

Delayed Fluorescence and Phosphorescence of 8-Aza-D-Homogonane in the Gas and Condensed Phases

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Abstract The delayed fluorescence spectrum for 8-aza-D-homogonane in the gas phase consists of a band of E-type delayed fluorescence of M-centers and a band of P-type delayed fluorescence of L-centers being the products of photo- and thermotransformations of a basic steroid. Triplet-triplet energy transfer from the M-centers to the L-centers is established and its efficiency is determined. For 8-aza-D-homogonane in frozen hexane solutions at $T = 77$ K only the phosphorescence of the M- and L-centers is revealed. The phosphorescence of the basic steroid itself ($\lambda_{\max}^{\text{phos}} = 415$ nm) as well as that of the M- and L-centers ($\lambda_{\max}^{\text{phos}} = 498$ and 532 nm, respectively) is seen in a mixture of frozen tetrahydrofuran and toluene solutions. This is evident of the fact that the basic steroid has the products of its transformations, whose amount grows due to irradiation and heating. The M- and L-centers are stable molecules.

Keywords: Delayed fluorescence · Phosphorescence · 8-aza-D-homogonane · Spectroscopic characteristics

Introduction

According to the data [1] 8-azasteroids are biologically active organic compounds and can either stimulate or suppress the immunity of living organisms depending on their structure. It is therefore important to investigate photophysical and pho-

tochemical processes in 8-azasteroid molecules, with the intent of establishing correlations between their spectroscopic characteristics and physiological properties.

The phosphorescence of one of the organic compounds of the steroid series, namely, 2,3-methoxy-8-azagona-1,3,5(10),13-tetraen-12,17-dione was revealed for the first time [2]. When microcrystal was subjected to exciting radiation with the wavelength $\lambda_{\text{exc}} = 250$ nm and at $T = 293$ K, the fluorescence was accompanied by the phosphorescence with the maximum wavelength $\lambda_{\max}^{\text{phos}} = 470$ nm and with the lifetime $\tau = 280$ ms. When this steroid was excited in the frozen acetonitrile solution ($T = 77$ K), $\lambda_{\max}^{\text{phos}} = 520$ nm and $\tau = 1.1$ s. In the ethanol solution of this steroid, in addition to the phosphorescence with $\lambda_{\max}^{\text{phos}} = 520$ nm and $\tau_1 = 1.5$ s, one more phosphorescence band with $\lambda_{\max}^{\text{phos}} = 400$ nm and $\tau_2 = 0.18$ s was observed [3]. The two-band nature of the phosphorescence was not explained.

For molecules with singlet ground state S_0 and a electronically excited triplet state T^* , two types of delayed fluorescence (DF) are known. First, E-type DF $S_1 \rightarrow S_0$ resulted from thermally activated intersystem crossing $S_1 \leftarrow T^*$, and second, P-type DF $S_1 \rightarrow S_0$ resulting from triplet-triplet annihilation (TTA) [4].

Of significance is the study of the spectral-luminescent properties of 8-azasteroid in the gas phase where the influence of the surrounding medium is absent. The experimental results on the absorption and fluorescence of the 8-azasteroid series in the gas phase are detailed in [5]. Fluorescence of acetonitrile solutions [6] and aqueous solutions (pH = 7.4) [7] of 2,3-dimethoxy-8-azagona-1,3,5(10),13-tetraen-12,17-dione is studied. The present work analyzes the delayed fluorescence and phosphorescence properties of 8-aza-D-homogonane-1,3,5(10),13-tetraen-12,17a-dione (hereinafter 8-aza-D-homogonane) in the gas and condensed phases. The structural formula of 8-aza-D-homogonane is given below:

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8-aza-D-homogonane has been prepared by the annelation of 3,4-dihydroisoquinone-2-acetil-1,3 with cyclopentadiene using the method described elsewhere in [8]. Samples for spectroscopic tests have been subjected to multiple recrystallizations from ethanol.

Experimental

Luminescence characteristics of 8-aza-D-homogonane in the gas and condensed phases were measured on an automated laser spectrometer, permitting the registration of the luminescence kinetics at different emission wavelengths as well as of instantaneous spectra at different luminescence decay stages over micro- and millisecond time ranges. The 10 ns pulses of the third harmonic of a YAG: Nd³⁺ laser ($\lambda_{\text{exc}} = 266$ nm) and the 30 ns pulses of the second harmonic of a sapphire-titanium laser ($\lambda_{\text{exc}} = 355$ nm) served as exciting radiation. Spectral characteristics of long-duration luminescence at low temperatures ($T = 77$ K) were measured also on a phosphorimeter described in [9].

