PHOTOINDUCED OXIDATION OF DIPHENYLBISANTHENE AND ITS SPECTRAL MANIFESTATIONS

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The absorption and fluorescence spectra of diphenylbisanthene (DPB) in n-octane and benzene at 300 and 77 K have been investigated. The appreciable Stokes shift of the fluorescence band (~180 cm⁻¹ in n-octane and ~440 cm⁻¹ in benzene) points to the nonplanar character of the aromatic skeleton of DPB, which has been confirmed by results of the optimization of the molecule geometry by the AMI quantum-mechanical method. It has been found that spectral manifestations of the products of photoinduced transformations of DPB molecules are observed in the UV region (200–350 nm), and it has been shown that the observed photochemical process is two orders of magnitude less effective than for diphenylhelianthrene. On the basis of the experimental data and the results of the quantum-chemical calculations of the end products of DPB phototransformations are its endobiperoxides in which -O-O- groups are added to the phenyl-substituted benzene rings of the aromatic skeleton.

Keywords: diphenylbisanthene, diphenylhelianthrene, absorption and fluorescence spectra, phototransformation, endoperoxides, quantum-chemical calculation.

Introduction. The investigation of hypericin-like molecules with an elementary chemical structure is important, first of all, for understanding the biological activity of many compounds of this class. The spectral and photochemical properties of the nonsubstituted bisanthene molecule as a fundamental system of the hypericin type have been the subject of many works [1–4]. Elementary symmetrically substituted bisanthenes from this point of view are undoubtedly of interest, since the hypericin molecule features symmetry of side groups (point group of symmetry $C_{2\nu}$) [5]. In the present paper, bisanthene substituted by phenyl groups in the *meso*-position — diphenylbisanthene (DPB) (the structure is given in Fig. 1) — has been investigated. The attachment of two phenyl rings to the molecule should lead to an interaction of the conjugate systems of the aromatic skeleton and substituents and, as a result, to a change in the energies of the electronic states of bisanthene, and, therefore, in the spectral-luminescent properties. The interest in phenyl-substituted hypericin-like compounds is also due to their possible practical application. For example, DPB has found application as a pigment of the passive shutter for the *Q*-switching of a ruby optical quantum generator [6] and its analog — diphenylhelianthrene (DPH) (see the structure in Fig. 2) — as a pigment of an actinometer sensitive to the light in the visible region of the spectrum [7]. In the first case, Gorelenko et al. [6] used the high photostability of DPB and in the second case [7] — on the contrary, the high efficiency of DPH transformations [2, 7–13].

For the first time, DPB was synthesized by G. Sauvage [8, 9], who only determined the maxima positions of the longwave absorption bands. The information on the DPB fluorescence given in [6, 10] is limited and contradicting. The photoinduced transformations of the diphenyl derivative of bisanthene were only mentioned in [6, 10].

The aim of the present paper was to investigate the spectral-luminescent properties of DPB, study its photochemical transformations (in comparison with the analogous process for DPH), and interpret the experimental data on the basis of quantum-chemical calculations of the molecule geometry of DPB and its endoperoxides, as well as of their electronic spectra.

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Experimental Procedure. The DPB was obtained by the method of [10] by irradiating diphenyldianthranyl for 5–6 h with light from a DKsSh-500 xenon lamp ($\lambda > 390$ nm). The DPB + DPH mixture formed was separated by chromatographing on aluminum oxide and silica gel (eluent — benzene). The diphenylanthranyl was synthesized by sequentially obtaining source products (anthrone–dianthrone–dihydroxydiphenyldianthranene–diphenyldianthranyl). The stages of this synthesis are described in [3, 10]. The chemical composition of DPB was confirmed by the results of the elemental analysis and the similarity of the obtained characteristic absorption spectra (Figs. 1 and 2) to the literature data [6, 8–10].

The organic solvents were preliminarily purified by multiple distillation and dried. The concentration of the solutions under investigation was chosen so that the optical density for the longwave absorption band of the pigment did not exceed 0.2.

