ELECTRONIC STRUCTURES AND SPECTRAL-LUMINESCENCE CHARACTERISTICS OF N-AMINONAPHTHALIMIDE AND NAPHTHALIC ACID HYDRAZIDE AND THEIR DERIVATIVES

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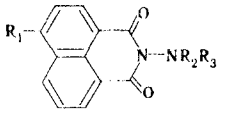
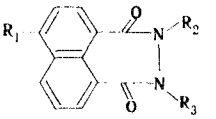
The π-electron structures and spectral characteristics of derivatives of N-aminonaphthalimide, naphthalic acid hydrazide, and their derivatives were subjected to quantum-chemical calculations by means of the Pariser—Parr—Pople method. The indexes of localization of the excitation on the atoms for the long-wave absorption of the investigated systems were calculated and analyzed. It was concluded that the naphthalene ring is responsible for the luminescence properties of derivatives of naphthalic acid hydrazide and N-aminonaphthalimide.

In connection with the fact that N-aminonaphthalimides (I) and naphthalic acid hydrazides (II) are luminophores of practical value, it seems of interest to make a more detailed study of the principles that exist between their structures and optical characteristics.



I a-c



II a-c

I a $R_1=R_2=R_3=H$, b $R_1=NH_2$, $R_2=R_3=H$, c $R_1=R_2=H$, $R_3=COCH_3$; II a $R_1=R_2=R_3=H$, b $R_1=NH_2$, $R_2=R_3=H$, c $R_1=H$, $R_2=R_3=COCH_3$

Naphthalic anhydride and its 4-nitro and 4-amino derivatives have served as intermediates in the synthesis of I and II. These anhydrides react with hydrazine to give the corresponding N-amino imides (I) and with salts of hydrazine to give hydrazides (II) [1, 2].

The difference in the structures of I and II has a substantial effect on the spectral-luminescence parameters. In contrast to hydrazides, N-amino imides do not luminesce. Acylation of the N-amino groups leads to the development of luminescence, and the introduction of the same grouping in the imino group of hydrazides increases the luminescence intensity significantly (Table 1) [3].

The electron density distributions in the ground and excited states determine the luminescence properties to a significant degree. In this connection, we performed quantum chemical calculations of systems I and II. The calculations were made by the self-consistent-field method within the π-electron approximation with the Pariser—Parr—Pople (PPP) parametrization. The two-electron coulombic replusion integrals ($\gamma_{\mu\nu}$) were calculated from the Mataga—Nishimoto formula [4]. The resonance integrals ($\beta_{\mu\nu}$) were varied in the process of achieving self consistency from the linear dependence $\beta_{\mu\nu} = A_0 + A_1 P_{\mu\nu}$ with A_0 and A_1 parameters [52]. To calculate the spectral characteristics we took into account the singly excited configurations within the framework of the configuration-interaction (CI) method. Allowance for 20 singly excited configurations proved to be sufficient to obtain reliable results.

The results of calculation of the spectral characteristics are presented in Table 1 along with the experimental data. The calculated spectrum of unsubstituted hydrazide IIa is shifted

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hypsochromically relative to unsubstituted N-amino imide Ia, in agreement with the experimental spectrum. The introduction of an amino group in the naphthalene ring in the para position relative to the carbonyl group, as expected, leads, in agreement with the calculated data, to a bathochromic shift of 0.6-0.7 eV of the long-wave absorption band in the spectrum of both the N-amino imide and the hydrazide. The observed experimental shift of the spectrum (0.8 eV) does not differ substantially from the calculated value. The fact that the spectral characteristics of N-amino imides and hydrazides remain virtually unchanged in the case of acylation is somewhat unexpected. To analyze this result and to determine the nature of the transitions in the investigated compounds we carried out calculations of the so-called indexes of localization of the excitation proposed in [6] and calculated as the diagonal matrix elements of the single-particle density transition matrix reduced to the diagonal form $L_{\mu\nu} = \mu|D_{\mu\nu}|\nu>$. The proposed estimate of the localization of the excitation has an advantage as compared with the widely known technique of determination of the change in the electron density on the atoms during excitation, since it makes it possible to quantitatively estimate the degree of localization of the excitation and is also suitable for the investigation of systems with an electron density that does not change during excitation (for example, for alternant hydrocarbons).