A test substance was placed into a vacuum quartz cell, from which air was pumped out to achieve 10^{-5} torr. A lower oven temperature T_1 predetermined vapor pressure. A filled with a substance cell branch was located in this oven. An upper optical part of the quartz cell was in another oven, via which a vapor temperature T_2 was predetermined. All studies of 8-aza-D-homogonane in the gas phase were made at $T_2 = 533$ K and $T_1 = 513$ K.

Results and discussion

When 8-aza-D-homogonane in the gas phase is excited by radiation with the wavelength $\lambda_{\text{exc}} = 266$ nm and at 10 ns pulses, the nanosecond fluorescence that repeats in time an exciting pulse as well as the long-duration luminescence that decays over the microsecond time range is registered. Figure 1a shows fluorescence spectrum (1) and the long-duration luminescence spectra measured at the time intervals $\Delta t = 0.7 \mu\text{s}$ (2) and $\Delta t = 1.7 \mu\text{s}$ (3) after the exciting pulse for $\lambda_{\text{exc}} = 266$ nm.

In [5] it is established that three independently fluorescing centers can contribute to the fluorescence spectrum of 8-aza-D-homogonane in the gas phase. These are: a short-wave (S) centers that are related to the basic steroid molecules itself and has a fluorescence band with the maximum $\lambda_{\text{max}} = 330$ nm, and middle-wave (M) and long-wave (L) centers that are the products of photo- and thermotransformations of basic 8-aza-D-homogonane and have fluorescence bands with the maxima $\lambda_{\text{max}}^{\text{fl}} = 370$ nm and $\lambda_{\text{max}}^{\text{fl}} = 470$ nm, respectively. In this case, the number of these bands and their contribution to the total fluorescence spectrum are affected

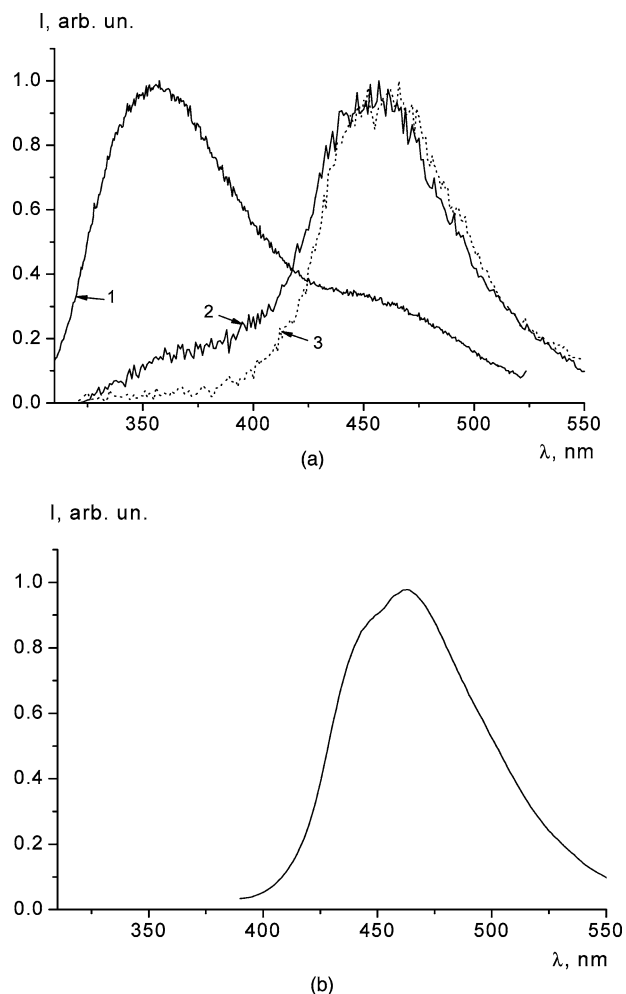


Fig. 1 Luminescence spectra of 8-aza-D-homogonane in the gas phase ($T_2 = 533$ K, $T_1 = 513$ K): **a** fluorescence spectra, $\lambda_{\text{exc}} = 266$ nm (1), long-duration luminescence spectra measured upon the exciting pulse at $\lambda_{\text{exc}} = 266$ nm at the time intervals $\Delta t = 0.7 \mu\text{s}$ (2) and $1.7 \mu\text{s}$ (3), respectively; **b** averaged long-duration luminescence spectrum at $\lambda_{\text{exc}} = 266$ nm, $\lambda_{\text{exc}} = 355$ nm, $\lambda_{\text{exc}} = 395$ nm; $\Delta t = 10 \mu\text{s}$

