sufficiently complex polyatomic molecule in solution and even in the gas phase occurs with the emission from the S_1 level rather than from the level to which it was excited. This is due to a high rate ($10^{12} - 10^{13}$ s^{-1}) of nonradiative transitions $S_i \rightsquigarrow S_1$ (it is

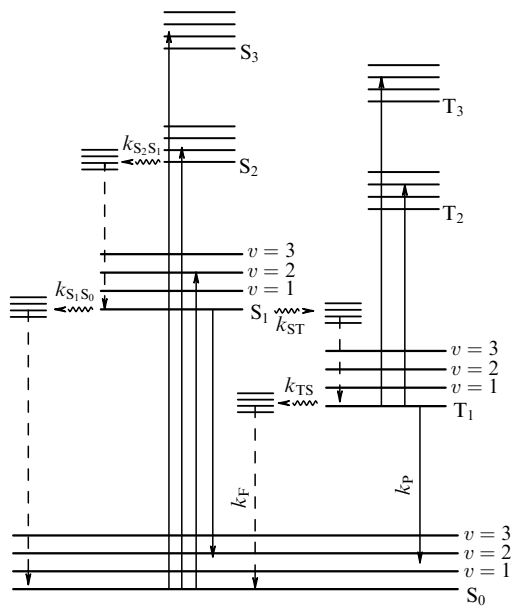

Figure 4. Diagram of energy levels and primary photophysical processes in an organic molecule. Wavy arrows indicate nonradiative processes, straight arrows symbolize transitions involving absorption and emission of light, and dashed arrows symbolize vibrational relaxation.

conceivable that they occur in a cascade manner: $S_i \rightsquigarrow S_{i-1}$, $S_{i-1} \rightsquigarrow S_{i-2}, \ldots, S_2 \rightsquigarrow S_1$) [13, 14]. The nonradiative transitions between different electronic levels without a change in spin are conventionally referred to as internal conversion. The distribution of excited molecules over the vibrational sublevels of the S_i state is controlled by yet another nonradiative process — vibrational relaxation. If the vibrational relaxation time is shorter than the lifetime of a given electronic state, it is commonly said that thermalization of the state occurs: the distribution over vibrational sublevels is characterized by a specific temperature (in solution, by the same temperature as the ambient temperature). As a result of the rapid and efficient course of internal conversion and vibrational relaxation, the fluorescence photons are emitted from the thermalized level S_1 irrespective of the level to which the molecule is excited. This is the reason why the spectrum of fluorescence and its quantum yield are independent of the wavelength of exciting light.

The quantum yield of the photoprocess is known to be the ratio between the number of events leading to a specific result and the number of absorbed photons. For instance, the quantum yield of fluorescence in the stationary mode is the ratio between the number of photons emitted per unit time and the number of photons absorbed during the same period. The independence of the luminescence quantum yield from the exciting light wavelength λ_{ex} is referred to as the Vavilov law (the term adopted in the Soviet and post-Soviet literature).

Transitions between singlet and triplet states are forbidden by the nonrigorous selection rule $\Delta S = 0$, called the intercombination selection rule. This prohibition is removed by the spin – orbit interaction. The probability of the nonradiative transition $S_1 \rightsquigarrow T_1$, called intersystem crossing, therefore turns out to be several orders of magnitude lower than the probability of the internal conversion $S_2 \rightsquigarrow S_1$, but can nevertheless efficiently compete with the radiative transition $S_1 \to S_0$. On the basis of a wealth of experimental data, Ermolaev and Sveshnikova formulated the rule $\varphi_F + \varphi_T = 1$ (where φ_F is the quantum yield of fluorescence and φ_T is the quantum yield of interconversion), which signifies that the intersystem crossing is the main channel of nonradiative deactivation of the S_1 level and the internal conversion $S_1 \rightsquigarrow S_0$ is insignificant [15]. In view of this, the expression for the fluorescence quantum yield

$$\varphi_F = \frac{k_F}{k_F + k_{S_1S_0} + k_{ST}}\,, \tag{1}$$

where k_F is the probability (the rate constant) of the spontaneous emission $S_1 \to S_0$, $k_{S_1S_0}$ is the probability of the internal conversion $S_1 \rightsquigarrow S_0$, and k_{ST} is the probability of the interconversion $S_1 \rightsquigarrow T_1$, can be rewritten as

$$\varphi_F \approx \frac{k_F}{k_F + k_{ST}}\,. \tag{2}$$

The corresponding formulas for the lifetime of the S_1 state, i.e., the fluorescence duration τ_F, are given by

$$\tau_F = \frac{1}{k_F + k_{S_1S_0} + k_{ST}}\,, \tag{3}$$

$$\tau_F \approx \frac{1}{k_F + k_{ST}}\,. \tag{4}$$

The direct $T_i \leftarrow S_0$ transitions are responsible for a weak absorption that is difficult to detect. By contrast, the radiative transitions $T_1 \to S_0$ quite frequently produce strong radiation — molecular phosphorescence (normally, at low temperatures). The reason lies, first, with the possibility of efficiently populating the T_1 state by interconversion under excitation in the singlet system and, second, with the fact that the nonradiative transition $T_1 \rightsquigarrow S_0$, like the radiative transition $T_1 \to S_0$, is spin-forbidden, and in many cases its probability k_{TS} turns out to be of the same order of magnitude as or even lower than the radiative intercombination transition probability k_P. The phosphorescence quantum yield φ_P is

$$\varphi_P = \frac{\varphi_T k_P}{k_P + k_{TS}}\,, \tag{5}$$

and its duration is

$$\tau_P = \frac{1}{k_P + k_{TS}}\,. \tag{6}$$

The spin-allowed $T_i \leftarrow T_1$ transitions are responsible for the transient triplet – triplet absorption.

Therefore, intercombination nonradiative transitions play two kinds of roles in the effect of molecular phosphorescence. The $S_1 \rightsquigarrow T_1$ intersystem crossing is responsible for the population of the phosphorescent level T_1 and the intercombination degradation $T_1 \rightsquigarrow S_0$ quenches the glow.

2.4 Intercombination transitions in atomic and molecular systems

As noted above, the reason underlying intercombination transitions is the spin – orbit interaction — an effect thoroughly studied in atomic spectroscopy. Generally speaking, this is a relativistic effect, but it can be adequately described in the framework of nonrelativistic quantum mechanics as the electromagnetic interaction between the spin magnetic moment of the electron orbiting a nucleus of charge $+Ze$ and the Coulomb field of this nucleus (this is the case of a hydrogen atom or a hydrogen-like ion) [16].

The quantum mechanical spin – orbit interaction operator for one electron in the field of a nucleus with charge $+Ze$ is given by [1, 17]

$$H_{SO} = \frac{e\mathbf{s}}{mc}\,\frac{\mathbf{E}\times\mathbf{p}}{2mc} = \frac{Ze^2}{2m^2c^2}\,\frac{1}{r^3}\,(\mathbf{ls})\,, \tag{7}$$

where e and m are the electron charge and mass, c is the speed of light, $\mathbf{E}$ is the nuclear electric field strength, and $\mathbf{p}$, $\mathbf{l}$, and $\mathbf{s}$ are the electron momentum, angular momentum, and spin momentum operators. We here use the relation

$$\mathbf{E} = -\frac{\mathbf{r}}{r}\,\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{Ze}{r}\right). \tag{8}$$

The correction to the energy level with a principal quantum number n is

$$\Delta E_{nlj} = \zeta_{nl}\,\frac{j(j+1) - l(l+1) - 3/4}{2}\,, \tag{9}$$

where the factor of the spin – orbit coupling is

$$\zeta_{nl} = \frac{R\alpha^2 Z^4}{n^3 l(l+1/2)(l+1)}\,. \tag{10}$$

Here, j and l are the inner and orbital quantum numbers, R is the Rydberg constant, and α is the fine structure constant $e^2/\hbar c \approx 1/137$.

A similar expression applies for one valence electron in the field of a nucleus with the charge $+Ze$ and $Z-1$ electrons of closed inner shells (the case of alkali metal atoms),

$$\zeta_{nl} = \frac{R\alpha^2 (Z^{\text{eff}})^4}{n^3 l(l+1/2)(l+1)}\,, \tag{11}$$

where $Z^{\text{eff}} < Z$ [17]. The effective nuclear charge Z^{eff} takes the screening effect of the inner-shell electrons into account.

Therefore, the energy of the spin–orbit interaction is proportional to $(Z^{\text{eff}})^4$. However, it is worth bearing in mind that in passing from the atoms of one alkali metal to the atoms of another alkali metal, the principal quantum number n of the ground level also changes, which moderates the $(Z^{\text{eff}})^4$ proportionality. It is nevertheless clear that the effect is strongly enhanced with Z, making it possible to emphasize the role of 'heavy' atoms, because the nuclear charge and mass are closely related. Because the radiative transition probability is proportional to the squared transition moment, the intercombination transition intensities would thus be expected to vary in proportion to Z^8. But because of the difference of Z^{eff} from Z and the occurrence of the factor $1/n^3$, the experimental dependence turns out to be weaker — proportional to Z^5 [1].

For multicentered systems, among which are molecules, the form of the spin–orbit interaction operator was found by Kramers [18] (cited from Ref. [19]):

$$H_{\text{SO}} = \frac{e^2}{2m^2c^2}\left(\sum_{\mu}\sum_{i}\frac{Z_\mu}{r_{i\mu}^3}(\mathbf{l}_i\,\mathbf{s}_i) - {\sum_{i,j}}'\,\frac{\mathbf{p}_i\times\mathbf{r}_{ij}}{r_{ij}^3}\,\mathbf{s}_i + 2{\sum_{i,j}}'\,\frac{\mathbf{p}_j\times\mathbf{r}_{ij}}{r_{ij}^3}\,\mathbf{s}_i\right). \tag{12}$$

Introducing Z^{eff} and neglecting the last term, one obtains H_{SO} in the form commonly used in the literature:

$$H_{\text{SO}} = \frac{e^2}{2m^2c^2}\sum_{\mu}\sum_{i}\frac{Z_\mu^{\text{eff}}}{r_{i\mu}^3}(\mathbf{l}_i\,\mathbf{s}_i)\,. \tag{13}$$

As is well known, the majority of organic luminescent compounds have molecules with conjugated single and double bonds, i.e., contain π-systems, in which the delocalization of π-electrons leads to the emergence of relatively low-lying excited electronic levels. Conjugated bond systems are structurally planar. In this case, the mixing of singlet and triplet states of the (π,π^*) type turns out to be substantially weakened, which was first shown by McClure [20]. The reason lies with the vanishing of one- and two-center integrals that enter the expressions for the matrix elements of H_{SO} in (13) involving one-electron wave functions (MOs) constructed from linear combinations of atomic orbitals (the MO LCAO method).

In the nonradiative transitions $T_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow T_1$, the spin–orbit interaction also plays the part of a perturbing factor that removes the intercombination prohibition $\Delta S = 0$. The nonradiative transition probability in the molecule is defined by Fermi's 'golden rule' or, more precisely, by its analog

$$k_{\text{nonrad}} = \frac{4\pi^2}{h}\,V_{\text{el}}^2 F_{\text{vibr}}\,\rho\,, \tag{14}$$

where V_{el} is the electron matrix element responsible for the mixing of the states between which the transition occurs, F_{vibr} is the Franck–Condon factor characterizing the overlap of vibrational wave functions, ρ is the final state density, and h is the Planck constant [21].

In the case of intercombination transitions, V_{el} is simply a matrix element of the operator H_{SO}. The probability of the intercombination degradation $T_1 \rightsquigarrow S_0$ is defined by the matrix element $\langle T_1|H_{\text{SO}}|S_0\rangle$, but the situation with the $S_1 \rightsquigarrow T_1$ transition probability may be more complicated. Specifically, between the levels S_1 and T_1, there may be levels T_i $(i > 1)$ for which the H_{SO} matrix element is larger than for T_1. However, effects arising from vibrational-electronic (vibronic) interaction may also play a significant part in nonradiative transitions.

The heavy-atom effect, which is the main concern of this review, arises from the following: when high-Z atoms are present in a molecular system, a relatively low probability of 'optical' electrons to find themselves close to these atoms is sufficient for making the contribution of these atoms to the total matrix elements H_{SO} dominant.

3. Luminescence of halogenated aromatic compounds

3.1 Discovery of the heavy-atom effect

The heavy-atom effect in the luminescence of polyatomic molecules was first investigated by McClure in 1949 [22]. Experimental measurements were made of the phosphorescence duration τ_{P} for several classes of organic compounds. The search for a correlation between τ_{P} and the spin–orbit coupling constants ζ for atoms that make up a molecule led to the determination of a clear relation between ζ_{Hal} and τ_{P} for halogenated derivatives of naphthalene (the Hal subscript denotes a halogen). Specifically, the quantity $\tau_{\text{P}}\zeta_{\text{Hal}}^2$ was found to be constant among mono-halogen-naphthalenes, i.e., τ_{P} shortens with enhancement of the spin–orbit interaction in accordance with predictions of the perturbation theory. At that time, McClure [22] did not subdivide the T_1-level deactivation probability $1/\tau_{\text{P}}$ into the radiative k_{P} and nonradiative k_{TS} parts and made an attempt to simultaneously determine τ_{P} from the absorption integral in the channel $T_1 \leftarrow S_0$. Although a qualitative agreement was reached, it is nevertheless pertinent to note that according to Ermolaev's more recent data [23, 24], the main contribution to the deactivation of the T_1 state of halogenated naphthalenes is made by the constant k_{TS}, whereas the absorption integral should correlate with k_{P}.

The $\tau_{\text{p}}-\zeta_{\text{Hal}}$ correlation obtained in Ref. [22] became in its time one of the most powerful arguments in support of the triplet nature of the phosphorescent level of organic molecules.

Two more circumstances are worthy of mention: (1) for ζ_{Hal}, McClure [22] employed a quantity ζ corresponding to the lowest-energy electronic configuration of an atom; (2) a less clear $\tau_{\text{P}}-\zeta$ correlation was also revealed for other series of compounds, in particular for Ph_nX-type compounds, where Ph is phenyl and X is the central atom, for instance X = O ($Z = 8$) and Se ($Z = 34$).

In subsequent measurements of the absolute quantum yields of fluorescence and phosphorescence of several benzene derivatives, McClure et al. discovered that the fluorescence of 1-bromonaphthalene was strongly quenched,

i.e., the internal heavy-atom effect enhanced deactivation of the S_1 state [25, 26].

It is noteworthy that the heavy-atom effect, as noted in Nickel's review [6], had earlier been observed by Pringsheim and Vavilov [10]. They had experimentally measured the τ_P values for fluorescein, eosin (tetrabromofluorescein), and erythrosine (tetraiodofluorescein) for 93 K as 5 s, 10 ms, and 1 ms, respectively.