The fragmentation of N-amino imides and hydrazides is shown in Fig. 1. The overall indexes of localization over the fragments are presented in Table 2. It is easy to see that the excited naphthalene ring makes the principal contribution to the first excited state. Thus, for example, the sum of the localization indexes for the N-amino imide is 0.8000, as compared with 0.9414 for the hydrazide. The localization of the excitation on the naphthalene fragment increases when an amino group is introduced (the corresponding values are 0.8412 and 0.9518). The acylation of N-amino imides and hydrazides also leads to an increase in the localization of the excitation on the naphthalene fragment. An examination of the molecular diagrams also leads to similar conditions.

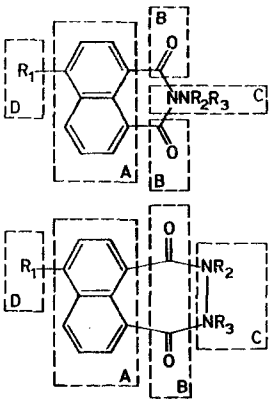

Fig. 1. Fragmentation of N-amino imides and hydrazides.

TABLE 1. Comparison of the Calculated and Experimental Energies of the Long-Wave Absorption of Derivatives of N-Aminonaphthalimide and Naphthalic Acid Hydrazide

Compound	Calc.			Exptl.			
	E, eV	λ, nm	f	E, eV	λ, nm	f *	η^r †
Ia	3,97	312	0,26	3,75	330	0,12	—
Ib	3,31	374	0,28	2,92	425	0,11	—
IIa	4,10	302	0,01	3,75	330	0,10	Weak luminescence
IIb	3,40	365	0,23	2,97	418	0,19	0,52
Ic	3,95	314	0,27	3,70	335	0,12	0,11
IIc	4,09	303	0,24	3,68	337	0,14	Weak luminescence

*The experimental value was determined from the approximate dependence $f = 10^{-4}\ \varepsilon_{max}$.
†The luminescence quantum yield.

TABLE 2. Overall Indexes of Localization over the Fragments

Fragment	Compound					
	Ia	Ib	IIa	IIb	Ic	IIc
A	0,8000	0,8412	0,9414	0,9518	0,8729	0,9608
B	0,1992	0,1500	0,0496	0,0402	0,1218	0,0342
C	0,0008	0,0003	0,0090	0,0031	0,0053	0,0050
D	—	0,0085	—	0,0049	—	—

TABLE 3. Spectral Characteristics of Naphthalene

E, eV	λ, nm	f
4,18	296	0,001
4,60	270	0,224
5,76	215	2,000

To illustrate the results let us present data from a calculation of the spectral characteristics of naphthalene. The energy of the first excited state of naphthalene differs very little from the energy of excitation of the N-amino imide ($\Delta E \approx 0.2$ eV) and, in particular, from the energy of excitation of the hydrazide ($\Delta E \approx 0.08$ eV).

The results make it possible to explain the luminescence properties of the investigated molecules. In all likelihood, the luminescence of N-amino imides and hydrazides is due to the luminescence of the naphthalene ring. In fact, the higher the degree of localization of the excitation on the naphthalene fragment, the more pronounced the luminescence properties of the molecule. Thus, for example, the N-amino imide has the lowest value of localization of the excitation on the naphthalene fragment and does not have luminescence properties. At the same time, the degree of localization of the excitation on the naphthalene fragment increases in the hydrazide, and the molecule luminescences in both the crystalline state and in solutions. Similar principles also arise in the case of acylation and when a donor amino group is introduced. These results are not in agreement with the widely held opinion of the direct relationship between the luminescence properties of molecules and the degree of intramolecular charge transfer and require further theoretical and experimental study.

EXPERIMENTAL

The absorption spectra of solutions of the compounds were recorded with an SF-4 spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission adapter, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which the light with wavelength 365 nm was isolated by means of a DMR-4 quartz monochromator. The absolute quantum yields of solutions in dioxane were determined by the equal absorption method [7].

Compounds I and II were synthesized by the method described in [2].

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