by the amount of substance placed into the vacuum cell, by the lower oven temperature T_1 that assigns vapor pressure and by the exciting radiation wavelength λ_{exc} . Under the experimental conditions for the fluorescence of 8-aza-D-homogonane vapors ($T_2 = 533$ K, $T_1 = 513$ K, $\lambda_{\text{exc}} = 266$ nm, substance is placed into the vacuum cell in the amount, providing the vapor saturation for all luminescence centers), two bands with the maxima $\lambda_{\text{max}}^{\text{fl}} = 355$ nm and $\lambda_{\text{max}}^{\text{fl}} = 465$ nm manifest themselves in fluorescence spectrum (1) in Fig. 1a. The first band is wide and incorporates the fluorescence of the S- and M-centers and the second is related to the L-centers.

Long-duration luminescence spectrum (2) in Fig. 1a measured at the interval $\Delta t = 0.7 \mu\text{s}$ after the exciting pulse consists of an intense long-wave band with $\lambda_{\text{max}}^{\text{lum}} = 465$ nm coinciding with $\lambda_{\text{max}}^{\text{fl}}$ of the fluorescence band of the L-centers, and a short-wave band with the maximum $\lambda_{\text{max}}^{\text{lum}} = 365$ nm

practically coinciding with the maximum of the fluorescence band of the M-centers [5].

It is important to note that in long-duration luminescence spectrum (3) measured at the interval $\Delta t = 1.7 \mu\text{s}$ after the exciting pulse, only the long-wave band $\lambda_{\text{max}}^{\text{lum}} = 465 \text{ nm}$ is registered and, hence, it is shared by the long-duration luminescence only of the L-centers.

This conclusion is supported by the data in Fig. 1b that demonstrates the spectrum for the long-duration luminescence of 8-aza-D-homogonane vapors measured with the time delay $\Delta t = 10 \mu\text{s}$ for the exciting radiation wavelength $\lambda_{\text{exc}} = 266 \text{ nm}$. Radiation with $\lambda_{\text{exc}} = 266 \text{ nm}$ is absorbed by all three luminescence centers, with $\lambda_{\text{exc}} = 355 \text{ nm}$ —by the M- and L-centers and with $\lambda_{\text{exc}} = 395 \text{ nm}$ —only by the L-centers. It has appeared that these long-duration luminescence bands normalized by the maximum to 1.0 for different λ_{exc} do not depend on λ_{exc} . The long-duration luminescence band with $\lambda_{\text{exc}} = 266 \text{ nm}$ (2) measured at the interval $\Delta t = 2 \mu\text{s}$ after the exciting pulse also coincides with the above-considered bands. Actually, Fig. 1b illustrates the averaged long-duration luminescence spectrum for the above-mentioned different excitation and registration conditions. The fact that the measured luminescence spectra for the L-centers of this steroid are not affected by λ_{exc} testifies that a vibrational equilibrium distribution is established during the lifetime in the excited electronic state. Hence, this state is triplet in nature.

P-type DF is characterized by the coincidence of the long-lived luminescence spectrum and the fluorescence spectrum. The conclusion about p-type DF of 8-aza-D-homogonane vapors is supported also by the fact that the long-duration luminescence intensity of the L-centers measured at the initial decay moment is proportional to the squared intensity of exciting radiation. P-type DF in the gas phase originates when two molecules interact in the lower triplet (T^*) state because of which molecules are formed in the ground (S_0) and excited singlet (S_1) states: $T^* + T^* \rightarrow S_1 + S_0$ [10].

The short-wave long-duration luminescence band of 8-aza-D-homogonane vapors with $\lambda_{\text{max}}^{\text{lum}} = 365 \text{ nm}$ practically coincides with the fluorescence band of M-centers. The intensity of long-duration luminescence linearly depends on the intensity of exciting radiation and so this luminescence is apparently E-type DF in nature. The vapor temperature is high ($T_2 = 533 \text{ K}$) and the M-centers can overcome the $T^* \rightarrow S_1$ barrier.