The absorption spectra were obtained on a Cary-500 Scan spectrophotometer (Varian, USA). The fluorescence excitation spectra were recorded on an SFL-1211A spectrofluorimeter (Solar, Belarus). The fluorescence spectra were measured at 300 and 77 K on a spectral facility assembled on the basis of a double monochromator and a recorder operating in the photon-counting regime. For fluorescence excitation, either filtered radiation from a xenon lamp or radiation from an LG-78 He–Ne laser ($\lambda_{exc} = 632.8$ nm) was used. In both cases, the excitation power density was $\approx 1 \text{ mW/cm}^2$.

Optimization of the geometry of the investigated molecules was performed using the AMI semiempirical method and the calculation of their electronic $S_i \leftarrow S_0$ absorption spectra — by the ZINDO/S semiempirical method.

Results and Discussion. On the face of it, the attachment of two phenyl groups in the *meso*-positions of the planar bisanthene molecule should not change the symmetry of its equilibrium configuration (D_{2h}) . However, as the results of the optimization of the DPH molecule geometry have shown, the planes of the phenyl groups make an angle $\Theta \approx 66^{\circ}$ with the plane of the aromatic skeleton. And the phenyl rings are tilted to one another so that their planes make an angle of $\approx 48^{\circ}$ (see the scheme in Fig. 1b). The rotation of the phenyl rings about single C—C bonds leads to a fair nonplanar "propeller-like" deformation of the aromatic skeleton itself (the planes of the end benzene rings of two anthracene fragments of the skeleton make an angle of $\approx 3^{\circ}$). As a result, the equilibrium configuration of the DPB molecule belongs approximately to the point group of the lower symmetry D_2 . It has no symmetry planes, as the bisanthene molecule does, but still has 2nd-order symmetry axes. Such a feature of the spatial structure of DPB is a consequence of the steric interactions of the phenyl and skeletal benzene rings. Note that an analogous orientation of the geometrical structure and excited states of phenyl derivatives of porphin by different quantum-mechanical methods [14–16] yielded values of $\Theta \approx 60-70^{\circ}$, which points to a small distortion of the planar structure of the porphyrin macroring as a result of the steric interaction of the phenyl and pyrrole rings.

The thorough chromatographic separation of DPB and the use of freshly prepared solutions have made it possible to obtain a qualitative absorption spectrum of this compound in the visible and UV regions. Figure 1a (curve 1) gives the absorption spectrum of DPB in *n*-octane at room temperature. The longwave region of the spectrum (550–700 nm) has a form characteristic of hypericin-like molecules, and the position and intensities of the bands agree with the literature data [6, 8–10]. The absorption spectrum of DPB in the UV region (200–350 nm) consists of a number of intense bands (in the literature, this region of the spectrum has not been investigated). That the observed bands belong to the phenyl derivative of bisanthene has been confirmed by the fluorescence excitation spectra (Fig. 1b), which simultaneously point to the purity of the compound being investigated. The fluorescence spectrum of DPB (Fig. 1a, curve 5) was obtained under excitation by the radiation from a He–Ne laser ($\lambda_{exc} = 632.8$ nm, $W_{exc} = 0.7$ mW/cm²).

Analyzing the spectra obtained, it is important to note that the longwave absorption band of DPB in *n*-octane at 679 nm is bathochromically shifted from the related band of nonsubstituted bisanthene [3] by 21 nm (for the benzene solution the shift is 23 nm). Moreover, a marked Stokes shift of the fluorescence bands ($\Delta v \approx 190 \text{ cm}^{-1}$ for *n*octane) compared to the corresponding shift for the planar molecule of bisanthene ($\Delta v \approx 40 \text{ cm}^{-1}$) is observed [3]. In the benzene solution (Fig. 2), Δv reaches 440 cm⁻¹ (for bisanthene in benzene $\Delta v \approx 340 \text{ cm}^{-1}$ [3]). In [3], the opinion was expressed that the large Stokes shift in the case of benzene was due to the fact that in the S₁-state of the hypericin-like molecule a dipole moment inducing dipoles in the solvent molecule arises, which, as a result, leads to a manifestation of universal intermolecular interactions (IMI) in such a system. The observed Stokes shift of the fluorescence bands and the bathochromic shift of the absorption bands of DPB are an additional indication of the aromatic



