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FLUORESCENCE OF N-TRIAZOLYL DERIVATIVES OF AZOMETHINES

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It was demonstrated by structural modeling that the long-wave band in the UV spectra of azomethine derivatives of o-methoxybenzaldehyde is associated with transfer of electron density in the aldehyde fragment. The development of luminescence in the azomethines is due to the planarity of the molecule, a consequence of which is exclusion of the quenching fluorescence of the $n-\pi$ interaction and a sufficient magnitude of the energy gap between the n,π^* and π,π^* states. In the investigated series 4-(2-methoxybenzylideneamino)-1,2,4-triazole molecules have such properties.

The absence of fluorescence of the benzenoid form of N-arylazomethine molecules is due to rapid intercombination conversion (ICC) [1]. It has been previously shown [2] that the following three conditions must be met for the realization of this emissiveless process: 1) localization of the lowest (or closest to it, $\Delta E \sim 3000$ cm^{-1}) electron transition in the amide fragment; 2) the possibility of the realization of bending and rotational deformations in this fragment; 3) the presence in this fragment of specific (for this type of molecule) interaction of the n electrons of nitrogen and the electrons of the aromatic π system (an $n-\pi_{Ar}$ interaction).

A sharp decrease in the rate of ICC and the development of fluorescence are observed when at least one of these necessary conditions is absent. It may be assumed that to obtain luminescing systems it is sufficient to replace the N-aryl group by an N-alkyl group in order to exclude the first and third condition. However, in this case the presence of a close n,π_N^* state [3] is also responsible for rapid emissiveless deactivation and the absence of fluorescence [4]. It should therefore be expected that fluorescing molecules can be obtained by attaching to the nitrogen atom of the C=N group a group (other than an aryl group) that, on the one hand, excludes the third condition and, on the other, creates a more favorable orientation of the n,π_N^* and π,π^* [or intramolecular charge transfer (ICT)] states. It seems to us that this situation can be realized by various methods.

One such method was previously examined in [5] in the case of methylphenyl- and diphenylhydrazone molecules, in which $n-\pi_{Ar}$ interaction is excluded, and the energy gap between the lowest singlet ICT state and the higher n,π_N^* state reaches 6000 cm^{-1}. As a consequence

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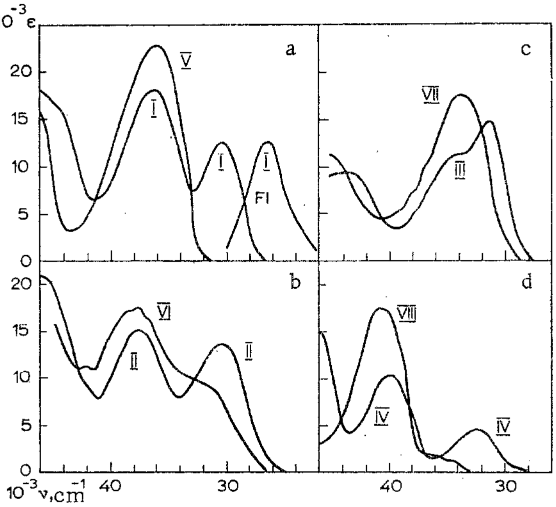
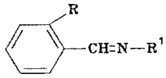


Fig. 1. Absorption spectra of I-VIII and fluorescence spectrum of I in ethanol at 293°K.

of this, phenylhydrazones have fluorescence with high quantum yields (0.8-0.9) in the crystalline state, in a polymer matrix, and in solution at 77°K. Nevertheless, because of the flexibility of the structure, fluorescence is absent in liquid solutions.