A significant stage in the investigation of the internal heavy-atom effect was a paper by Ermolaev and Svitashev [27]. They measured the absolute quantum yields of the fluorescence (φ_F) and phosphorescence (φ_P) of several 1-substituted naphthalenes, including F-, Cl-, Br-, and I-derivatives, and the quantum yield of phosphorescence of unsubstituted naphthalene. The measurements were made with a relative technique from the known value of φ_F for naphthalene. They observed a strong fluorescence quenching and a sharp rise in the probability of the intercombination conversion $S_1 \rightsquigarrow T_1$ (k_{ST}) with increasing Z_{Hal}. The estimate of k_{ST} was made assuming that $k_{TS} = 0$. It was shown that k_{ST} increases faster than $1/\tau_P$: at each step in F–Cl–Br–I, the value of $1/\tau_P$ increases approximately 10-fold and that of k_{ST} by about a factor of 35–70.

In a series of works, beginning with Ref. [23], Ermolaev, in collaboration with Sveshnikova, determined [15] that a large number of organic molecules obey the relation $\varphi_F + \varphi_T = 1$, as noted above. The halogenated derivatives of naphthalene were among the objects of this kind, and the values of k_P and k_{TS} determined for them in Ref. [24] are collected in Table 1.

Table 1. Deactivation probabilities of the T_1 state of naphthalene and its 1-halogenated derivatives [24].

Compound	k_P, s^{-1}	k_{TS}, s^{-1}
Naphthalene	1.6×10^{-2}	4.2×10^{-1}
1-fluoronaphthalene	3.6×10^{-2}	6.3×10^{-1}
1-chloronaphthalene	5.7×10^{-1}	2.7 †
1-bromonaphthalene	7.0	4.3×10
1-iodonaphthalene	1.0×10^2	4.0×10^2

† The value $1.7\ s^{-1}$ is given in Ref. [24], but this is supposedly a misprint, because the sum $k_P + k_{TS}$ does not correspond to τ_P according to Refs [22, 27].

It is pertinent to note that in Ref. [24], use was made of the φ_P values from Ref. [23], which differ from the data in Ref. [27] due to the employment of different φ_F values for naphthalene, which served as the reference: the value $\varphi_F = 0.53$ borrowed from Refs [25, 26] was assumed in Ref. [27], while Ermolaev [23] obtained the value $\varphi_F = 0.29$ for naphthalene. According to the data in Table 1, the $k_P^{Cl} : k_P^{Br} : k_P^{I}$ ratio is 1 : 12.3 : 176 and the $k_{TS}^{Cl} : k_{TS}^{Br} : k_{TS}^{I}$ ratio is 1 : 15.9 : 148. The squared spin–orbit coupling constants ζ_{Hal} (borrowed from Ref. [22]) are in the ratio $\zeta_{Cl}^2 : \zeta_{Br}^2 : \zeta_I^2 = 1 : 17.6 : 73.9$. It is valid to say that in the case of the iodinated derivative, the heavy-atom effect is stronger than expected. Supposedly manifested in this case are the changes in the electronic structure of the naphthalene nucleus upon introduction of an iodine atom into the molecule.

In 1952, Kasha discovered the external heavy-atom effect [28]. On merging two colorless organic liquids (1-chloronaphthalene and ethyl iodide), he observed a yellow coloring. Measurements of the absorption spectrum showed that the 1-chloronaphthalene absorption became stronger in the $T_1 \leftarrow S_0$ channel.

The external heavy-atom effect and related phenomena were systematically studied by McGlynn et al. for both absorption and fluorescence [29–33]. We note that the terms external and internal heavy-atom effects, which we use, were introduced in Ref. [29]. The external heavy-atom effect is not considered in our review. This effect is described at length in the monograph in Ref. [1]. Here, it is only worthy of note that, according to the data in Refs [29, 31, 33], the two effects, internal and external, are mutually enhanced when a halogen atom is present in the naphthalene molecule.

3.2 Polarized phosphorescence of halogenated derivatives of naphthalene

The data of spectral-polarization phosphorescence investigation of the halogenated derivatives of naphthalene performed by El-Sayed and Pavlopoulos [34, 35] are of significance in understanding the mechanism of the internal heavy-atom effect. They investigated 1- and 2-monosubstituted (Cl, Br, I) and two dibromosubstituted 1,4- and 2,3-derivatives. It was found that the phosphorescence spectra contained two systems of bands, which were denoted as I and II: I is the 0–0 transition polarized perpendicular to the plane of a macrocycle and its vibrational repetitions; II is the vibration-induced system of bands that begins with a vibronic transition shifted by $\sim 250\ cm^{-1}$ to the long-wavelength side from the 0–0 transition and is polarized in the plane of the molecule. The frequency of the inducing vibration depends on the nature of a halogen in an irregular manner, and its nature was not elucidated.

El-Sayed [19] performed a theoretical analysis of the above data. We enlarge on this analysis, because it lays the groundwork for the discussion of more recent works.

The consideration of the problem in Ref. [19] relies on the approach earlier proposed by Albrecht [36] for vibronic transitions in the phosphorescence spectrum of benzene, including three types of vibronic effects: the spin-vibronic interaction (the dependence of the operator H_{SO} on nuclear coordinates) in the first-order of the perturbation theory (to be termed type 1) and the mixing of the T_1 state with the S_i states in the second order of the perturbation theory via an intermediate state S_j (type 2) or T_j (type 3).[1] The Hamiltonian of the problem is of the form

$$H = H_0^0 + H_{SO}^0 + \sum_a \left(\frac{\partial H_0}{\partial Q_a}\right)_0 Q_a + \sum_a \left(\frac{\partial H_{SO}}{\partial Q_a}\right)_0 Q_a\,, \qquad (15)$$

where the superscript '0' in the first two terms refers to the equilibrium position of the nuclei for which the partial derivatives are evaluated (the subscript '0'), and the summation in the last two terms is performed over $3N - 6$ normal coordinates of the corresponding electronic state.

The operator H_{SO} mixes the S and T states in the first order, the operator $\sum_a (\partial H_{SO}/\partial Q_a) Q_a$ gives type-1 vibronic transitions, and the operators H_{SO} and $\sum_a (\partial H_0/\partial Q_a) Q_a$ are jointly responsible for the vibronic transitions of types 2 and 3 in the second order.

El-Sayed [19] chose to consider 1,4- and 2,3-dibromonaphthalene molecules, which belong to the point symmetry group C_{2v}, allowing an efficient use of the group-theoretical approach. This analysis was performed using one-electron

[1] In principle, account should also be taken of the mixing of the ground state S_0 with the triplet states T_i, but this is commonly neglected as in Ref. [19].

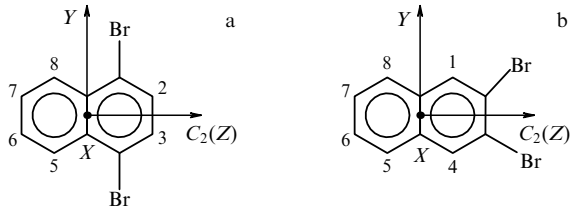

Figure 5. Structures of the isomers of 1,4- (a) and 2,3-dibromonaphthalene (b).

wave functions — molecular orbitals in the LCAO form. The spin–orbit interaction operator was, as usual, taken in the one-electron form (with the superscript 'eff' at Z_μ omitted)

$$H_{\mathrm{SO}} = \alpha^2 \sum_\mu \sum_i \frac{Z_\mu}{r_{i\mu}^3} (L_i S_i) \,. \tag{16}$$

Figure 5 shows the structure of dibromonaphthalene isomers. It is pertinent to note that although the choice of coordinate axes in the diagram is customary for the C_{2v} symmetry (the axis C_2 is selected as the Z axis), it contradicts the traditional use of the notation p_z for atomic orbitals that constitute the π electronic MOs in conjugated bond systems. Here, the 'eights' of π electrons are p_x.

We outline the main results of the analysis performed in Ref. [19]. From experiment, it follows that (1) admixed to the T_1 state are singlet states of the (σ, π^*) type [or of the (π, σ^*) type] with the symmetry B_1, which gives the $0-0$ transition polarized perpendicular to the plane of the molecule; and (2) type-1 vibrational-electronic interaction does not show up in the spectra and can be omitted from consideration.

The analysis shows that for types 2 and 3, the perturbing vibration belongs to the symmetry type A_2, inactive in optical spectra, and accordingly the Z-component operates in H_{SO}. The ensuing diagram of the most probable mixed state couplings is represented in Fig. 6 (the capital letters B denote the symmetry of electronic states and the lowercase letter a the symmetry of vibrations).

A detailed analysis shows that this diagram explains the emergence of the Y component of the phosphorescence oscillator of the subspectrum II for the 1,4-derivative and of both Y and Z plane components for the 2,3-derivative. But without a specific calculation, it is impossible to determine what states, (σ, σ^*) or (π, π^*), are more actively mixed with the T_1 state to give the specified components of the $T_1 \to S_0$ transition moment. Because the heavy-atom effect is involved, it is nevertheless probable that a significant part is played by the (σ, σ^*) states formed by σ-MOs localized on the C–Br bonds.

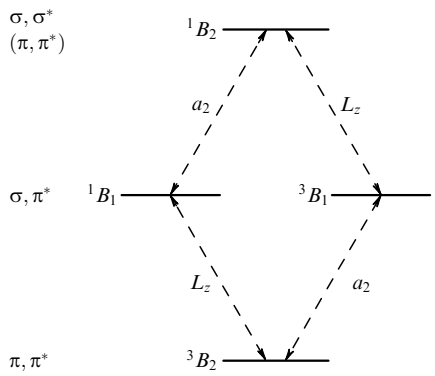

Figure 6. Diagram of the most probable bonds of the mixing states for 1,4-dihalogenated naphthalene. The dashed arrows show the mixing of electronic states.

Two coupling versions are possible:

$$^1B_2(\sigma, \sigma^*) \cdots L_z \cdots > {}^3B_1(\sigma, \pi^*) \cdots a_2 \cdots > {}^3B_2(\pi, \pi^*) \tag{17}$$

(spin–orbit coupling with vibronic coupling in the triplet system, type 3) and

$$^1B_2(\sigma, \sigma^*) \cdots a_2 \cdots > {}^1B_1(\sigma, \pi^*) \cdots L_z \cdots > {}^3B_2(\pi, \pi^*) \tag{18}$$

(spin–orbit coupling with vibronic coupling in the singlet system, type 2).

Pertinent to the former case are the matrix elements

$$\left\langle {}^1B_2(\sigma, \sigma^*) | H_{\mathrm{SO}} | {}^3B_1(\sigma, \pi^*) \right\rangle . \tag{19}$$

Because H_{SO} is a one-electron operator, the spatial part of such a matrix element reduces to the one-electron integral

$$\langle \sigma^* | H'_{\mathrm{SO}} | \pi^* \rangle \,, \tag{20}$$

where

$$H'_{\mathrm{SO}} = \alpha^2 \sum \frac{Z_\mu}{r_{i\mu}^3} (L_{x\mu} + L_{y\mu} + L_{z\mu}) \,. \tag{21}$$

The orbital π^* can be represented as the LCAO,

$$\pi^* \approx N_1 \left\{ \left[a p_{x(\mathrm{C}_1)} + \ldots + a p_{x(\mathrm{C}_4)} \right] + b \left[p_{x(\mathrm{Hal}_1)} + p_{x(\mathrm{Hal}_2)} \right] \right\} , \tag{22}$$

and the orbital σ_4, which is estimated to play the major part in this coupling version, as

$$\sigma_4 = N_2 \left[k_1 p_{y(\mathrm{Hal}_1)} + l_1 (sp^2)_{\mathrm{C}_1} + l_1 (sp^2)_{\mathrm{C}_4} + k_1 p_{y(\mathrm{Hal}_2)} \right] . \tag{23}$$

Matrix element (20) is then obtained as the sum of one-, two-, and three-center integrals (with the corresponding coefficients), of which the following terms are the most significant for the heavy-atom effect:

$$2 N_1 N_2 k_1 b \left\langle p_{x\mathrm{Br}_1} \left| \frac{Z_{\mathrm{Br}}}{r_{\mathrm{Br}_1}^3} (L_{x\mathrm{Br}_1} + L_{y\mathrm{Br}_1} + L_{z\mathrm{Br}_1}) \right| p_{y\mathrm{Br}_1} \right\rangle \tag{24}$$

(one-center) and

$$2 N_1 N_2 k_1 a \left\langle p_{x\mathrm{C}_1} \left| \frac{Z_{\mathrm{Br}}}{r_{\mathrm{Br}_1}^3} (L_{x\mathrm{Br}_1} + L_{y\mathrm{Br}_1} + L_{z\mathrm{Br}_1}) \right| p_{y\mathrm{Br}_1} \right\rangle \tag{25}$$

(two-center).

Similar terms are also obtained for the second coupling version. The first integral is greater, but the magnitude of b is small, and these terms would be expected to play roles of comparable significance in the vibration-induced removal of intercombination prohibition.

It is stated in Ref. [19] that the mixing of singlet and triplet (π, π^*)-type states in planar conjugated bond systems is quite insignificant because one- and two-center integrals of the $\langle p_{x\mathrm{Br}} | H'_{\mathrm{SO}} | p_{x\mathrm{Br}} \rangle$ and $\langle p_{x\mathrm{Br}} | H'_{\mathrm{SO}} | p_{x\mathrm{C}} \rangle$ types vanish (we recall that the X axis is perpendicular to the molecular plane). In this connection, it is pertinent to note that this conclusion for

aromatic molecules (containing only C and H atoms) had previously been made by McClure [20].

3.3 Fluorescence of halogenated derivatives of azulene

Manifestations of the internal heavy-atom effect were also revealed in the investigation of the 'anomalous' $S_2 \to S_0$ fluorescence of azulene. Azulene, an isomer of naphthalene (Fig. 7), belongs to the so-called nonalternant hydrocarbons. Its ordinary $S_1 \to S_0$ fluorescence is strongly quenched for still debated reasons, but the fluorescence in the $S_2 \to S_0$ channel is rather intense in defiance of the well-known Kasha rule, which states that transitions with emission of a photon take place from the lowest level of a given multiplicity. In Refs [37–39], it was found that the introduction of Cl, Br, or I atoms into the azulene molecule quenches the $S_2 \to S_0$ fluorescence. In Ref. [40], which was published after Ref. [39], it was shown that the nonradiative S_2-state deactivation probability for molecular azulene derivatives containing light atoms (including F) is correlated with the S_2-S_1 interval by the 'energy gap law', i.e., the main contribution to deactivation is made by the internal conversion $S_2 \rightsquigarrow S_1$. On separating the corresponding quantity from the total constant for Cl- and Br-derivatives, the authors gave a model estimate of the $S_2 \rightsquigarrow T_i$ intersystem crossing probabilities and showed that they are qualitatively correlated with the quantity $\sum \zeta^2$.