The luminescence kinetics of the L-centers has appeared nonexponential at high intensities of exciting radiation. In this case, the triplet states in the gas phase decay due to both the bimolecular collisions of triplet molecules and the monomolecular decay processes [11]. When large molecular concentrations are formed in the triplet state the bimolecular processes of triplet-triplet annihilation (TTA) become dominant during decay. At weak exciting radiation intensities

the decay of triplet states is mainly monomolecular, and the decay curve is close to the exponential one. The P-type DF decay time of the L-centers measured under weak excitation is $100 \mu\text{s}$. Hence, the triplet state lifetime, τ , of the 8-aza-D-homogonane L-centers in the gas phase is equal to $200 \mu\text{s}$.

The important specific feature of the DF kinetics of the 8-aza-D-homogonane vapors is the growth of the DF intensity of the L-centers during the first $2 \mu\text{s}$ after the exciting pulse. Figure 2 illustrates the first stage of the DF kinetics when emission is registered at the maximum of the P-type DF band of the L-centers ($\lambda_{\text{reg}} = 470 \text{ nm}$) excited by radiation with $\lambda_{\text{exc}} = 266 \text{ nm}$ (curve 1). This figure shows that when the molecules are excited by radiation with $\lambda_{\text{exc}} = 266 \text{ nm}$ that is also absorbed by the S- and M-centers, the DF kinetics of the L-centers points to the growth of the DF intensity. The DF intensity does not grow when the 8-aza-D-homogonane vapors are excited by radiation with $\lambda_{\text{exc}} = 395 \text{ nm}$ that is absorbed only by the L-centers (curve 2). In this case, the time of increasing the DF intensity of the L-centers approximately corresponds to the decay time of the DF of the M-centers, which follows from both the start kinetics of the L-center DF (curve 1) and the DF spectra measured at the time intervals $\Delta t = 0.7 \mu\text{s}$ and $\Delta t = 1.7 \mu\text{s}$ (Fig. 1a).

In general, no long-duration luminescence of the S-centers is observed. The fast decay of the long-lived luminescence of the M-centers is associated with quenching their triplet states by the L-center molecules due to radiationless triplet-triplet energy transfer from the M-centers to the L-centers. As known, the intermolecular electronic energy transfer in the gas phase is a highly efficient process [12] and occurs because of diffusional collisions of donor molecules in the triplet state and of acceptor molecules in the ground state.

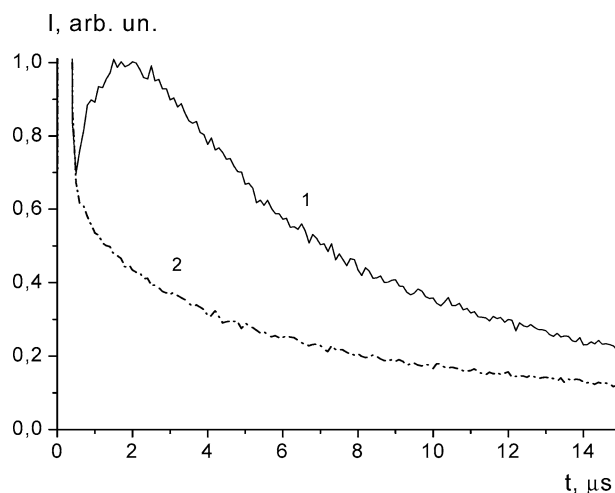


Fig. 2 Long-duration luminescence kinetics of 8-aza-D-homogonane in the gas phase: $\lambda_{\text{exc}} = 266 \text{ nm}$ (1), and $\lambda_{\text{exc}} = 395 \text{ nm}$ (2); the luminescence registration wavelength is $\lambda_{\text{reg}} = 465 \text{ nm}$

This conclusion also follows from the measurements of the intensity ratio of fluorescence and P-type delayed fluorescence of the L-centers. Previously it has been shown [11] that under intense laser excitation of organic compounds, when the decay of the triplet states is completely determined by the TTA processes, the integrated over time intensity ratio of P-type DF (I_{ADF}) and fluorescence (I_{fl}) is equal to the product of the efficiency, p , of the TTA of excited singlet molecules and the quantum yield, φ_T , of triplet states:

