ORGANIC LUMINOPHORS OF THE AZOMETHINE SERIES WITH FLUORINE-CONTAINING SUBSTITUENTS

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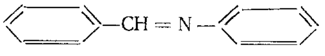
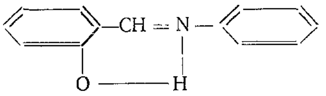
UDC 621.3.032.35

Azomethines of the aromatic series are among the intensely luminescent compounds with simplest structures. However, luminescent properties are displayed only by compounds whose molecules have a structure that is planar or nearly so. Thus, benzalaniline,


(I)

does not luminesce either in crystal or solution form when subjected to UV irradiation. One reason for this is the noncoplanarity of the benzalaniline molecule produced by the competitive influence of π,π- and n,π-conjugation.

Luminescence develops when intramolecular hydrogen bonds are present (II), binding the unshared electron pair of the azomethine nitrogen and thus weakening the n,π-conjugation.


(II)

This effect also appears on introduction of electron-donating substituents such as the dimethylamino group into the "aldehyde" ring of the azomethine, in the para-position with respect to the azomethine group. This results in intensification of the conjugation effect between the aromatic rings and produces a more planar molecular structure. Such luminescent compounds include

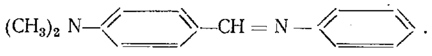

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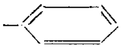
TABLE 1. Positions of Absorption and Luminescence Maxima of Compounds III and V-X in Dimethyl Formamide $(CH_3)_2N$–  –CH = N–Y

Compound No.	Y	λmax for absorption at K band, nm	λmax for luminescence, nm
III	C_6H_5	355	455
V	p-C_6H_4–SO_2CF_3	395	495
VI	p-C_6H_4–CF_3	365	460
VII	p-C_6H_4–NO_2	405	Weak luminescence
VIII	p-C_6H_4–Cl	360	460
IX	м-C_6H_4–CF_3	360	460
X	3,5-$C_6H_3(CF_3)_2$	340, 375 (Inflection)	460

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 17, No. 1, pp. 101-104, July, 1972. Original article submitted April 13, 1971.

TABLE 2. Melting Points, Analytic Results, and Compound Yields

Compound No.	M. p., °C	Yield, %	Empirical formula	N, %	
				observed	calculated
V	130—131	32	$C_{16}H_{15}O_2N_2SF_3$	8,27	7,85
IX	81—82	40	$C_{16}H_{15}N_2F_3$	9,23	9,58
X	57	45	$C_{17}H_{14}N_2F_6$	8,00	7,77

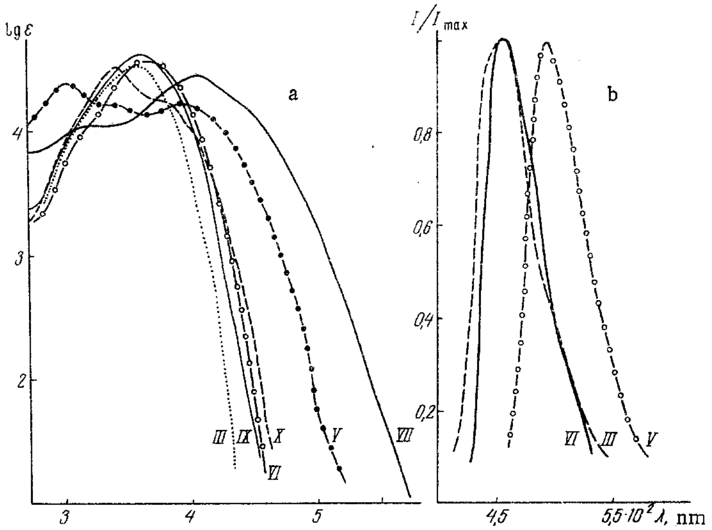
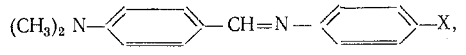


Fig. 1. Absorption (a) and luminescence (b) spectra of azomethines (the curve numbers correspond to the compound numbers).