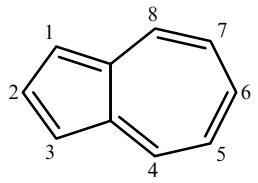

Figure 7. Azulene structure and position numbering.

3.4 Fluorescence of halogenated derivatives of phenanthrene

The internal heavy-atom effect in the molecules of halogenated derivatives of phenanthrene was investigated by Goodman et al. [41, 42] from the spectral-polarization characteristics of phosphorescence. In Ref. [42], investigations were made of 3-chloro-, 9-bromo-, and 4-bromophenanthrene. Figure 8 shows the phenanthrene structure, the coordinate axes, and position numbering.

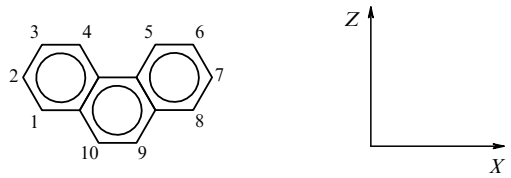

Figure 8. Phenanthrene structure, coordinate axes, and position numbering.

Similarly to the case of halogenated naphthalene, two subspectra can be distinguished in the phosphorescence spectra: I — the 0–0 transition with vibronic repetitions, and II — the vibration-induced transitions with a substantial X component. In contrast to halogenated naphthalenes, the subspectrum II becomes stronger with the enhancement of the spin–orbit interaction (in passing from the 3-chloro- to the 9-bromoderivative). The authors attempt to attribute this to the emergence of low-lying electronic states of the (σ, σ^*) type localized on the C–Hal bond.

We emphasize that the angles between the transition moments may differ strongly from 0 and 90° for molecules not having the C_{2v} or D_{2h} symmetry. In this case, the long-wavelength transition need not be polarized along the X or Z axes, which seriously hinders the analysis of experimental dependences.

An abnormally broadened phosphorescence spectrum with a Z-component was obtained for 4-bromophenanthrene. The authors justly attribute this to the violation of planarity of the conjugated bond system due to steric interactions.

Miller, Meek, and Strickler [43] measured the T_1-state lifetimes for a large number of mono- and dihalogenated phenanthrene and naphthalene in order to verify that $1/\tau_P$ is proportional to ζ^2 and elucidate the influence of the position of the substituent on the heavy-atom effect, as well as the additivity of the effect. The authors had no way of dividing $1/\tau_P$ into k_P and k_{TS}; however, they assumed that both of these constants should be proportional to ζ^2 (in the foregoing, we showed that this is not entirely correct). The results of measurements in the coordinates $\lg(1/\tau_P)$ and $\lg(\zeta^2)$ yield straight lines. But a close examination of the drawing in Ref. [43] shows that the straight lines are not parallel, i.e., that $1/\tau_P$ is not strictly proportional to ζ^2.

The effect depends only slightly on the heavy-atom position in the case of naphthalene and significantly in the case of phenanthrene. $1/\tau_P$ is highest for position 9 and lowest for position 2 (see Fig. 8). Assuming that the position dependence is determined by the electron density at the C atom in a specific position, the density belonging to 'optical' orbitals (the upper completed MO — HOMO and the lower vacant MO — LUMO), the authors endeavored to find the correlation with the published coefficients c_μ of these orbitals obtained by the Hückel method for unsubstituted naphthalene and phenanthrene (it is likely that use was made of the sum of the moduli of c_μ^{HOMO} and c_μ^{LUMO}). A qualitative agreement was reached for naphthalene (the electron density is higher at position 1), but the order of increase in the electron density and the magnitude of the effect did not quite coincide for phenanthrene. For phenanthrene, a better agreement of the heavy-atom effect was obtained for the spin density in the state T_1 determined by the photo-EPR technique in Ref. [44]. However, for naphthalene, such a comparison with the corresponding photo-EPR data [45] impaired the agreement in comparison with the Hückel coefficients (the spin density is very low in position 2).

The internal heavy-atom effect was shown to be almost completely nonadditive for disubstituted derivatives of phenanthrene, with the exception of 2,7-dibromophenanthrene. The authors noted that this behavior departs from the additivity observed in the deuteration of these and other samples in different molecular positions [46–48]. It was hypothesized that steric factors and the participation of charge transfer states in the heavy-atom effect were responsible the above effect.

We note that Ref. [43] contains a number of references to earlier works on the luminescence of halogenated derivatives of naphthalene and phenanthrene that concern special cases. The authors corroborate the conclusion in Ref. [42] that the 4-derivatives of phenanthrene are nonplanar molecules.

3.5 Halogenated naphthalenes: deactivation data on spin sublevels of the T_1 state

To gain a deeper understanding of the influence of substituent position on the heavy-atom effect, Flatscher and Friedrich [49] investigated halogenated naphthalenes using the method of microwave-induced delayed phosphorescence (MIDP), allowing determination of the decay constants of individual spin sublevels of the T_1 state: $k_i = k_P^i + k_{TS}^i$, where $i = x, y, z$ (at helium temperatures, i.e., in the conditions of the so-called spin polarization, when there is no redistribution over sublevels arising from spin–lattice relaxation). The diagram of these sublevels is shown in Fig. 9 (the symmetry is C_{2v} and the directions of the coordinate axes are the same as in Fig. 5).

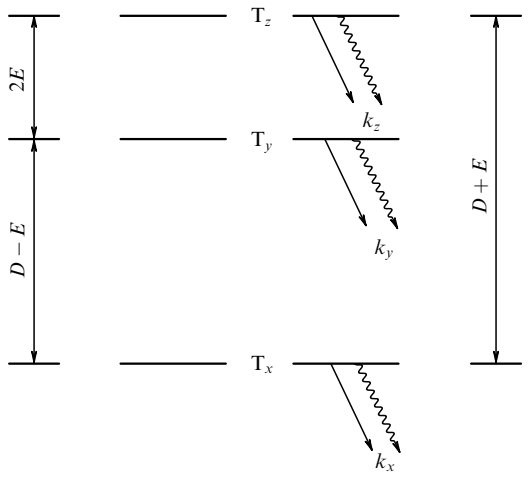

Figure 9. The T_1-state sublevel diagram from Ref. [49].

The spacing of the sublevels was determined by the stationary method of optically detected magnetic resonance (ODMR). The MIDP method also allowed measuring the relative values of k_P^i.

The objects of investigation were dichloronaphthalenes: 1,4-; 1,5-; 2,3-; and 2,6. The main results were obtained for naphthalene matrices. The phosphorescence spectra proved to be fine-structured (which is significant for the application of microwave techniques), but the vibrational structure was not analyzed. In particular, no attempts were made to separate the I and II subspectra as in El-Sayed's paper [19], which is not mentioned at all. In the MIDP measurements, monitoring was carried out in the 0–0 transition region in an interval of about 100 cm^{-1}.

From selection rules for the spin–orbit interaction, it follows that in the case of the C_{2v} symmetry, the T_x sublevel of the T_1 state of symmetry B_2 can mix with the singlet (π, π^*) states of symmetry A_1, the T_z sublevel with the (σ, π^*) and (π, σ^*) states of symmetry B_1, and the T_y sublevel with the A_2 states inactive in electronic spectra, i.e., with the states that cannot contribute to k_P^y.

The results and conclusions in Ref. [49] can be summarized as follows:

(1) the substitution type (1,4,5 — α, 2,3,6 — β) has a stronger effect on the T_1 state deactivation than the symmetry of molecules;

(2) the averaged value of $k_P + k_{TS}$ (which corresponds to $1/\tau_P$ for 77 K) is 45% greater for α-derivatives than for β-derivatives, i.e., the difference is greater than for monochloronaphthalenes;

(3) the probabilities k_x and k_P^x are substantially lower than the others, which corresponds to the expectations for (π, π^*) interactions;

(4) the constants k_z are greatest for α-derivatives and the constants k_y for β-derivatives;

(5) the ratios between the magnitudes of k_P^i are more or less similar for all the samples under study;

(6) the probability of the $T_y \to S_0$ transition prohibited for the C_{2v} symmetry is rather high, which the authors attribute to distortion of the molecules in the naphthalene matrix.

We note that in discussing the results, the authors do not invoke Albrecht's approach but resort to the operator $(\partial H_{SO}/\partial Q)Q$ (the so-called spin–vibronic coupling) in the first and second approximations. It is stated that apart from the LCAO coefficients, the overlap of heavy-atom AOs with hydrogen atoms participating in nonplanar promoting symmetry' vibrations must be taken into account.

The authors of Ref. [49] borrow the substantiation of this viewpoint from an earlier work of the same group with the participation of a theorist (Metz) [50]. In Ref. [50], which was concerned with the polarization of monohalogenated naphthalenes, the degree of polarization at the peak of the 0–0 phosphorescence band of derivatives with substitution at position 1 (in other words, α) was found to increase in the series F-, Cl-, Br-, I-naphthalene and become positive for the I-derivative. An analysis shows that the nonplanar constituent of the phosphorescence oscillator increases approximately in proportion to ζ_{Hal}^2 and the planar ones increase more steeply. The planar components of vibronic transitions increase even more strongly. For 2(or β)-derivatives, the degree of phosphorescence polarization remains negative throughout the series. However, the authors state (without going into details) that the planar component also increases in this case, although for the direction approximately perpendicular to the $G \to L_a$ transition. For 2-derivatives, this direction is close to the direction of the $G \to L_b$ transition moment. We note that there is good reason to investigate the symmetric dihalogenated derivatives with substitution at the β-positions in order to eliminate the ambiguity in this matter. It is not improbable that the effect of the increase in the planar constituent is simply weaker for β-monohalogenated naphthalenes.

The enhancement of the planar component in the 0–0 phosphorescence transition in the internal heavy-atom effect is attributed by the authors of Ref. [50] to the manifestation of the Herzberg–Teller vibronic interaction for zero-point oscillations in the second order of the perturbation theory. For one of the sublevels of the T_1 level with the spin polarization aligned with the τ axis, the dependence of the $T_1^\tau \to S_0$ transition moment on the normal vibrational coordinates is written as a Taylor series up to second-order terms,

$$M_{S_0T_1}^{\tau,\alpha}(Q) = M_{S_0T_1}^{\tau,\alpha}(0) + \sum_{p}\left[\frac{\partial}{\partial Q_p} M_{S_0T_1}^{\tau,\alpha}\right]_0 Q_p + \frac{1}{2}\sum_{p,p'}\left[\frac{\partial}{\partial Q_p}\frac{\partial}{\partial Q_{p'}} M_{S_0T_1}^{\tau,\alpha}\right]_0 Q_p Q_{p'}, \quad (26)$$

where $\alpha = (x, y, z)$, and Q_p and $Q_{p'}$ are the perturbing vibrations.

The excitation of nonplanar vibrations in the $T_1 \to S_0$ transition may yield vibronic transitions polarized in the

molecular plane, as considered above (subspectrum II), which corresponds to first-order terms in (26).

In the internal heavy-atom effect, the enhancement of the spin – orbit interaction results in an increase in the nonplanar constituent of the phosphorescence oscillator due to a relatively large one-center integral comprising σ- and π-orbitals. The authors show that three-center integrals responsible for the mixing of singlet and triplet (π, π^*) states do not increase under the heavy-atom effect. The increase in the planar 0 – 0 transition components is attributable to the contribution of the second-order terms in expansion (26), involving expressions of the type

$$\left\langle \frac{\partial}{\partial Q_{\mathrm{p}}} S_j \middle| H_{\mathrm{SO}} \middle| \frac{\partial}{\partial Q_{\mathrm{p}}} T_1^{\tau} \right\rangle ,$$

which are responsible for the mixing of singlet and triplet (π, π^*) states. Expanding these integrals in molecular orbitals gives terms that are similar to those encountered in the theory of nonradiative transitions and are not small. Further expansion in atomic orbitals gives a term containing a one-center integral at the halogen atom and the factors

$$\left\langle \varphi_{\pi}(\mathbf{R}_{\mathrm{C}_1}) \middle| \frac{\partial}{\partial z_{\mathrm{C}_1}} \middle| \varphi_{\mathrm{s}}(\mathbf{R}_{\mathrm{C}_1}) \right\rangle \quad \text{and} \quad \left\langle \frac{\partial}{\partial z_{\mathrm{H}_8}} \varphi_{\mathrm{s}}(\mathbf{R}_{\mathrm{H}_8}) \middle| \varphi_{\pi}(\mathbf{R}_{\mathrm{C}_8}) \right\rangle , \tag{27}$$

where z is the coordinate along the axis perpendicular to the molecular plane, φ denotes atomic orbitals (π — $2p_z$, s — 2s for C and 1s for H), and the indices correspond to the atoms C and H in the specified positions.

It is significant that this contribution does not contain the LCAO coefficient on the halogen atom, which should be small, resulting in a weakening of the heavy-atom effect for the direct spin – orbit interaction.

Therefore, the nonplanar vibrations Q_{p} may make a contribution to the $T_1 \to S_0$ 0 – 0 transition in the second order of the vibronic interaction and be responsible for the enhancement of its planar constituents.

The second factor in (27) points to the role of vibrations of a hydrogen atom, which was employed in the derivation in Ref. [49]. The authors of Ref. [50] predicted that deuteration should affect the planar component of the $T_1 \to S_0$ 0 – 0 transition for Br- and I-derivatives and confirmed this in the subsequent paper [51]. They showed that the deuteration of 1,4-dichloro-, 2,7-dibromo-, and 2,7-diiodonaphthalene lowers the 0 – 0 phosphorescence transition probability primarily due to the weakening of planar components (especially for the bromoderivative).

At the same time, it must be mentioned that the rise of the planar phosphorescence oscillator component for halogenated naphthalenes may have a simpler cause — the violation of molecular planarity upon the introduction of bulky halogen atoms owing to steric interactions (in a condensed medium).