$$\frac{I_{ADF}}{I_{fl}} = p\varphi_T$$

Measuring the ratio I_{ADF}/I_{fl} by this formula permits the estimation of the quantum yield φ_T . Our estimates are made from the analysis of the emission kinetics at the band maximum of the L-centers ($\lambda_{reg} = 465$ nm) for different exciting radiation wavelengths. The following data are obtained: for $\lambda_{exc} = 266$ nm $p\varphi_T = 0.5$; for $\lambda_{exc} = 355$ nm $p\varphi_T = 0.13$; for $\lambda_{exc} = 355$ nm $p\varphi_T = 0.022$. If p is considered to be independent of λ_{exc} , then when the molecules are excited by radiation absorbed by the M-centers ($\lambda_{exc} = 266$ nm) the quantum yield, φ_T , of the triplet states of the L-centers will be approx. 20 times higher as against the one under the excitation of molecules in the absorption band of the L-centers ($\lambda_{exc} = 355$ nm). This means that when the molecules are excited by short-wave radiation, the triplet states of the L-centers are populated not only due to the intersystem crossing $S_1 \rightarrow T_1$ but also due to the $T-T$ energy transfer from the M-centers to the L-centers. Also note that the measured lifetime, τ , of the triplet states of the L-centers equal 200 μ s is typical for the vapors of organic compounds at a given temperature ($T_2 = 533$ K).

After 8-aza-D-homogonane has been investigated at high temperatures in the gas phase, the vacuum cell substance is dissolved in hexane and its spectra are measured. Figure 3a shows the absorption spectrum for the hexane solution at $T = 293$ K (1), the long-duration luminescence spectra at $T = 77$ K for $\lambda_{exc} = 305$ nm (2), $\lambda_{exc} = 393$ nm (3) and $\lambda_{exc} = 414$ nm (4) and also the phosphorescence excitation spectrum for $\lambda_{reg} = 500$ nm (5). Absorption spectrum (1) much differs from that of the hexane solution of basic 8-aza-D-homogonane [13]. The latter has weaker absorption in the spectral 320–360 nm region. Spectrum (1) clearly shows a band with $\lambda_{max} = 348$ nm. Long-duration luminescence spectrum (2) for the frozen 8-aza-D-homogonane solution has two phosphorescence bands with $\lambda_{max}^{phos} = 465$ nm and $\lambda_{max}^{phos} = 495$ nm. When the hexane solution is excited by more long-wave radiation with $\lambda_{exc} = 393$ nm and 414 nm, there is only one band with $\lambda_{max}^{phos} = 495$ nm (3, 4). The phosphorescence excitation spectrum at $\lambda_{reg} = 500$ nm differs from the absorption one, its maximum falls on the absorption band with $\lambda_{max} = 348$ nm. The coincidence of spectra (3) and (4)