Fig. 1. Absorption spectra: 1) initial; 2–4) upon photoirradiation for 1 (2), 4.5 (3), and 10 h (4) and fluorescence spectra (5, 6) at $\lambda_{exc} = 632.8$ nm of DPB in *n*-octane at 300 (1–5) and 77 K (6) (a). Fluorescence excitation spectra of DPB in *n*-octane at 300 K ($\lambda_{reg} = 688$ (1) and 750 nm (2)) (b), as well as a three-dimensional image of the chemical structure of DPB (a) and its projection in the aromatic skeleton plane (b)

skeleton deformation. The appreciable deviation from the mirror symmetry of the obtained spectra of absorption (longwave region) and fluorescence, as well as the considerable Stokes shift of the fluorescence bands, can be due to the restructuring of the DPB molecule in the excited electronic S_1 -state (possibly, to the enhancement of nonplanarity upon photoexcitation due to the reorientation of the phenyl groups). At the same time, it is not excluded that in the region of the absorption band at 620 nm the band of the $S_2 \leftarrow S_0$ transition is localized, as in the case of bisanthene [4, 17].

Freezing of the *n*-octane solution of DPB to 77 K does not lead to the appearance of the quasi-line structure of the fluorescence spectrum (Fig. 1a, curve b), although the bands markedly narrow. The absence of the structural spectra, unlike the nonsubstituted bisanthene [3, 4, 17], is due to the noncoplanarity of the planes of the phenyl groups to the aromatic skeleton plane, creating an obstacle to the isomorphous penetration of DPB molecules into the crystal-lographic cells of *n*-octane. The latter does not lead to the removal of inhomogeneous broadening of the spectral bands by limiting the number of types of impurity centers in the Shpolski matrix.

In [9], it was stated that DPB was not capable of phototransformations. However, as mentioned above, in [6, 10] it was revealed that prolonged irradiation leads to a slow decomposition of DPB. And Maulding [10] erroneously argued that the arising absorption bands with a center at 400 nm corresponded to the formation of DPB photooxide (most probably, the investigated solution contained a certain quantity of DPH, to whose photooxide the new absorption bands belonged [2, 7, 10, 12, 13]). As our experiments have shown (Fig. 1a, curves 1–4), under a prolonged irradiation of the *n*-octane solution of DPB by the light of an SVDSh-500 mercury lamp ($\lambda_{exc} \approx 200-500$ nm, $W_{exc} \approx 1.6$ mW/cm²), the observed photochemical processes lead to the appearance of new bands in the UV region: a rather narrow band at 262 nm and a low-intensity background in the 300–400-nm range. In so doing, the absorption bands belonging to DPB completely disappear (see curve 4). The family of curves corresponding to various times of preliminary photoirradiation of the DPB solution has a number of isobestic points (241, 279, 309, and 530 nm), which definitively points to the formation of a binary mixture of DPB and its photoproduct.



Fig. 2. Absorption spectra: 1) initial; 2) upon 5-min photoirradiation of benzene solution of DPB with DPH; 3) fluorescence spectrum of DPB in benzene ($\lambda_{exc} = 632.8 \text{ nm}$) at 300 K. In insets: change in the relative fluorescence intensity of benzene solution of DPB (1) at $\lambda_{reg} = 708 \text{ nm}$ and DPH (2) at $\lambda_{reg} = 600 \text{ nm}$ depending on the photoirradiation time in the 200–500-nm range, as well as a three-dimensional image of the chemical structure of DPH.

For quantitative estimation of the phototransformation efficiency of DPB, we investigated a benzene solution containing DPB and DPH (nonchromatographed mixture), whose absorption spectrum is given in Fig. 2 (curve 1). Besides the DPB bands (longwave band at 686 nm), in the spectrum of the nonirradiated solution intense bands of DPH (for example, at 582 nm) and low-intensity bands of its endoperoxide with a center at 400 nm are observed [7, 12, 13]. Upon irradiation of the solution by the light of the mercury lamp for 5 min the DPH absorption bands disappeared from the absorption spectrum and the bands of its endoperoxide sharply gained in intensity (Fig. 2, curve 2). This confirms the effective process of DPH phototransformations [2, 7–13]. In [12], such a photochemical reaction of DPH was investigated and the rate constant of phototransformations $k = (7.0 \pm 0.3) \cdot 10^9 \text{ sec}^{-1}$.mole⁻¹.liter was measured. The inset in Fig. 2 shows the kinetics of DPH phototransformations, obtained under experimental conditions as a change in the relative fluorescence intensity at $\lambda_{\text{reg}} = 600 \text{ nm}$ (fluorescence-band maximum) depending on the phototradiation time. The experiment has shown that in ~15 sec the concentration of DPH molecules in the solution is reduced by one-half. Under the same photoexcitation conditions, the relative fluorescence intensity of DPB at $\lambda_{\text{reg}} = 708 \text{ nm}$ remains practically unchanged (see Fig. 2, curve 3, insert). Analysis of the obtained kinetic curves has shown that the phototransformation efficiency of DPB is two orders of magnitude lower than that of DPH.