The authors of Ref. [52] studied the decay kinetics of sublevels of the T_1 level and recorded a well-resolved excitation spectrum of phosphorescence in the $T_1 \leftarrow S_0$ channel for the 1,4-dichloronaphthalene crystal at 4.2 K. The frequency of the vibration most active in the excitation spectrum (263 cm^{-1}) was found to form developed progressions both from the 0 – 0 transition and in combination with totally symmetric skeleton vibrations. Comparing this frequency with the frequency 327 cm^{-1} in the ground state and ascribing them to the nonplanar γCCl vibration, the authors interpret the frequency lowering in the T_1 state as a result of the vibronic interaction of the T_1, $^3(\pi, \pi^*)$ state with the $^3(\pi, \sigma^*)$ state, in which the excitation is localized on the C – Cl bonds. However, it is questionable whether nonplanar vibrations can form developed progressions. This is possible only if the molecule in the T_1 state is nonplanar. It is more likely that the above vibrations are planar, supposedly with the participation of δCCl deformations.

3.6 Luminescence of halogenated derivatives of naphthalene and quinoline: experimental and theoretical analysis

In a series of papers by Polish authors [53 – 55] (Najbar et al.), including the well-known American spectroscopist Hochstrasser [54], the luminescence of halogenated derivatives of naphthalene and its aza-analog quinoline (Fig. 10) was investigated. The analysis and interpretation of their own and literature data were made on the basis of simultaneously performed model calculations of the Franck – Condon factor entering the expression for k_{TS}.

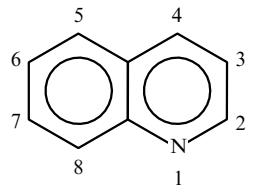

Figure 10. Quinoline structure and position numbering.

The measurements were carried out for frozen ethanol solutions at 77 K and in mixtures of C_2H_5OH with H_2SO_4 (D_2SO_4) [54]. The authors believe that aromatic molecules in amorphous vitreous media experience smaller deformations than in crystal matrices of naphthalene and durene (see Ref. [49]), i.e., they are closer to free molecules. The phosphorescence spectra of the derivatives of quinoline and naphthalene are similar. The substituent (halogen) position affects the 0 – 0 transition frequency and the spectra broaden in some cases. The constants k_{P} and k_{TS} were determined from the values of φ_{F}, φ_{P}, and τ_{P} (τ_{P} is virtually independent of the temperature in the 77 – 150 K range) assuming that $\varphi_{\mathrm{F}} + \varphi_{\mathrm{T}} = 1$. Comparing the quantities k_{P} and k_{TS} for chloronaphthalenes and chloroquinolines [53] shows the absence of a correlation between these constants. The quantity k_{TS} is greater than k_{P} and determines τ_{P}. Accordingly, the dependences of τ_{P} on the substituent position are determined by changes in the values of the k_{TS} constants; the lower the T_1 level, the greater these constants.

To qualitatively analyze this relation, the authors of Ref. [56] performed a model calculation of the Franck – Condon factor in the formula

$$k_{\mathrm{TS}} = \sum_k |C_{\mathrm{TS}}^k|^2 \frac{\omega_k}{2\hbar} \exp\left(-\sum_j X_j\right) \times \int_{-\infty}^{\infty} \mathrm{d}t \, \exp\left(-\mathrm{i}\,\frac{\Delta E - \hbar\omega_k}{\hbar}\, t + \sum_j X_j \exp(\mathrm{i}\omega_j t)\right) , \tag{28}$$

where $\Delta E = E_{\mathrm{T}}$ is the energy of the T_1 state, ω_j are the frequencies of accepting vibrations j, X_j are the dimensionless displacements of the surfaces involved in the $T_1 \rightsquigarrow S_0$

transition, and ω_k are the frequencies of promoting vibrations, for which it was assumed that $X_k = 0$.

The vibronic factors $C^k_{T_1S_0}$ are given by

$$C^k_{T_1S_0} = \sum_m \left| \frac{\langle \Phi_{T_1} | H_{SO} | \Phi_m \rangle}{U_{T_1}(Q) - U_m(Q)} J^k_{mS_0} + J^k_{T_1m} \frac{\langle \Phi_m | H_{SO} | \Phi_{S_0} \rangle}{U_m(Q) - U_{S_0}(Q)} \right| , \quad (29)$$

where, for instance,

$$J^k_{mS_0} = \hbar (M_k)^{-1/2} \left\langle \Phi_m(q, Q) \middle| \mathrm{i} \frac{\partial}{\partial Q_k} \middle| \Phi_{S_0}(q, Q) \right\rangle . \quad (30)$$

Here, H_{SO} is the spin–orbit interaction operator, and $U_{T_1}(Q) - U_m(Q)$ and $U_m(Q) - U_{S_0}(Q)$ are the spacings between the potential surfaces of the states coupled by the H_{SO} operator.

In the model calculation, it was assumed that there existed two types of promoting (inducing a nonradiative transition) nonplanar oscillations: C–Cl (one in monochloroderivatives) and C–H [assumed to be local, their number d_2 ('degeneracy') being equal to the number of CH groups]. It was assumed that $\nu_1 = 250$ cm^{-1} and $\nu_2 = 800$ cm^{-1}. The result was

$$k_{TS} = \frac{|C^{(1)}_{TS}|^2}{2\hbar} F_1 + \frac{d_2 |C^{(2)}_{TS}|^2}{2\hbar} F_2 = BF_2 , \quad (31)$$

where

$$B = \frac{|C^{(1)}_{TS}|^2 a + d_2 |C^{(2)}_{TS}|^2}{2\hbar} , \qquad a = \frac{F_1}{F_2} .$$

The reason for the last transformation lies with the approximate constancy of the ratio F_1/F_2 obtained in calculations ($a \approx 0.15$). The Franck–Condon factors F_1 and F_2 were calculated in Ref. [53] for all compounds investigated [the stretching C–H vibrations (3065 cm^{-1}) and two skeleton vibrations with the frequencies 1470 cm^{-1} (averaged over two vibrations) and 500 cm^{-1} were taken as 'accepting' vibrations].

A graphic representation of the data showed that the experimental points (values of k_{TS} versus F_2) for chloroquinolines fit nicely in two straight lines corresponding to α- and β-substitution (with the exception of 2- and 8-derivatives, in which the chlorine atom is located in the immediate vicinity of the nitrogen atom). This is good evidence of the significance of the Franck–Condon factor in the dependence of k_{TS} on the substituent position. Refining the calculation of the F_2 factors by way of empirical inclusion of the difference in length changes of different C–H bonds under electronic excitation has the effect that all points for quinolines fit in a common straight line passing through the origin, and the two points corresponding to 1-chloro- and 2-chloronaphthalene also fit in a similar straight line. The latter may imply that the lowering of k_{TS} in going from 1-chloro- to 2-chloronaphthalene is due to the vibrational factor rather than the electronic (vibronic) one.

At the same time, it is clear that the differences in electronic factors cannot be disregarded. This is evidenced, in particular, by the data in Ref. [49]: the values of k_z and k_y for which the Franck–Condon factors are equal behave in a different manner for α- and β-derivatives.

In the next paper [54], the electronic factor received more attention. The authors used the same approach as in Ref. [53] for a combined analysis of their own data on monochloronaphthalenes and the literature data for dichloronaphthalenes [43, 49] and tetrachloronaphthalenes [57]. The model was somewhat changed: instead of the 800 cm^{-1} frequency for promoting CH vibrations, the value 930 cm^{-1} averaged over vibrational spectra was used.

For an arbitrary number of chlorine atoms in the molecule, expression (31) becomes

$$B = \beta^2_{CH} d_H + \beta^2_{CCl} a d_{Cl} . \quad (32)$$

The solution of the system of such equations shows that the contribution of the C–Cl vibration as the promoting one (β^2_{CCl}) is significant for α-derivatives and is dominant for β-derivatives.

Experimental investigation in Ref. [54] was made of the same chloroquinolines as in Ref. [53], although in an acid medium, the mixtures of C_2H_5OH and H_2SO_4 (D_2SO_4). The points for different media fit rather well in straight lines in the $k_{TS}-F_{930}$ coordinates.

Deuteration occurs in the N^+–H group: $ClQH^+ \rightarrow ClQD^+$. The deuteration is responsible for the τ_P lengthening and, accordingly, for the lowering of k_{TS} (determined under the assumption that k_P remained invariable under deuteration). The degree of this influence depends on the position of the chlorine atom in the chloroquinoline molecule. For β-substituted derivatives, k_{TS} decreases by about a factor of 1.1 on the deuteration, but the effect is stronger for α-derivatives: k_{TS} decreases by a factor of 1.6. The authors of Ref. [54] provide the following explanation. In the presence of an NH group, the valence N–H vibrations are additional accepting vibrations and formula (31) becomes

$$B = \beta^2_{NH} n + \beta^2_{CH} d_H + \beta^2_{CCl} a d_{Cl} , \quad (33)$$

where $n = F(N-H)/F_{930}$ and $a = F_{250}/F_{930}$.

Deuteration decreases both the Franck–Condon factor $F(N-H)$ and the electronic factor β^2_{NH}. The magnitude of F_{930}, as evidenced by model calculations, also decreases (1.1-fold). That is why for β-derivatives, when the quantity β^2_{CCl} prevails, the effect of deuteration on k_{TS} involves primarily a change of F_{930}. For α-derivatives, of significance is the quantity β^2_{NH}, which characterizes the promoting action of the deformation NH vibrations. A model calculation was also used to estimate the relative β^2_{NH} values for QH^+, 4-$ClQH^+$, 5-$ClQH^+$, and 8-$ClQH^+$: 0.15, 0.4, 0.3, and 1.1, respectively. It follows that the introduction of a heavy atom increases β^2_{NH}, and the closer it is to the NH group, the greater this increase.

As a development of Refs [53, 54], the authors of Ref. [55] investigated a similar series of bromoquinolines and made a quantum-chemical calculation for chloroquinolines using the INDO/S method for the purpose of using its results to interpret experimental data. Three main results were obtained.

1. The dependence of k^{Br}_{TS} on the Br atom position is similar to that for k^{Cl}_{TS}. Experimental points fit reasonably well in a straight line when plotted in the $k^{Br}_{TS}-k^{Cl}_{TS}$ coordinates with the introduction of a correction for the Franck–Condon factor, i.e., actually for the quantities β^2_{Br} and β^2_{Cl}. At the same time, the slope of this straight line is somewhat steeper than the ratio $\zeta^2_{Br}/\zeta^2_{Cl}$ and the line does not pass through the origin:

the action of Br is weaker for low k_{TS} and is stronger for high k_{TS} than would be expected for a simple proportionality between k_{TS} and ζ^2.

2. There exists a rather good, also linear, correlation between the values of k_{TS}^{Br} and k_P^{Br}, which the authors anticipated on the strength of the similarity between expression (31) and the formula defining the probabilities of vibronic radiation transitions.

3. Calculations of chloroquinoline molecules using the INDO/S method, which reproduce the S_1 and T_1 energy levels rather well, predict the emergence of a relatively low-lying level of the (π, σ^*) type, which is denoted by S_x. The S_x state is inherently an intramolecular charge transfer (ICT) state. Calculations were made of the parameter X,

$$X = \left| \frac{\langle T_1 | H_{SO} | S_x \rangle}{{}^1E_{S_x} - {}^3E_{T_1}} \right|^2 , \tag{34}$$

which, as one might expect, should correspond to the quantities k_{TS} corrected by the Franck – Condon factor. Indeed, the experimental data points in the k_{TS} (with a correction by the Franck – Condon factor) and X coordinates satisfactorily lay on a straight line. This demonstrates the significance of (π, σ^*) states of the ICT type for the internal heavy-atom effect.

Furthermore, Jarzeba et al. [55] noted the dependence of the fluorescence lifetime on the position of the chlorine atom (the fluorescence yield is low). It is hypothesized that this may be determined by the relative position of excited levels, but no specific conclusions were drawn.

Recently, in the investigation of 3-methyl- and 3-bromoquinoline phosphorescence, Marquez et al. [58] observed the shortening of τ_P and the enhancement of planar constituents of the phosphorescence oscillator for the bromoderivative. They attributed this to vibronic interactions with the participation of the ${}^3(\pi, \pi^*)$, ${}^3(n, \pi^*)$, ${}^1(\pi, \pi^*)$, and ${}^1(n, \pi^*)$ states, while the heavy-atom effect was not discussed at all.

3.7 Halogenated derivatives of quinoxaline

Another group of Polish authors [59] investigated the heavy-atom effect in the molecules of chloro- and bromoderivatives of quinoxaline with substitution in the carbon ring at positions 5 and 6 (Fig. 11). Previously, 2,3-chloroderivatives of quinoxaline were investigated in Refs [60 – 62].

Well-resolved quasi-line phosphorescence and phosphorescence excitation spectra were obtained and their vibrational analysis was performed. The frequencies were determined for the nonplanar vibrations forming subspectrum II (according to El-Sayed's terminology), which is more pronounced with 6-derivatives. The vibration with the frequency about 250 cm^{-1} is interpreted, following Michaelian and Ziegler [63], as the result of interaction of the skeleton deformation vibration and the C – Hal bond vibration. The special features of this interaction in different compounds result in variations in the frequency. The vibration with a frequency above 500 cm^{-1} is conceivably attributable to the A_2 vibration of quinoxaline near 450 cm^{-1}, whose frequency is supposedly increased upon attachment of a halogen atom. The relative intensity of vibrationally induced transitions (relative to the 0 – 0 transition) was found to rise upon the introduction of a halogen atom and it was higher for bromoderivatives.

The authors of Ref. [59] also performed a quantum-chemical calculation by the INDO/S method. As in Ref. [55], they revealed low-lying ${}^1(\pi, \sigma^*)$ levels. An analysis of the available experimental data invoking the calculated data led the authors to conclude that the distinctions between the photophysical properties of the 5- and 6-derivatives of quinoxaline arise primarily from the position of the lowest triplet level T_1 ${}^3(\pi, \pi^*)$ via both the Franck – Condon factor and the change in energy difference between the given level and the perturbing ones.

3.8 Heavy-atom effect in anthracene derivatives

In the photophysical investigations of the molecules of anthracene derivatives, significant data about the internal heavy-atom effect were obtained and interesting features were revealed for halogenated derivatives.

The energy and kinetic characteristics of chloro- and bromoderivatives of anthracene were determined by Cherkasov et al. [64 – 66]. It turned out that a rather strong heavy-atom effect for 9-bromoanthracene ($\varphi_F = 0.02$ versus $\varphi_F = 0.22$ for anthracene, Fig. 12) becomes weaker upon the introduction of the second Br atom into the opposite meso-position 10 ($\varphi_F = 0.09$).

However, the heavy-atom effect is significant compared to 9,10-dichloroanthracene ($\varphi_F = 0.48$). Upon introduction of an alkyl or phenyl group into position 10 of the 9-bromoanthracene molecule, fluorescence increases still further ($\varphi_F = 0.16$ for 9-bromo-10-phenylanthracene). All this may be attributed to the fact that the main S_1-state deactivation channel is the $S_1 \rightsquigarrow T_2$ transition, while the $S_1 \rightsquigarrow T_1$ transition probability is low; the T_2 level position is sensitive to the substitution and its rise 'disengages' the $S_1 \rightsquigarrow T_2$ channel (see below).