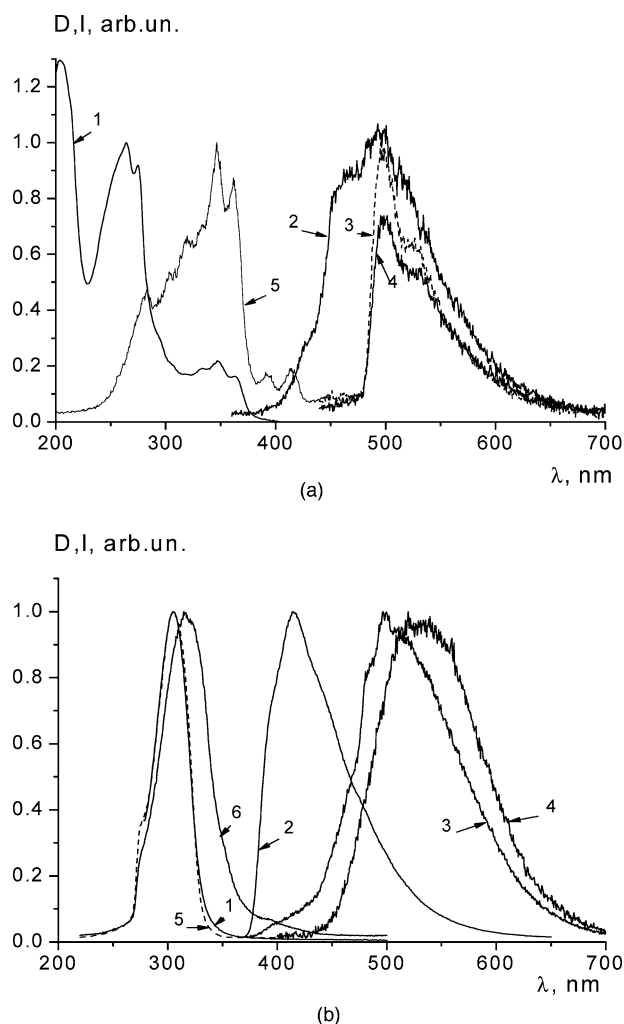


Fig. 3 Absorption spectra ($T = 293$ K), phosphorescence spectra ($T = 77$ K) and phosphorescence excitation spectra for 8-aza-D-homogonane solutions: **a** 8-aza-D-homogonane hexane solutions for substance extracted from the vacuum cell after its heating in the gas phase up to a high temperature $T_2 = 533$ K: absorption (1), phosphorescence (2–4), $\lambda_{exc} = 305, 393, 414$ nm, respectively; phosphorescence excitation (5) spectra, $\lambda_{reg} = 500$ nm; **b** basic 8-aza-D-homogonane in the tetrahydrofuran-toluene solutions mixed with the ratio 3:1: absorption (1), phosphorescence (2–4) spectra, $\lambda_{exc} = 305, 360, 391$ nm, respectively; phosphorescence excitation (5, 6) spectra, $\lambda_{reg} = 405, 550$ nm, respectively

means that the long-duration luminescence band with the maximum of $\lambda_{max}^{phos} = 495$ nm is the phosphorescence of the L-centers in nature. The long-duration luminescence band with $\lambda_{max}^{phos} = 465$ nm corresponds to the phosphorescence band of the M-centers.

Figure 3b demonstrates the spectra for basic 8-aza-D-homogonane in tetrahydrofuran-toluene solutions. To improve the substance solubility and to increase the luminescence intensity, the mixture of tetrahydrofuran and toluene in the ratio 3:1 is used. The absorption spectrum measured at $T = 293$ K in the spectral 225–360 nm region practically consists of one intense band with $\lambda_{max} = 348$ nm, on the

short-wave wing of which a shoulder with $\lambda = 275$ nm is seen. On the long-wave side of the absorption spectrum is seen very weak, slowly decreasing absorption typical of the solutions of other steroids. The intense band with $\lambda_{\max} = 261$ nm is observed in the neutral hexane solution.

The phosphorescence spectra for basic steroid solutions in Fig. 3b are measured at $T = 77$ K. When a solution is excited by short-wave radiation with $\lambda_{\text{exc}} = 275$ nm and 305 nm, there is one coinciding intense phosphorescence band with $\lambda_{\max}^{\text{phos}} = 415$ nm (2), whose excitation spectrum (5) at $\lambda_{\text{reg}} = 415$ nm practically coincides with absorption spectrum (1). This phosphorescence band should be related to the luminescence of 8-aza-D-homogonane itself. This band is not available in the spectrum for the hexane solution of the substance extracted from the vacuum cell after heating at high temperatures in the gas phase. Exciting the basic steroid solutions by long-wave radiation with $\lambda_{\text{exc}} = 360$ and 391 nm causes two phosphorescence bands with $\lambda_{\max}^{\text{phos}} = 498$ nm (3) and $\lambda_{\max}^{\text{phos}} = 532$ nm (4) to appear, that belong to the M-centers and the L-centers, respectively. From this point of view, phosphorescence excitation spectrum (6) for the L-centers ($\lambda_{\text{reg}} = 550$ nm) does not coincide with absorption spectrum (1). A distinction in the position of the phosphorescence bands of the M-centers and the L-centers in hexane and in the mixture of tetrahydrofurane with toluene is attributed to the properties of solvents since in the first and second cases a difference in the maxima of these bands remains 30 and 28 nm within the accuracy, respectively.

Conclusion

The study of the long-duration luminescence of 8-aza-D-homogonane in the gas phase has established that there exist the E-type delayed fluorescence of M-centers and the P-type delayed fluorescence of L-centers being the products of photo- and thermotransformations of a basic steroid. Triplet-triplet energy transfer from the M-centers to the L-centers is proved and its efficiency is determined. The luminescence of the steroid itself in the gas phase is not revealed.

The long-duration luminescence spectrum for 8-aza-D-homogonane in frozen hexane solutions ($T = 77$ K) does not reveal the phosphorescence band of the steroid itself (S-centers) and has the phosphorescence bands of the M-centers and the L-centers.

The spectrum for basic 8-aza-D-homogonane in frozen mixed tetrahydrofurane-toluene solutions ($T = 77$ K) has the phosphorescence band with $\lambda_{\max}^{\text{phos}} = 415$ nm, that is char-

acteristic for the steroid itself, and also the phosphorescence bands with $\lambda_{\max}^{\text{phos}} = 498$ nm and $\lambda_{\max}^{\text{phos}} = 532$ nm for the M-centers and the L-centers, respectively.

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