On the basis of the quantum-chemical calculation of the DPH molecule geometry it has been established that the aromatic skeleton has no planar structure (Fig. 2). The reason for this is the steric obstacles of two "internal" hydrogen atoms, which force the end benzene rings of anthracene fragments to leave the plane of the aromatic system in opposite directions. Such structural distortions disturb the π -electron conjugation in the DPH molecules, which leads to a considerable shortwave shift of the absorption band from the DPB bands.

In [2, 7, 10, 12, 13], it has been found that phototransformations of DPH are a self-sensitized process of its photooxidation with the formation of endoperoxides in which the oxygen bridges are attached to the phenyl-substituted benzene rings. Moreover, in [18] it is stated (by an example of nonsubstituted helianthrene molecules) that exactly the skeleton deformation (the going of the end benzene rings out of the plane) creates favorable conditions for the addition of oxygen in *meso*-positions of the aromatic skeleton, An experimental proof of such a chemical structure of DPH endoperoxide is the NMR [2] and mass spectrometric [2, 10] data.

By analogy with nonsubstituted bisanthene [1, 3], helianthrene [2, 18], and DPH [2, 7, 10, 12, 13] we assume that the process of phototransformations of DPB is also due to the formation upon photoexcitation of its endoperoxides. This is evidenced by the considerable retardation of the photochemical reaction of DPB in degassed solutions. To additionally confirm such a mechanism, we have performed a quantum-chemical calculation (ZNDO/S semiempirical method) of energies of the singlet states and oscillator strengths of transitions for molecules of DPB and its endoperoxides. Figure 3 shows the optimized molecule geometries of DPB and its most probable, as to chemical structure (see below), endoperoxides in which the -O-O- group (groups) is attached to the benzene rings containing phenyl groups of endomonoperoxide (Fig. 3b) and two isomers (*cis-* and *trans-*) of endobiperoxides (Fig. 3c and d). The results of the calculation of their electronic $S_i \leftarrow S_0$ spectra are also given here (bold vertical lines).

According to the calculations performed, the addition of two phenyl fragments to the bisanthene molecule increases the energy of the highest occupied molecular orbital (MO), whereas the energy of the lowest unoccupied orbital remains practically unaltered. This explains the experimentally observed bathochromic shift of the longwave absorption band of DPB ($\Delta\lambda \approx 20$ nm) from the corresponding bisanthene band. In so doing, the oscillator strength of the longwave transition of DPB is somewhat greater than in the nonsubstituted bisanthene ($f \approx 1.03$ and ≈ 0.81 , respectively). The calculation also shows that the oscillator strength of the $S_2 \leftarrow S_0$ transition of DPB is negligible (f < 0.001). Despite the fact that the calculated value of the S_2-S_1 energy interval turned out to be fairly large ($\sim 6000 \text{ cm}^{-1}$), it may be stated that the experimentally observed breaking of the mirror symmetry of the longwave absorption and fluorescence band intensities of DPB (see Fig. 1a and Fig. 2) is due to the localization of the S_2 -level of DPB in the region of the electronic-vibrational levels of the S_1 -state, as is the case with nonsubstituted bisanthene [4, 17]. For the shortwave region, good agreement between the experimental data and the results of the quantum-chemical calculation of the electronic spectra of DPB is observed (Fig. 3a).