Amirav and Jortner [67] investigated the fluorescence of 9-bromoanthracene and 9,10-bromoanthracene molecules cooled in a supersonic jet. Fine-structure excitation spectra were obtained and the absolute fluorescence quantum yields were measured for different wavelengths λ_{ex} of exciting light. For isolated molecules, the $\varphi_F(\lambda_{ex})$ dependence was found to oscillate near the 0 – 0 transition; for a higher frequency (ν_{exc}), $\varphi_F \approx$ const for 9-bromoanthracene and φ_F decreases sharply for 9,10-dibromoanthracene. Interestingly, at the excitation in the 0 – 0 transition, $\varphi_F = 0.72$ for 9,10-dibromoanthracene and $\varphi_F = 2.4 \times 10^{-3}$ for 9-bromoanthracene, i.e., the difference amounts to almost three orders of magnitude. This is attributable to the existence of two intercombination conver-

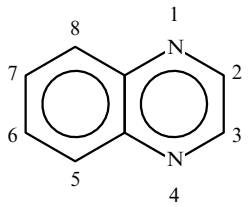

Figure 11. Numbering of atoms in the quinoxaline molecule.

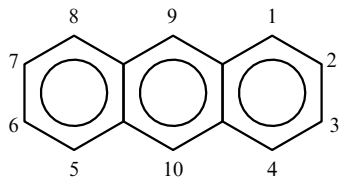

Figure 12. Anthracene structure and position numbering.

sion channels, the direct $S_1 \rightsquigarrow T_1$ channel and the $S_1 \rightsquigarrow T_2 \rightsquigarrow T_1$ mediated one (the authors use T_x to denote the intermediate triplet state and T_x^k to denote its individual vibronic levels), the former being ineffective. This concept has long been under development, beginning in the 1960s (see the references in Ref. [67]).

The data in Ref. [67] allow determining the T_2 level position: it should be located near the $S_1 + 202$ cm^{-1} level. For 9-bromoanthracene, the T_2 level is located below the S_1 level, which favors the manifestation of the internal heavy-atom effect. To confirm the above concept, Amirav and Jortner [67] also employed the external heavy-atom effect in Van der Waals complexes of anthracene, anthracene-d_{10}, and 9,10-dichloro- and 9-cyanoanthracene with Ar and Xe. It should be mentioned that the $\varphi_F(\lambda_{exc})$ dependence in the condensed phase was noted in Ref. [68] for 9,10-dibromoanthracene (as well as for 1-iodonaphthalene) as a violation of the Vavilov law.[2] The decrease in φ_F with decreasing λ_{exc} in the 320–280 nm range (above the region of the first electronic transition) is due to the high probability of the intercombination conversion $S_2 \rightsquigarrow T_i$ and in the higher-frequency domain due to the C–Br bond predissociation. For 1-iodonaphthalene, only the C–I predissociation is assumed.

An anomalous external heavy-atom effect was discovered for 9,10-dibromoanthracene: upon the addition of ethyl iodide or bromobenzene to the alcoholic or hexane solution, it was possible to observe the enhancement of fluorescence [69, 70]. On the basis of systematic investigation of the effect of solvent on φ_F and τ_F, Wu and Ware [71] showed that this effect is due to the rise in the triplet level close to S_1, denoted by T_2 by the authors. The weakening of the $S_1 \rightsquigarrow T_2 \rightsquigarrow T_1$ intercombination transition more than compensates for the strengthening of the low-probability direct $S_1 \to T_1$ transition under the influence of external heavy atoms, which accounts for the above anomaly.

Tanaka et al. [72] investigated the temperature dependence of k_{ST} for 9-bromoanthracene and 9,10-dibromoanthracene in the 77–296 K range. The quantity k_{ST} obeys the Arrhenius dependence

$$k_{ST} = A_{ST} \exp\left(-\frac{\Delta E}{kT}\right). \quad (35)$$

The resultant values of ΔE are approximately 300 cm^{-1} higher than the corresponding energy differences determined from the $T_i \to T_1$ fluorescence in Ref. [73]. The authors of Ref. [72] attribute this to the effect of Stokes shifts (the level positions are determined from the peaks of the 0–0 bands). However, it is not inconceivable that the quenching level T_q and the level T_i from which the emission of light occurs are different, i.e., a rapid transition to a relatively long-lived level T_i occurs after the $S_1 \rightsquigarrow T_q$ transition.

The authors of Refs [74, 75] investigated the effect of temperature and the internal heavy-atom effect on the inverse intercombination conversion $T_i \rightsquigarrow T_2 \rightsquigarrow S_1$ observed in the fluorescence occurring under the stepwise excitation $S_0 \to S_1 \rightsquigarrow T_1$ (a flashlamp) and $T_1 \to T_i$ (a ruby laser). This technique was developed by the same group of authors [76]. The reverse intersystem crossing probability was shown to be proportional to the quantity $\sum \zeta^2$ for 9-methylanthracene, 9,10-dichloroanthracene, and 9,10-dibromoanthracene.[3]

Another group of Japanese authors found that the direct intercombination conversion probability is not negligible for 9-bromoanthracene and 9,10-dibromoanthracene [77]. The authors employed the method in Ref. [78] to study the T–T absorption in the excitation by the second harmonic of a ruby laser ($\lambda = 347.2$ nm). They discovered the T–T absorption at 90 K, when the indirect thermally activated population is hardly possible, and determined the k_{ST} values for 3-methylpentane (MP) and EPA-mixture solutions. For 9-bromoanthracene, $k_{ST} = 1.2 \times 10^7$ s^{-1} (MP) and 1.7×10^7 s^{-1} (EPA); for 9,10-dibromoanthracene, $k_{ST} = 1.9 \times 10^7$ s^{-1} in both solvents ($k_F^{DBA} = 6.7 \times 10^7$ s^{-1}). The fluorescence quantum yield of 9,10-dibromoanthracene at 90 K is equal to 0.78, which is in good agreement with the above-given data for jet-cooled molecules [67]. For 9-bromoanthracene, the average value is $\varphi_F \approx 0.8$, while in the gas phase, $\varphi_F \approx 10^{-3}$. It is likely that the quenching level T_2 (for generality, T_x) in this molecule in the gas phase is located below the S_1 level.

In our laboratory, the internal heavy-atom effect in halogenated anthracene molecules was investigated by Pavlovich [79–81]. For 9,10-dibromoanthracene, it was discovered [79, 80] that the temperature dependence of k_{ST} is described by two exponentials

$$k_{ST} = k_{ST}^0 + A_1 \exp\left(-\frac{\Delta E_1}{kT}\right) + A_2 \exp\left(-\frac{\Delta E_2}{kT}\right). \quad (36)$$

Here, the quantity k_{ST}^0, which corresponds, as already noted in the discussion of other papers, to the direct $S_1 \rightsquigarrow T_1$ interconversion, is low, and the quantity A_1 is four orders of magnitude higher than A_2, while $\Delta E_1 \approx 1600$ cm^{-1} and $\Delta E_2 \approx 275$ cm^{-1}. The high activation barrier is associated with the $S_1(^1B_{2u}) \rightsquigarrow T_3(^3B_{3u})$ transition and the low one with the $S_1(^1B_{2u}) \rightsquigarrow T_2(^3B_{1g})$ transition, prohibited by the symmetry of the coordinate wave function. The prohibition of the latter transition is removed by participation of a nonplanar vibration (γCCBr), supposedly with the frequency 202 cm^{-1}, in accordance with the data for jet-cooled molecules [67]. The difference 275–202 cm^{-1} is filled up with low-frequency matrix vibrations.

For 9,10-dibromoanthracene at room temperature, $\varphi_F = 0.08$ and $\tau_F = 1.6$ ns. Substitution of iodine atoms for bromine atoms results in a drastic shortening of τ_F and a decrease in φ_F, which is evidently due to a strong internal heavy-atom effect: $\varphi_F = 0.018$, $\tau_F = 0.2$ ns [81]. A sharp dependence of φ_F on λ_{exc} (quenching with a decrease in λ_{ex}) was noted within the region of the first electronic transition. In the foregoing, it was mentioned that such dependence had been observed for 9-iodoanthracene earlier. Using the method of picosecond kinetic absorption spectroscopy, Pineault et al. [82] showed that the main channel of the absorbed light energy conversion in 2- and 9-iodoanthracenes is photodissociation in the triplet state T_n with the production of an anthracene radical $A^\bullet$ and atomic iodine. In this connection, Pavlovich et al. [81] made the following note: if this mechanism operates in the case of 9,10-diiodoanthra-

[2] S I Vavilov's papers and his name are not mentioned in Ref. [68], but that work actually verified the validity of Vavilov's law for six organic compounds in solutions.

[3] However, the atoms taken into account were not mentioned; only the peripheral ones (and the carbon atom of the methyl group for the methylderivative) were supposedly included.

cene, the photodissociation should be reversible, because no changes in the optical density of the solutions are observed during measurements. They proposed a different explanation: the production of singlet oxygen in stable Van der Waals complexes of 9-iodoanthracene with O_2.

Although the external heavy-atom effect is not considered systematically in our review, worthy of mention is Ref. [83], which is thematically close to the works cited above. In the supercritical Xe liquid, the fluorescence of 9-cyanoanthracene is quenched due to the external heavy-atom effect. However, the quenching vanishes in passing from room temperature to 15 K. Based on the experiments with 9-cyanoanthracene fluorescence in a cooled supersonic jet, the authors show that the quenching is related to the population of the vibrational S_1-state sublevel with $\nu_{\text{vibr}} = 376\ \text{cm}^{-1}$. For 15 K, this sublevel is barely populated due to rapid vibrational relaxation in the S_1 state.

3.9 Other aromatic and heteroaromatic molecules

The internal heavy-atom effect was also investigated in the molecules of anthraquinone derivatives (Fig. 13), where the photophysics is complicated by the occurrence of n-electrons of the O atoms of carbonyl groups (see Ref. [84] and the references therein). Hamanoue et al. [84] showed that the introduction of a chlorine or bromine atom into the β-position of the anthraquinone molecule has a weak effect on phosphorescence (77 K), which continues to belong to the $^3(\text{n},\pi^*) \to S_0$ type [the weak effect of heavy atoms on the (n,π^*) phosphorescence has long been recognized]. By contrast, in the case of the α-substitution by one or two chlorine or bromine atoms (including the mixed chlorine–bromine substitution), the phosphorescence is quenched (φ_F and τ_F are decreased by about a factor of 100) and the spectrum is blurred. The authors attribute these changes to the nonplanarity arising from steric interactions between the O and Hal atoms. Noted in this case is the internal heavy-atom effect: the quantities k_P and k_{TS} are proportional to $\sum \zeta^2$ for the atoms H, C, O, Cl, and Br. It should be added to the conclusions of the authors of Ref. [84] that the manifestation of the internal heavy-atom effect should be favored by the overlap of the electron clouds of O and Hal atoms.

Zander and Kiesch [85] and Zander [86] investigated the somewhat special case of an intra-annular heavy-atom effect, i.e., the effect on molecular photophysics exerted by a heavy atom incorporated into the cycle of a heteroaromatic compound. Investigations were made of the spectral-luminescent properties of benzo- and dibenzoderivatives of furan, thiophene, selenophene, and tellurophene [85] (Fig. 14), as well as of dibenzoperylene derivatives containing the furan, thiophene, or selenophene type grouping [86]. In the series O–S–Se–Te, they observed a clearly pronounced heavy-atom effect. The results were interpreted on the basis of the

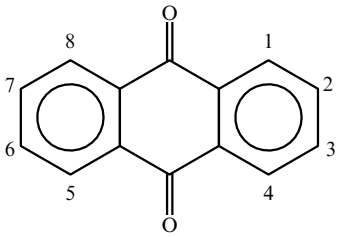

Figure 13. Anthraquinone structure and position numbering.

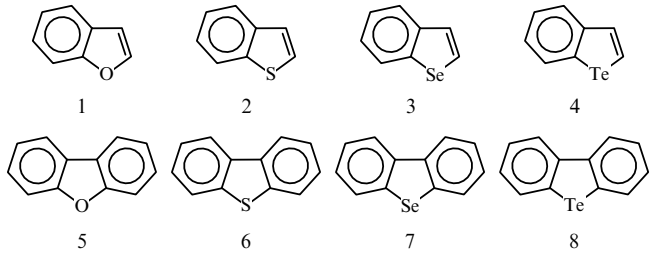

Figure 14. Structures of benzo- and dibenzoderivatives of furan (1, 5); thiophene (2, 6); selenophene (3, 7), and tellurophene (4, 8), respectively.

formula

$$k_P = B\left(\sum_k c_k^2 \zeta^2\right), \tag{37}$$

where c_k is the Hückel HOMO coefficient of an allied carbocyclic molecule (styrene, diphenyl, dibenzoperylene) for a carbon atom k directly bonded to a heavy heteroatom (there are two such atoms).

Although formula (37) has not been substantiated theoretically,[4] experimental points in the coordinates $\lg k_P$ and $\lg K$, where $K = \sum_i c_i^2$, fit nicely on a straight line with a slope of 45°, with a common straight line for benzo- and dibenzoderivatives. Furthermore, k_{TS} obeys the same dependence reasonably well, although somewhat worse. The values of k_P and k_{TS} correlate still worse (with a large scatter). The fact that the points fall on a common straight line in logarithmic coordinates signifies that the magnitude of B is the same for different classes of compounds, i.e., that formula (37) is supposedly valid in this case. It comes as no surprise that the probability k_P is proportional to the value of ζ^2.

For dibenzoperylene derivatives [86], the above dependence is also linear, but the straight line is shifted upwards, i.e., B is greater in magnitude, which may result from the rise in k_{TS} due to the lowering of the level T_1.