I–VIII

I—IV R=OCH_3; V—VIII R=H; I, V R^1=1,2,4-triazol-4-yl;II, VI R^1=Ph; III, VII R^1=$N(CH_3)_2$; IV, VIII R^1=CH_3

In this paper we propose a different method for the realization of the above-described favorable situation by the attachment of a triazolyl group (to give I) to the nitrogen atom. The structural similarlity between the investigated hydrazone molecule I and the analogous arylimine molecule II is due to the similarity in their absorption spectra (Fig. 1, spectra *a* and b) as a consequence of the identical nature of the most intense electron transitions. An intense long-wave band at 30,000 cm^{-1} is also present in the spectra of model compounds that do not contain a π system in the amide part (III, IV), except that it is shifted somewhat (1000 and 2000 cm^{-1}) to the short-wave region (Fig. 1, spectra c and d). At the same time, this band is absent in the spectra of molecules that do not contain an o-OCH_3 group (V-VIII) (Fig. 1). The longest-wave transition should therefore be associated primarily with redistribution of the electron density from the aldehyde ring to the C=N group and should partially involve the π system of the amine (triazole or phenyl) ring.

A characteristic structural difference between the I and II molecules consists in a significant decrease in I of the steric interaction of the hydrogen atom of the CH=N group and the N ring. As a consequence of this and as a result of interaction of the p orbitals of the sp^2-hybridized imine (N_I) and amine (N_A) nitrogen atoms a planar structure of the I molecule is realized. It is apparent that the characteristic (for the II molecule) n–π interaction and the resulting quenching long-wave ICT transition localized on the amide fragment (n_N–$\pi_{Ar} \to \pi^*_{C=N}$) are absent in this structure. In fact, the long-wave band in the spectrum of I is the only electron transition, since it is distinguished by an appreciably smaller width and greater symmetry with respect to the corresponding band in the spectrum of II (Fig. 1, spectra *a* and b), for which it has been shown [2] that it is the superimposition of bands of two transitions ($\Delta\bar{\nu} \sim 750$ cm^{-1}), viz., an intense long-wave transition, as in the case of I (see above) and a low-intensity short-wave ICT transition localized on the amine fragment.

Similar superimposition of the transitions is also observed in the long-wave band of model compound III. In this case the intense ICT transition, which is similar in nature to a transition of the $l \to a^*_\pi$ type (n_{N_I}–$l_{N_{Asp^3}} \to \pi^*_{C=N}$) and is localized on the amine fragment, is shifted to the short-wave side and stands out clearly, although it is extremely close ($\Delta\bar{\nu} \approx 2500$ cm^{-1}) to the common (to the molecules under consideration) long-wave transition localized on the aldehyde fragment (see above). It should be noted that delocalization of the n electrons that participate in the ICT transition over the overlapped sp^2 and sp^3 orbitals of the nitrogen atoms is observed in this molecule and in II. Thus conditions for ICC similar to 1–3 are observed in the III molecule, as a consequence of which the III molecule, like II, does not fluoresce. (Satisfaction of condition 1 is similar to manifestation of the "proximity effect" [3].)

In contrast to II and III, conditions 1 and 3 are not satisfied in the I molecule, and exclusion of the n_{N_I} electrons from interaction is responsible for the development of an n,π* state, which, as in the case of alkylimines IV, is capable of completely quenching fluorescence. However, in I as compared with IV one observes a substantial shift of the long-wave transition to the low-energy side, in which case the energy gap between the n,π* and π,π* states, in contrast to alkylimine IV [4], should exceed 4000 cm^{-1}. Thus, as expected, the attachment of a triazole ring to the imine nitrogen atom, on the one hand, excludes the ICC condition and, on the other, creates a favorable orientation of the n,π* and π,π* states. In contrast to the II-IV molecules, hydrazone molecule I, like phenylhydrazones, has intense fluorescence (Fig. 1, spectrum *a*). In contrast to the latter, as a consequence of structural flexibility, the fluorescence of triazole derivatives is manifested not only in rigid matrixes but also in liquid solutions at room temperature.

The results obtained in this research constitute yet another convincing piece of evidence in favor of the fruitfulness of the application of structural modeling in the directed approach to the synthesis of luminescing molecules.

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