The formation of endomono- and endobiperoxides of DPB (Fig. 3b–d) leads, on the contrary, to a marked decrease in the energy of the two highest occupied MOs and an increase in two lowest vacant MOs. The calculation shows that in the case of endomonoperoxide the longwave absorption band experiences a hypsochromic shift to 437 nm (see Fig. 3b). In so doing, the oscillator strength of this transition, as in the case of transitions that manifest themselves in the UV region, does not exceed a value of $f \approx 0.75$. The calculation of the electronic spectra of endobiperoxides (Fig. 3c and d) yields a different result: an appreciable hypsochromic shift of the longwave bands (to 320 nm for the *cis*- and 315 nm for the *trans*-isomer) and a negligible oscillator strength of the corresponding transitions (0.001 and 0.009), as well as intense bands in the UV region ($f \approx 1-2$). As a result, as is seen from Fig. 3c and d, the calculated spectra of the two isomers of DPB endobiperoxides most closely agree with the experimentally observed absorption spectrum of the irradiated DPB solution (see also Fig. 1a, curve 4), which can serve as a corroboration of the dominant formation of endobiperoxides under the action of light.

Concurrently with the above calculations, we also calculated the electronic spectra of DPB endoperoxides in which the oxygen bridges were attached to the central benzene rings of the aromatic skeleton (such structures of endoperoxides were supposed in [2, 11] for helianthrene and DPH). In this case, a wide discrepancy between the experimental and calculated spectra is observed. Obviously, such a chemical structure of endoperoxide is unlikely, since the high reactivity of the two *meso*-positions of bisanthene and its derivatives to oxygen [1] favors the formation of the structures depicted in Fig. 3b–d. Moreover, as the results of the quantum-mechanical calculation of the geometry have shown, in this case an excessive distortion of the aromatic skeleton plane takes place.

Analysis of the results obtained permits stating that endomonoperoxide makes no appreciable contribution to the formation of the absorption spectrum of the irradiated DPB solution (Fig. 1, curve 4 and Fig. 3d). Its insignificant concentration is indicative of a fast attachment by the DPB molecule of the second oxygen bridge. As is seen from Fig. 3b, the presence of one bridge —O—O— leads to an expansion of the kink of the second oxygen-nonsubstituted anthracene fragment, which increases the reactivity of its *meso*-positions [18] and favors fast formation of endobiper-oxide.

The whole set of the data obtained and the literature data on the photoexcitation of hypericin-like compounds indicates that in the case of DPB molecules the mechanism of self-induced phototransformations is realized. This mechanism is reduced to the formation of endoperoxides through the interaction of DPB molecules with high-reactivity singlet oxygen. In this case, ${}^{1}O_{2}$ is formed through the energy transfer from the T_{1} -state of DPB to the unexcited oxygen molecule. It should be noted that in [18] the formation of nonsubstituted helianthrene endoperoxide in the dark through the realization of a unique (spin-forbidden) reaction between helianthrene in the S_{0} -state and molecular oxygen in the ground triplet (${}^{3}O_{2}$) state was revealed. And Seip and Brauer [18] thereby postulate that, as a result of the collision of such molecules, a bound complex is formed, via which on the spin-forbidden path, through the charge trans-



Fig. 3. Absorption spectra of DPB (a) and its photoproducts (d) in *n*-octane at 300 K and calculated electronic spectra of DPB (a) and its endoperoxides (b–d) (bold lines — calculated spectra), as a well as three-dimensional image of the chemical structure of DPB (a) and its endoperoxides (b–d).

fer from helianthrene to oxygen, a witterion arises (the formation of a single bond between them). And the latter is immediately transformed to the end product — endoperoxide. In our experiments, the dark reaction of DPB endoper-oxide formation has not been revealed.

Conclusions. For one of the elementary representatives of hypericin-like molecules — diphenyl-substituted bisanthene — a complex of spectral-luminescent studies has been carried out. The analysis of the obtained spectral data and of the results of the quantum-chemical calculation of the DPB molecule geometry has permitted the conclusion that its aromatic skeleton has a nonplanar structure. The spectral region of the appearance of products of photoin-duced transformations of DPB in oxygen-containing solutions has been revealed. On the basis of the quantum-chemical calculation of the energies and intensities of the electron $S_i \leftarrow S_0$ transitions of DPB and its peroxides it has been concluded that as a result of the photooxidation of the aromatic molecule, its endoperoxides, in which the oxygen bridges are attached to the phenyl-substituted benzene rings, are mainly formed.

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