Gallivan [87] investigated the heavy-atom effect in molecules with partially isolated conjugated bond systems for 1-halogenphenylnaphthalenes. One *para*-derivative (chlorine) and three *ortho*-derivatives (chlorine, bromine, iodine) were investigated. The introduction of a chlorine atom into the *para*-position of phenyl results in small changes in the fluorescence spectra and in the shortening of τ_T by $\sim 40\%$, i.e., in a weak heavy-atom effect. By contrast, observed in the case of an *ortho*-derivative is an increase in τ_T and the (hypsochromic) shift of the phosphorescence spectrum towards unsubstituted naphthalene. The author attributes this to steric effects, i.e., evidently, to the rotation of the phenyl ring and a weakening of its conjugation to the naphthalene one. Substitution of bromine and iodine atoms for the chlorine atom produces

[4] Reference is made to monograph Ref. [1], but the formula in Ref. [1] applicable to the case where the spin–orbit interaction is relevant for only one (heavy) atom is different in form:

$$\langle S_p | H_{SO} | T_1 \rangle = \frac{c^*_{r\mu K} c_{s\nu K} \left(\zeta_{(\mu\nu)K}\right)}{2},$$

where the coefficients c pertain to the heaviest atom K, r and s are the numbers of the relevant MOs, μ and ν are the AO numbers, and S_p is the 'perturbing' singlet state. In the discussion of a specific example in Ref. [1], it is assumed that these coefficients may be proportional to the LCAO coefficients for the neighboring carbon atoms.

an appreciable heavy-atom effect, but it is weaker than for the corresponding 1-halogenated naphthalenes by a factor of 25, judging by the shortening of τ_T. It is noteworthy that no appreciable strengthening of the 0–0 transition is observed in the phosphorescence spectrum of the iododerivative, which one might expect when the halogen atom is located outside the naphthalene ring plane due to the above-indicated rotation of the phenyl group.

Here, it is pertinent to note that investigations into the excitation of molecules by monoenergetic electron beams revealed an increase in electron energy losses for europium chelates in the region between the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ bands in the optical absorption spectrum upon introducing Br and I atoms into the ligand; this effect was attributed to the strengthening of the intercombination $T_i \leftarrow S_0$ transitions under the influence of heavy atoms [88, 89].

4. Internal heavy-atom effect in porphyrin and metalloporphyrin molecules

4.1 Phosphorescence of tetrapyrrole pigments

Of interest are the manifestations of the internal heavy-atom effect in the case of tetrapyrrole pigments — porphyrins, chlorins, phthalocyanines, etc. In a tetrapyrrole macrocycle, a heavy atom may reside both at the center (a metal atom) and at the periphery. The class of tetrapyrroles attracts considerable attention from researchers for several reasons, first of all, due to the biological significance of molecules of this type (the structures are depicted in Fig. 15).

Although the phosphorescence of metalloporphyrins and metal-chlorines, including chlorophyll *b*, has been known since 1947 [90, 91], it was not until 1955 that Becker and Kasha [92] noted the role of the central metal atom as the spin–orbit perturbing factor. Subsequently, Becker and Allison performed a systematic study of the effect of the nature of metal on the phosphorescence of metalloporphyrins [93–95] (by the example of complexes of mesoporphyrin IX dimethyl ether). They showed that complexes with completed metal d-shells exhibit the internal heavy-atom effect: τ_T shortens as Z of the metal grows, φ_F decreases, and φ_P may increase. Zinc complexes have the optimal fluorescence–phosphorescence yield ratio. The photophysics of transition metal complexes is more complicated. Many of them do not luminesce at all. An important result was the discovery of intense phosphorescence for virtually nonfluorescent Pd and Pt complexes. More recently, it was shown that φ_P for Pd- and Pt-etioporphyrin I is equal to 0.5 and 0.9, respectively [95]. For comparison, $\varphi_P = 0.07$ for Zn-etioporphyrin [97].

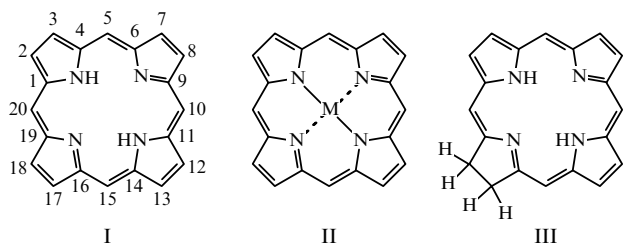

Figure 15. Structural formulas of tetrapyrroles. I — porphin, II — metal porphin, III — chlorin (dihydroporphin). Various porphyrins and chlorins differ from I and III by the presence of organic radicals at positions $2, 3, \ldots, 17, 18$ of pyrrole rings and at positions 5, 10, 15, 20 of methine bridges (*meso*-positions).

We do not enlarge on the general issues of the photophysics of metalloporphyrin molecules, because they are adequately discussed in the monographic literature [98–100]. We emphasize only two points.

1. Reproducible data on the phosphorescence spectra of the free bases of porphyrins and their complexes with light metals (Mg, Al) were obtained as late as 1974 [101, 102]. Obtained earlier, in 1973, were reproducible data on the position of the 0–0 band in the fluorescence spectra of chlorophyll *a* and pheophytins[5] *a* and *b* (the data in Ref. [91] for chlorophyll *b* were not confirmed: obtained in lieu of 860–890 nm was 920–930 nm) [103, 104]. However, complete corrected phosphorescence spectra of chlorophylls, pheophytins, and their close analogs were later reported in Ref. [105].

2. An observation of fundamental importance was reported by Gurinovich, Patsko, Solov'ev, and Shkirman [106]. They found that the phosphorescence of Zn- and Cu-porphyrins has a degree of polarization close to 1/7 and is independent of λ_{exc}. This implies that the phosphorescence oscillator is planar. For Mg-porphin and Mg-*meso*-tetraphenylporphin (MgTPP), they showed the existence of a nonplanar component of the phosphorescence oscillator [107]. For Zn-porphyrins of symmetry C_{2v}, for instance Zn-chlorins, the phosphorescence polarization P_P^{00} amounts to $-1/3$ and the phosphorescence oscillator is oriented in the molecular plane [108], and it is therefore valid to say that the selection rules for spin–orbit interaction are strictly fulfilled in the case of zinc complexes of porphyrins. Hence, it follows that there occurs mixing of the $^3(\pi, \pi^*)$ T_1 state with the singlet $^1(\pi, \pi^*)$ states both for the D_{4h} symmetry ($P_P^{00} \cong 1/7$) and for the C_{2v} symmetry ($P_P^{00} \cong -1/3$), which is in seeming contradiction to the general properties of planar π-electronic systems (see above). This contradiction is resolved as follows: for the Zn atom, the d-orbitals for which one-center integrals are nonzero (see below about the role of extraligands) can participate in the spin–orbit interaction.

In the subsequent discussion, the emphasis is placed on the photophysics of the molecules of heavy halogen atoms covalently associated with porphyrin molecular systems.

4.2 Photophysics of halogen-phenyl-porphyrins

4.2.1 Luminescence of *para*-halogenated tetraphenylporphin and tetraphenylchlorine and their metal complexes. In the work of our laboratory [109, 110], it was discovered that the attachment of heavy halogen atoms at the *para*-positions of the phenyl groups of *meso*-tetraphenylporphin molecules (H_2TPP) and its metal complexes has a significant effect on the photophysics of the porphyrin macrocycle. This marked the beginning of a series of works to investigate the internal heavy-atom effect in porphyrin molecules. We discuss their findings step by step, beginning with Refs [109, 110].

In Refs [109, 110], the spectral-luminescent properties of *para*-halogenated H_2TPP and its complexes with Mg and Zn were studied, wherein the heavy halogen atoms were separated by phenyl groups from the main conjugated bond system. In abbreviated form, these compounds are denoted as H_2TPP-(*p*-Cl)$_4$. Owing to the noncoplanarity of the benzene

[5] Chlorophylls *a*, *b*, etc. are magnesium chlorins of a complicated structure, and the corresponding metal-free compounds are termed pheophytins.

and porphyrin rings, the halogen atoms are largely isolated from the chromophore conjugated bond system. Despite this fact, a significant intramolecular perturbation of intercombination transitions was discovered, which was responsible for fluorescence quenching and the shortening of the triplet state lifetime. The phosphorescence of metal complexes was analyzed in detail and the probability k_P was shown to rise with Z_{Hal} due to the strengthening of the vibronic phosphorescence band. A conclusion was reached that the singlet character is transferred to the triplet state T_1 via an intermediate triplet level, i.e., the rise in k_P is caused by second-order effects.

Borisevich et al. [111] widened the range of subjects under investigation by including *meso*-tetraphenylchlorin (H_2TPC) and its *para*-halogenated derivatives (Cl, Br, I) and investigated the spectral, energy, and kinetic characteristics of the phosphorescence of free bases. The fluorescence and phosphorescence spectra of *para*-halogenated H_2TPP exhibit dependence on the nature of the halogen atom: the vibronic band gains in intensity relative to the $0-0$ band with an increase in the atomic number of the halogen. For *para*-halogenated derivatives of H_2TPC, the halogenation has only a slight effect on the relative band intensities in the fluorescence and phosphorescence spectra. The $0-0$ band positions in the fluorescence spectra (the S_1 level) and the phosphorescence spectra (the T_1 level) for the halogenated derivatives of both H_2TPP and H_2TPC are only slightly dependent on the nature of the halogen, and the $S-T$ interval is conserved. At the same time, the intensity rise of the vibronic band in the phosphorescence spectrum of the free bases of bromo- and iododerivatives is substantially weaker than for MgTPP and ZnTPP investigated in Refs [109, 110].

With an increase in the atomic number of a halogen, φ_F of *para*-halogenated derivatives of H_2TPP and H_2TPC decreases [by almost a factor of 30 for H_2TPP-(*p*-I)$_4$ in comparison with H_2TPP and by a factor of 16 for H_2TPC-(*p*-I)$_4$ in comparison with H_2TPC] and φ_P increases [16-fold for H_2TPP-(*p*-I)$_4$ in comparison with H_2TPP and 64-fold for H_2TPC-(*p*-I)$_4$ in comparison with H_2TPC]. It is noteworthy that φ_F decreases faster in the series of H_2TPP and its halogenated derivatives than their φ_P increases, while the reverse holds for the series of H_2TPC and its halogenated derivatives. As Z_{Hal} grows, the fluorescence lifetime (τ_F) for H_2TPP, H_2TPC, and their halogenated derivatives shortens proportionally to the decrease in φ_F, and hence the fluorescence probability k_F is virtually unchanged, which was earlier noted for the metal complexes of halogenated derivatives of H_2TPC in Ref. [112].

The probabilities k_{ST} and k_P (in the calculation, it was assumed that $\varphi_F + \varphi_T = 1$, which was substantiated for H_2TPP and its metal complexes in Refs [109, 110]) rise sharply upon introducing heavy halogen atoms into the *para*-positions of phenyl groups [k_{ST} is 32 times higher for H_2TPP-(*p*-I)$_4$ than for H_2TPP and 20 times higher for H_2TPC-(*p*-I)$_4$ than for H_2TPC]. The rise in k_P is only partly due to the strengthening of the vibronic band of the phosphorescence spectrum as opposed to the metal complexes of H_2TPP [110].

Based on the analysis of experimental data, a conclusion was drawn that the effect of heavy halogen atoms on the photophysics of the examined molecules of free bases was due to the mixing of singlet and triplet macrocycle states in the first order of the perturbation theory.

This conclusion was borne out by the results of spectral-polarization investigations into the phosphorescence of para-halogenated derivatives of H_2TPP and H_2TPC [113]. As the atomic number of a halogen increases, a transformation of the phosphorescence polarization spectrum occurs, testifying to the increase in planar components of the three-dimensional phosphorescence oscillator. For H_2TPP, the introduction of heavy halogen atoms into the *para*-positions of benzene rings strengthens the *Y*-component, which is forbidden for the D_{2h} symmetry, to a greater degree than the allowed *X*-component. For H_2TPC, the *X*-component allowed for the C_{2v} symmetry is primarily strengthened under the effect of heavy atoms. The observed behavior was interpreted on the basis of the low symmetry of the molecules under investigation, which was due to the nonplanar arrangement of benzene rings relative to the macrocycle plane.

A comparison of the data for the halogenated derivatives of H_2TPP and H_2TPC [111] shows that hydrogenation of the pyrrole ring has only an insignificant influence on the internal heavy-atom effect. For H_2TPC derivatives, the heavy atoms affect k_{ST} somewhat more weakly and $1/\tau_P$ somewhat more strongly, and the influence on k_P is about the same, to say nothing of the fact that k_P is very low for the unsubstituted H_2TPC and rises sharply in passing to the chloroderivative. However, when it is considered that the intensity of the long-wavelength $S_1 \leftarrow S_0$ absorption band, commonly denoted as $Q_1(0,0)$, for chlorins is higher and the $T_1 \rightarrow S_0$ transition intensity is largely determined by the admixture of the $S_1(^1Q_1)$ state, it is valid to say that the mixing of the states S_1 and T_1 is weaker for the halogenated derivatives of H_2TPC than for those of H_2TPP. Here, a certain part may be played by steric factors, which have the effect that two benzene rings of the H_2TPC molecule neighboring on the hydrogenated pyrrole ring are perpendicular to the macrocycle plane.

4.2.2 Cancellation of the spin – orbit perturbations introduced by the atoms of a halogen and a metal. The luminescence of the free bases and zinc complexes of *meso*-tetraarylporphyrins, which contain halogen atoms in *para*-, *meta*-, and *ortho*-positions of phenyls, was investigated by Quimby and Longo [114]. The fluorescence quenching (most pronounced in the case of *ortho*-substitution in free bases) was attributed to intensification of the $S_1 \rightsquigarrow T_n$ intercombination transitions. The observed intensity lowering of the $0-0$ absorption and fluorescence bands of the Zn-derivatives on the *ortho*-substitution was, as for the free bases, attributed to steric interactions of the halogen atom and the pyrrole rings and, as a consequence, to the increase in HOMO a_{1u} of the porphyrin macrocycle. For ZnTPP-(*o*-Cl)$_4$, they discovered a lowering of the intercombination conversion probability in comparison with unsubstituted ZnTPP and provided a conjectural explanation (in a note, following the idea of the paper referee M Gouterman): the observed lowering is due to the destructive interference of the constituents of the matrix element of the spin – orbit interaction operator that belong to the metal atom and to the chlorine atom in *ortho*-positions. It was noted that attempts to record the phosphorescence of free bases did not meet with success.

The spectral-luminescent and photophysical characteristics of *para*-, *meta*-, *ortho*-chloro-, and *ortho*-bromoderivatives of H_2TPP, as well as of their complexes with Zn, Pd, and In, were comprehensively investigated by Egorova et al. [115]. They traced the effect of the position of a halogen atom in the phenyl group on the probabilities of radiative and nonradia-

tive transitions from the S_1 and T_1 states. A substantial strengthening of the heavy-atom effect in the case of *ortho*-substitution was attributed to efficient mixing of the singlet (π, π^*) states with the T_1 state arising from the influence of the heavy atom. Complexes of H_2TPP and H_2TPP-(*o*-Cl)$_4$ with In(OH) were specially synthesized to elucidate the feasibility of cancellation of the contributions of the spin – orbit interaction. It was found that the enhancement of fluorescence upon introducing chlorine atoms is significantly more pronounced for indium complexes (φ_F increases five-fold) than for the zinc ones. A conclusion was drawn that the constituents of the matrix element of the spin – orbit interaction operator that belong to the metal and chlorine atoms in *ortho*-positions were different in sign. In that work, the phosphorescence spectra of H_2TPP and its halogenated derivatives were recorded for the first time.

As a development of Ref. [115], the authors of Ref. [112] investigated the zinc and indium complexes of halogenated derivatives of H_2TPC, where the radiative $S_1 \rightarrow S_0$ transition probability is increased owing to pyrrole-ring hydrogenation. The energy and time luminescence characteristics are largely dependent both on the chlorine atom position in the phenyl group and on the atomic number of the metal introduced into the center of the molecule. Passing from ZnTPC to ZnTPC-(*p*-Cl)$_4$ lowers the quantum yield of fluorescence by a factor of 1.3. Passing to ZnTPC-(*o*-Cl)$_4$, on the contrary, increases φ_F by nearly a factor of 2. Passing from In(OH)TPC to In(OH)TPC-(*o*-Cl)$_4$ also increases φ_F, although the increase is far smaller — 1.4-fold. The fluorescence lifetime changes in parallel with the changes in φ_F such that k_F is hardly changed, i.e., the observed effects arise from the differences in the interconversion probability k_{ST}. The magnitude of k_{ST} depends strongly on the chlorine atom position in the phenyl group and lowers twofold in passing from ZnTPC to ZnTPC-(*o*-Cl)$_4$. Upon substituting In for Zn, the k_{ST} probability rises by nearly an order of magnitude, and *ortho*-chlorosubstitution in the indium complex lowers k_{ST} 1.4-fold.

The findings in Ref. [112] confirmed the existence of the interference effect described by Egorova et al. [115]. According to the data in Ref. [115], passing from the zinc complex to the indium one was accompanied by a significant strengthening of the effect, which was, strictly speaking, the demonstration of its verity. The experimental data in Ref. [112] signify that the manifestation of the interference of spin – orbit perturbations introduced by a metal atom and chlorine atoms is more pronounced for ZnTPC-(*o*-Cl)$_4$ than for the indium complex. This difference between MTPC and MTPP (where M stands for metal) is not fundamental; it merely implies that the contribution of Cl atoms to k_{ST} in the case of MTPC-(*o*-Cl)$_4$ is smaller than in the case of MTPP-(*o*-Cl)$_4$. Moreover, this feature of MTPC provides yet another confirmation of the existence of the effect, because the general picture persists under different relations of the spin – orbit perturbations.

By the example of metal complexes of the H_2TPP *para*-bromoderivative with Zn, In, and Pd, it was shown that the cancellation of spin – orbit perturbations occurs not only for *ortho*-halogenated derivatives of H_2TPP but also for *para*-halogenated derivatives [116]. The introduction of Br atoms into the zinc complex of H_2TPP decreases φ_F by an order of magnitude and in the case of the complex with the heavier indium atom, by only a factor of two, φ_F for In(OH)TPP-(*p*-Br)$_4$ being only slightly smaller than for ZnTPP-(*p*-Br)$_4$. For unsubstituted compounds, φ_F becomes 4.4 times smaller in passing from Zn to In. For complexes with the palladium atom, which is a very strong spin – orbit perturbing factor, even an increase in φ_F is observed upon the introduction of bromine atoms. However, this is also accompanied by a shortening of the singlet – triplet interval. It is conceivable that the position of the T_2 level also changes. The transition to this level makes a significant contribution to the intercombination conversion; the shift of this level away from 'resonance' may be entirely or partly responsible for the enhancement of fluorescence. In the case of indium complexes this explanation fails, because the fluorescence and phosphorescence spectra shift only slightly under bromination.

The introduction of bromine atoms has a weak effect on the luminescence spectra of metal complexes. The energy characteristics (for the indium complex) are changed more significantly. The magnitude of k_P for In(OH)TPP is small, and it rises sharply upon the introduction of the bromine atom; the resultant k_P values are comparable to the data for the free basis. For PdTPP, the k_P value also increases upon introducing bromine atoms, although much more weakly. By contrast, the k_P value for the zinc complex rises upon bromination only due to the enhancement of the $0-1$ phosphorescence spectral band, and the k_P value for ZnTPP-(*p*-Br)$_4$ is two times smaller than for In(OH)TPP-(*p*-Br)$_4$. The effect of bromine atoms is supposedly weakened by the effect of Zn atoms, i.e., destructive interference of spin – orbit perturbations also occurs in this case.

The conclusion that the contributions to the dipole moment of the $0-0$ $T_1 \rightarrow S_0$ transition may cancel was recently drawn in Ref. [117] on the basis of a direct calculation by the perturbation theory [118] for the chloroderivatives of dibenzo-*para*-dioxine. It was determined that the sings of contributions of chlorine atoms to the transition moment for the Y-component of the H_{SO} operator (the Y axis is aligned with the long axis of the molecule) are different for positions α and β. This is the reason why, for instance, the transition moment is greater for the β-tetrachloroderivative than for the $\alpha\beta$-tetrachloroderivative and the octachloroderivative. That work continued the series of several interesting publications by the same group of authors concerned with the quasi-line phosphorescence spectra of *para*-dioxine and its derivatives (ecologically hazardous toxicants) [119 – 123]. We nevertheless discuss that paper in this section rather than the previous one, because it has the cancellation effect in common with our earlier publications.

It is pertinent to note that Klimenko et al. [117] arrive at one more significant result. In their calculations, account was taken of not only the T_1 state interaction with excited singlet states but also the interaction between the S_0 state and triplet states, which is quite often neglected. The contribution of the latter mechanism was then found to be greater than that of the former one.

We emphasize that the cancellation effects for the contributions to the spin – orbit interaction of the destructive interference type may be a rather widespread occurrence. For instance, they may underlie the special features of phenanthrene derivatives revealed in Ref. [43] (see Section 3.4).

In concluding this section, we note that the effect of molecular structure, of halogenation for different positions of the phenyl group of H_2TPP in particular, on the quenching of triplet porphyrin states by molecular oxygen was investigated in Ref. [124]. When the atomic number of the halogen introduced into the *para*-position of phenyl

increases, the quantum yield of singlet oxygen production rises, which is due to the increase in the quantum yield of interconversion. However, the constant of excited-state quenching by molecular oxygen (k) is then barely affected by the atomic number of the halogen in the *para*-position of phenyl. This is attributed to the weakness of the interaction between the π-electronic system of the porphyrin macrocycle and the halogen atoms residing in the *para*-positions of phenyls. Introduction of halogen atoms into the *ortho*-position of phenyl results in a decrease of the quenching constant k. A conclusion was drawn that the approach of the halogen atom to the conjugated porphyrin system increases the oxidation potential, i.e., the constant k is more sensitive to the halogen position in the phenyl ring relative to the conjugated bond system of the porphyrin molecule and not to the atomic number of the halogen (the change of spin – orbit interaction).

4.3 Heavy-atom effect in pyrrole-ring halogenated porphyrins

The authors of Ref. [125] investigated the spectral-luminescent properties of halogenated derivatives of deuteroporphyrin IX and their zinc complexes in which the halogen atoms are attached directly to the conjugated bond system of the porphyrin macrocycle (at 3,8-positions of pyrrole rings, which are 2,4-positions in the old notation).

Attachment of halogen atoms to the pyrrole rings increases the intercombination transition probabilities much more strongly (per single halogen atom) than for *para*-halogenated H_2TPP and is comparable to the effect of *ortho*-halogenation of H_2TPP. A substantial transformation of phosphorescence spectra with an increase in the atomic number of the halogen was discovered for zinc complexes, which was caused by the intensification of the vibronic bands with frequencies ~ 150 and ~ 700 cm^{-1}. The rise in the probability k_P was attributed, as for *para*-halogenated derivatives of H_2TPP, to second-order effects arising from vibrational-electronic interactions.

Investigations were made of the bromoderivatives of octaethylporphin (H_2OEP) — 2-bromo-3,7,8,12,13,17,18-heptaethylporphin (H_2-I) and 2,12-dibromo-3,7,8,13,17,18-hexaethylporphin (H_2-II) — wherein the heavy bromine atoms reside at the β-positions of the pyrrole rings and are directly bound to the conjugated bond system of the porphyrin macrocycle [126]. Noted in this case was the possibility of the constructive interference of the contributions to the spin – orbit interaction made by two bromine atoms. In the molecules investigated, a rather strong internal heavy-atom effect occurs: introducing bromine atoms results in a drastic shortening of the S_1 and T_1 excited-state lifetimes and a lowering of the fluorescence yield; the influence of one bromine atom in the H_2-I molecule on the probabilities k_{TS} and k_{ST} is then comparable to the influence of four bromine atoms for H_2TPP-(p-Br)$_4$. Introducing one bromine atom into the H_2OEP molecule lowers the phosphorescence yield approximately proportionally to the shortening of τ_T, and introducing the second bromine atom somewhat increases the phosphorescence yield. The data for H_2-II correspond well with the data obtained for 3,8-dibromodeuteroporphyrin in Ref. [125]. For the nonradiative intercombination transitions $T_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow T_1$, Borisevich et al. [126] demonstrated the nonadditivity of the internal heavy-atom effect for the introduction of the second bromine atom. This was interpreted as the constructive interference of spin – orbit perturbations (they all appear in the expression for the matrix element with the same sign).

It is noteworthy that some photophysical parameters of H_2-I and H_2-II were investigated in parallel in Ref. [127] (only at room temperature). In general, the picture of the strong internal heavy-atom effect proves to be the same, but there is quantitative disagreement with the data in Ref. [126], which is primarily due to the values of φ_F and φ_T for the H_2OEP reference employed in Ref. [127].

4.4 Effect of heavy halogen atoms — acidoligands — on the photophysics of metalloporphyrins

Because the heavy-atom effect is clearly manifested when heavy halogen atoms are far enough from the porphyrin macrocycle (for *para*-halogenated derivatives of H_2TPP), attachment of a halogen to the very center of a metalloporphyrin molecule as the so-called acidoligand would be expected to produce a significant effect. But investigations of the luminescence of etioporphyrin I ('etio') aluminum complexes, namely AlCletio, AlBretio, and AlIetio, yielded a negative result: the photophysical characteristics were independent of the nature of the halogen atom [128]. This result was, as is now evident, erroneous. The employment of chromatography to purify the complexes underlay the error. At present, it has been determined (see, e.g., Ref. [129]) that acidoligands are substituted by the OH group in the chromatography on Al_2O_3. Moreover, it has been shown that Br- and I-acidoligands are especially labile (see below).

The significant influence of heavy halogen atoms as acidoligands was demonstrated by Gouterman, Schwartz, Smith, and Dolphin [130] for porphyrin complexes with IVth group elements. To saturate the valence 4, suchlike complexes affix two acidoligands on either side of the macrocycle plane, with the result that a metal atom is located in this plane [131]. The authors of Ref. [130] investigated the complexes $SiCl_2$OEP, $GeCl_2$OEP, $SnCl_2$OEP, SnF_2etio, $SnCl_2$etio, $SnBr_2$etio, SnI_2etio, and some others, including $SnCl_2$TPP. In the spectroscopy of porphyrins, it is well known that the electronic structure and associated properties of the metal complexes of H_2OEP and etioporphyrin I are very close, which is borne out by the identity of the data for $SnCl_2$OEP and $SnCl_2$etio obtained in Ref. [130]. This signifies that the above complexes may be regarded as complexes of the same porphyrin, while all the distinctions may be attributed only to the state of the central part of the molecule — the metal atom and two acidoligands. In connection with what was stated above about aluminum complexes, it should be mentioned that the authors of Ref. [130] specially emphasize the extreme lability of Br- and I-acidoligands: their dissociation occurs in solvents containing alcohol or ester groups, and direct synthesis from $SnBr_2$ and SnI_2 yielded $Sn(OH)_2$ complexes (for the investigations, $SnBr_2$etio and SnI_2etio were obtained by shaking the chloroform solution of $Sn(OH)_2$etio with 6M HBr or 6M HI, respectively; the chloroform layer was separated and stored above water-free Na_2SO_4).

Measuring the photophysical parameters φ_F, φ_P, φ_F/φ_P, and $\tau_P \equiv \tau_T$ clearly revealed the internal heavy-atom effect in two series: $SiCl_2$OEP ($Z_{Si} = 14$), $GeCl_2$OEP ($Z_{Ge} = 32$), $SnCl_2$OEP ($Z_{Sn} = 50$) (this series is referred to as 'series I') and SnF_2etio ($Z_F = 9$), $SnCl_2$etio ($Z_{Cl} = 17$), $SnBr_2$etio ($Z_{Br} = 35$), SnI_2etio ($Z_I = 53$) (series II). The variations in Z in these two series are comparable, and experiment shows

that the perturbation introduced by the acidoligand is stronger than that introduced by the metal atom.

The influence of heavy atoms on the photophysical parameters for the above-specified series of compounds can be judged by the data collected in Table 2. It is noteworthy that the variations in absorption spectra in these series are moderate: in series I, a small bathochromic shift in the Q bands is observed for $SnCl_2OEP$, the $Q(0,0)$ band intensity decreasing in this series; in series II, the Q bands behave in a similar manner, while for the B band (the so-called Soret band, an intense band at the visible–UV region boundary) a broadening with increasing Z_{Hal} is observed, which is accompanied by a lowering of the peak intensity, i.e., the oscillator strength is conserved (for the designation of the bands, see Fig. 3b).

Table 2. Photophysical parameters of porphyrin complexes with IVth group elements for 77 K [130].

Complex	$\varphi_F \times 10^2$	$\varphi_P \times 10^2$	φ_P/φ_F	τ_P, ms
$SiCl_2OEP$	20	1.8	0.1	95
$GeCl_2OEP$	7.4	4.2	0.6	42
$SnCl_2OEP$	0.7	6.8	9.7	30
SnF_2etio	0.9	3.8	4.3	50
$SnCl_2etio$	0.7	6.8	9.7	28
$SnBr_2etio$	0.3†	3.5	11.3	6
SnI_2etio	0.02†	0.4	15.8	1

† Data for 293 K.

The manifestation of the internal heavy-atom effect is clearly seen from Table 2, the quantity φ_F being more sensitive than φ_P in series I and the relative changes in these quantities being comparable in series II. The value of φ_P in series I increases but not sharply. In series II, it initially increases and then decreases.

To interpret the observed effects, the matrix elements of the spin–orbit interaction were calculated in Ref. [130] with the help of the extended Hückel method (EHM). From the theory of spin–orbit interaction in metalloporphyrin molecules [132], it follows that the main part in the mixing of the lower singlet and triplet (π, π^*) states is played by the one-center integrals

$$\langle nd_{xz} | \zeta_M(r) l_z^M | nd_{yz} \rangle \equiv \frac{\zeta_M}{i} , \tag{38}$$

$$\langle np_x | \zeta_L(r) l_z^L | np_y \rangle \equiv \frac{\zeta_L}{i} , \tag{39}$$

whose contribution is determined by the interaction of the lower vacant π-orbital of symmetry e_g with the d_{xz}-, d_{yz}-orbitals of the metal atom and with the p_x-, p_y-orbitals of the ligand atom located near the plane of the macrocycle. In formulas (38) and (39), $\zeta_M(r) l_z^M$ is the spin–orbit interaction at the metal atom and $\zeta_L(r) l_z^L$ at the ligand atom. The spin–orbit interaction integral, denoted by Z in Ref. [130] and by Ω in this paper to avoid confusion with the atomic number, is given by

$$\Omega = -c_M^2 \zeta_M - 2c_L^2 \zeta_L , \tag{40}$$

where c_M and c_L are the respective coefficients of the e_g-orbital for the metal and the ligand atom. The quantities ζ_M and ζ_L are determined from the atomic spectra. The EHM was employed precisely for the calculation of c_M and c_L.

For experimental data analysis, the well-known relations of molecular photophysics were modified assuming that intercombination transition probabilities are proportional to Ω^2,

$$k_P = B_P \Omega^2 ; \quad k_{ST} = A_{ST} \Omega^2 ; \quad k_{TS} = B_{TS} \Omega^2 ,$$

where A_{ST}, B_P, and B_{TS} are constants [the probability k_F is assumed to be constant relying on absorption spectra and $k_{S_1S_0}$ (denoted as A_F) relying on general considerations].

The following relations were obtained:

$$\varphi_F^{-1} - 1 = k_F^{-1}(A_F + \Omega^2 A_{ST}) , \tag{41}$$

$$\tau_P^{-1} = \Omega^2 (B_P + B_{TS}) , \tag{42}$$

$$\frac{\varphi_P}{\varphi_F} = \frac{\Omega^2 A_{ST} B_P}{k_F (B_P + B_{TS})} , \tag{43}$$

$$\frac{\varphi_P}{\varphi_F} \tau_P = \frac{A_{ST} B_P}{k_F (B_P + B_{TS})^2} . \tag{44}$$

Here, the following note is in order. By the time Ref. [130] was carried out, at the Institute of Physics of the BSSR Academy of Sciences, in our laboratory [133–135], and in the Laboratory of Photochemistry [136, 137], it was determined for porphyrins and metalloporphyrins that $\varphi_F + \varphi_T \approx 1$, i.e., the quantity $k_{S_1S_0}$ can be neglected, which simplifies the photophysical data analysis. However, M Gouterman disregarded these results, relying on his data on φ_T determined by the pulsed calorimetry technique [138] (in particular, the value $\varphi_T = 0.57$ was obtained for $SnCl_2$, i.e., $\varphi_F + \varphi_T \approx 0.6$).

A comparison of the theory with experimental parameters according to relations (41)–(44) shows the following: (1) the quantity $(\varphi_P/\varphi_F)\tau_P$ should be constant but is not. We note that this comes as no surprise: for nonradiative transitions, as shown above, (σ, π^*)- or (π, σ^*)-states play a significant part unrelated to the value of Ω; (2) a decrease in Ω is predicted in the series $SiCl_2$, $GeCl_2$, and $SnCl_2$, which is in apparent contradiction to experimental data; (3) predictions for $SnBr_2$ and SnI_2, on the contrary, overrate the values of Ω. Items 2 and 3 lead the authors of Ref. [138] to a somewhat imprecise formulation that the EHM may underestimate the contribution of the metal and overestimate the contribution of the ligand; it would supposedly be well to formulate the conclusion more precisely. For $SnCl_2$, for instance, the contribution of the metal is estimated at only 5%. Were it about 50%, the increase in Ω that follows from experiment in series I — $SiCl_2$, $GeCl_2$, and $SnCl_2$ — would be natural, in the view of the authors of Ref. [130].

4.5 Halogenated derivatives of Zn-phthalocyanine

Closely related to porphyrins are phthalocyanines — synthetic dyes that enjoy important and diversified applications in science and technology. Halogenation is widely used to modify the physicochemical properties of these compounds. Nevertheless, as far as we know, there is only one publication [139] on the photophysics of halogenated phthalocyanine molecules.

For Zn-phthalocyanine (ZnPc) and its tetra-halogenated derivatives containing one halogen atom per each isoindole ring (Fig. 16), Xian-Fu and Hui-Jun [139] determined the photophysical parameters of S_1-state deactivation, intermolecular associative processes, and interaction with oxygen. As in the case of halogenated porphyrins, the internal heavy-

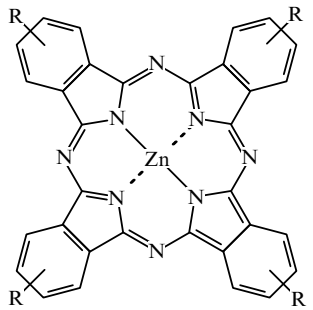

Figure 16. Structure of Zn-phthalocyanine and its halogenated derivatives (R = H, Cl, Br, I).

atom effect is clearly manifested here — the intercombination conversion probability rises with Z_{Hal}, which makes itself evident in a lowering of φ_{F} and a shortening of τ_{F}. It was of interest to compare the degree to which heavy atoms affect the photophysics of ZnPc and the halogenated derivatives of H_2TPP, investigated in our work, whose molecules also contain one halogen atom in each of the four fragments of the molecule. For this, we determined the quantities $\Delta k_{\mathrm{ST}}^{\mathrm{Hal}} = k_{\mathrm{ST}}^{\mathrm{Hal}} - k_{\mathrm{ST}}^{\mathrm{H}}$ from the data in Ref. [139] using the formula

$$\Delta k_{\mathrm{ST}}^{\mathrm{Hal}} = \frac{1}{\tau_{\mathrm{F}}^{\mathrm{H}}}\left(\frac{\varphi_{\mathrm{F}}^{\mathrm{H}}}{\varphi^{\mathrm{Hal}}} - 1\right). \tag{45}$$

We here assumed that the relative fluorescence yield for compounds with similar emission spectra is determined with a high accuracy and that the same is true for τ_{F} of unquenched fluorescence. Experimental data for ZnTPP [110] and H_2TPP [111] were processed in a similar way (in doing this, there emerged a small discordance with the values of k_{ST} given in these papers). The results of such comparative analysis for the three molecules are collected in Table 3.

One can see from Table 3 that the values of $\Delta k_{\mathrm{ST}}^{\mathrm{Hal}}$ for ZnPc derivatives are significantly smaller than for ZnTPP derivatives; for Br and I, this is so for H_2TPP as well. However, consideration must be given to the difference in $k_{\mathrm{ST}}^{\mathrm{H}}$ magnitudes, i.e., primarily the Franck – Condon factor (for zinc complexes). That is why we determined the quantities $r^{\mathrm{Hal}} = \Delta k_{\mathrm{ST}}^{\mathrm{Hal}}/k_{\mathrm{ST}}^{\mathrm{H}}$ (for ZnPc) and similarly r_1^{Hal} for ZnTPP and r_2^{Hal} for H_2TPP. Also given in Table 3 are the values of r_1/r and r_2/r, which characterize the difference between the molecules. It is evident that the internal effect of heavy halogen atoms in ZnTPP is approximately four times stronger than in ZnPc, r_1/r being greatest for Br. A comparison with the free bases shows that the difference is even larger for I and is smaller for Cl.

Therefore, attachment of heavy halogen atoms to the benzene fragments of isoindole groups, which form the planar phthalocyanine macrocycle, has a weaker effect on molecular photophysics than halogenation of the *para*-positions of benzene rings noncoplanar with the macrocycle. This supposedly occurs because noncoplanarity removes the nonrigourous prohibition imposed on the mixing of S_1 and T_1 states of the (π, π^*) type for planar systems, which was discussed in the foregoing.

5. Application of the internal heavy-atom effect in molecular photonics

One can see from the preceding material that transition probabilities in different deactivation channels of excited electronic states are specifically dependent on molecular structure in the case of the internal heavy-atom effect. This allows controlling the parameters of chromophores and luminophors in optical devices and systems.

In particular, the authors of Ref. [140] proposed the use of phthalocyanine complexes with heavy metals (indium and lead) to improve the parameters of optical limitation on the basis of reverse saturable absorption (RSA). The RSA effect is due to the emergence of transient absorption in the $S_i \leftarrow S_1$ and $T_i \leftarrow T_1$ channels induced by a light (laser) pulse. Optical limiters are developed for eye and photodetector protection from high-power radiation. The enhancement of intercombination transitions under the action of a heavy atom improves the speed of response and the degree of protection. Another example of material that provides efficient RSA is Zn-octabromo-TPP, which combines the action of heavy bromine atoms with the influence of macrocycle nonplanarity on photoprocesses [141].

As noted in Section 4.1, a specific feature of the internal heavy-atom effect in Pd- and Pt-porphyrin molecules is a high quantum yield of phosphorescence. This is due to the preferred increase in k_{P} in comparison with k_{TS} accompanied by a 100% population of the T_1 state; this was demonstrated for Pd-porphyrins in Ref. [142]. This phosphorescence has found several practical uses, because it is also observed at room temperature.

Of interest is the physics of PtOEP employment in electroluminescent devices based on organic compounds. In the electron excitation of the molecules of an organic luminophor, 75% of the energy is lost due to the production of triplet excitons, which emit virtually no radiation. A small addition of a well-radiating PtOEP with the T_1 level located below the T levels of the base has the effect that the triplet excitons are entrapped with subsequent reemission (in the red spectral region) [143, 144].

The phosphorescence of Pd- and Pt-porphyrins is quenched by molecular oxygen (O_2) and, accordingly, air.

Table 3. Influence of halogen atoms (Hal) on the probability of the $S_1 \rightsquigarrow T_1$ intersystem crossing (k_{ST}) in ZnPc, ZnTPP, and H_2TPP molecules.

Hal	ZnPc [139]		ZnTPP [110]			H_2TPP [111]		
	$\Delta k_{\mathrm{ST}} \times 10^{-7}$, s^{-1}	r	$\Delta k_{\mathrm{ST}} \times 10^{-7}$, s^{-1}	r_1	r_1/r	$\Delta k_{\mathrm{ST}} \times 10^{-7}$, s^{-1}	r_2	r_2/r
(H)	(11.6)	—	(44)	—	—	(7)	—	—
Cl	2.2	0.2	30.4	0.7	3.5	2.7	0.4	2.0
Br	19	1.6	339	7.7	4.8	53	7.6	4.7
I	54	4.6	774	17.6	3.8	238	34.0	7.4

Notes. 1. $r = \Delta k_{\mathrm{ST}}^{\mathrm{Hal}}/k_{\mathrm{ST}}^{\mathrm{H}}$ for ZnPc, r_1 — the same for ZnTPP, r_2 — the same for H_2TPP (the superscript Hal with r, r_1, and r_2 is omitted).
2. The values of $k_{\mathrm{ST}}^{\mathrm{H}}$ (in parentheses) are given for H. 3. For ZnPc, $k_{\mathrm{ST}}^{\mathrm{H}}$ was determined from the data in Ref. [135].

The quenching is diffusive in character and is therefore much stronger for liquid solutions (nearly complete quenching for nondeaerated solutions) than for solid-state systems. This effect is harnessed to make O_2 sensors of different kinds. Both the intensity of phosphorescence and its duration $\tau_P \equiv \tau_T$ may be the measured quantity.

Investigations have shown that the H_2TPP derivative with fully fluorinated phenyl rings [tetrakis-(pentafluorophenyl)porphin (H_2TFPP)] and its metal complexes exhibit high photostability. On this basis, a fiber-optical O_2 sensor was proposed [145] and an air pressure-sensitive paint (PSP) was developed. This paint as a component of a polymer film is deposited on the wing of an airplane, which is then tested in a wind tunnel. The intensity of PtTFPP phosphorescence at a given point of the aerofoil surface is determined by the air pressure (see Ref. [146] and the references therein). Khalil et al. [146] proposed a new pigment, PtTFPP lactone, whose emission spectrum is shifted to the red side. It turned out that the PSP phosphorescence intensity is also affected by the temperature. For a temperature sensor, use can be made of the luminescence of europium complex, but this was hampered by the overlap of the Eu^{3+} and PtTFPP emission spectra. Passing to lactone permits 'separating' these two spectra.

In the work at our laboratory, the use of oxygen quenching of water-soluble Pd-porphyrin phosphorescence was proposed for reliability checks of airproofing of medical vials and other reservoirs [147] and for the study of hypoxia (lowering of O_2 content) in solutions and cells [148, 149]. Analytical uses of PtOEP were described in Ref. [150], which is partly a review paper in character. In particular, special emphasis was placed on the uses of Langmuir – Blodgett film-based phosphorescent coatings as SO_2 and nitrogen oxide sensors in conditions of a large excess of oxygen. Ways of improving the sensitivity of the O_2 sensors containing Pd and PtOEP were proposed in Ref. [151].

The phosphorescence of Pd-porphyrins may be employed in luminescent immunoanalysis with temporal resolution [152, 153]. When millisecond-range luminophors are employed as the luminescent markers, the temporal resolution allows eliminating the background almost completely. At present, complexes of rare-earth elements are used validly for this purpose (see, e.g., review Ref. [154]). Pd-porphyrins may offer some advantages, but they have not been realized to date.

6. Conclusion

The material in this review shows that the internal heavy-atom effect is a certain range of phenomena exhibiting structurally determined specific features. Application of new and presently developing experimental techniques to this range of problems results in the acquisition of information that finds theoretical interpretation. At the same time, despite remarkable advances in the understanding of the mechanism underlying the internal heavy-atom effect, state-of-the-art science does not make it possible to quantitatively predict the photophysical parameters of polyatomic molecules. Moreover, there is disagreement on the form of the operator responsible for vibronic transitions in phosphorescence spectra and nonradiative transitions. Accumulation of experimental material on the spectral-luminescent properties of diverse molecular systems bearing heavy atoms remains a topical problem.

Addition to the proof.
Work at the Karpov Research Institute of Physical Chemistry (Moscow) on the spin – orbit interaction in molecules and the heavy-atom effect [119 – 123] is going on well. The results of calculations for heterocyclic analogs of fluorene have been outlined in new publications [155, 156].

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