When electron-accepting substituents are introduced into the "amine" ring (X), bound into a conjugation chain with the dimethylamino group,



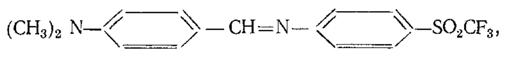
(IV)

there should be an intensification of the conjugation between the aromatic rings. On the other hand, it is also possible for there to be an increase in the conjugation of the unshared electrons of the nitrogen with the π-electrons of the "amine" ring, whose electron-accepting properties are more strongly manifested under the influence of substituent X. The question of which of these types of conjugation occurs in compounds of the type of IV to a greater extent can be answered by comparing the optical characteristics of compounds containing substituents X with electron-accepting effects of different strengths.

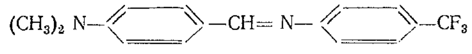
The most strongly electron-accepting substituents include those containing fluorine. Thus, we previously gave the Hammet–Taft σ-constants for a number of substituents and these permitted us to rank them in the following order for conjugated systems [1]: $CF_3 < NO_2 < CF_3SO_2$. Thus, the SO_2CF_3 group is a stronger electron-accepting substituent than the nitro group.

Introduction of the nitro group into the molecule of a luminescent substance is known to lead to an attenuation of luminescence in most cases. This effect is due both to the electron structure of the NO_2 group [2] and to the low dissociation energy of the $C-NO_2$ valence bond [3].

Investigation of compounds with a similar structure containing the NO_2 and CF_3SO_2 groups would aid in solution of the problem of the factors responsible for the damping effect of the nitro group. For this purpose, we synthesized compounds V and VI, which had fluorine-containing substituents:

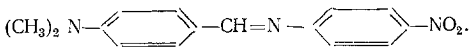


(V)



(VI)

and compared their absorption and luminescence spectra with those of compounds III and VII [4] (Table 1):



(VII)

All the azomethines investigated were synthesized by the method described in the literature [5], fusing equimolecular amounts of the corresponding amine and aldehyde. The resultant azomethines were purified by double recrystallization from petroleum ether. Data on the melting points and yields of the new compounds after purification and the results of analysis of the final compounds for nitrogen are given in Table 2.

The absorption spectra of the azomethines in dimethyl formamide were measured in an SF-4 spectrophotometer at 20°C. Azomethines generally do not luminesce in organic solvents at room temperature; as a result, the luminescence spectra of the compounds were measured at 77°K in an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 photomultiplier, and an M-95 microammeter. The radiation source was an SVDSh-500 bulb, from whose spectrum we isolated the 365 nm excitation line. Table 1 and Fig. 1 characterize the optical properties of the compounds obtained.

The absorption spectrum of compound III, which contained no substituent in the "amine" ring, contained one band with a distinct maximum in the 270-400 nm region. Introduction of a chlorine atom in the p-position with respect to the nitrogen of the azomethine group caused almost no change in the character of the spectrum and had very little effect on the position of the absorption maximum. Replacement of the chlorine by a CF_3 group, which has a pronounced but comparatively weak electron-accepting effect, also left the form of the spectrum unchanged, displacing it slightly in the long-wave direction.

On moving to compounds containing strong electron-accepting substituents, i.e., the NO_2 and SO_2CF_3 groups, the spectra became considerably more complex. The K bands exhibited a bathochromic shift of 30-40 nm and shorter-wave bands appeared in the spectral region investigated.

At the same time, compound VII, which contained the nitro group, did not luminesce in crystal form and exhibited very weak luminescence in solution, while compound V luminesced strongly in powdered form and in solution even at room temperature. This gives us grounds for concluding that the damping effect of the nitro group is not related to its electronic structure, since the SO_2CF_3 group has stronger electron-accepting properties.

Compounds containing the CF_3 group and chlorine as substituents, like compound III (with no substituent in the "amine" ring) and in contrast to compound V, did not luminesce in crystal form or solution at room temperature; its luminescence in frozen solutions was weaker than that of compound V. The luminescence spectra of frozen dimethyl formamide solutions of all these compounds had the same form.

The luminescence thus became more intense as the electron-accepting influence of the substituent in the "amine" ring became stronger, apparently as a result of an intensification of the donor–acceptor interaction of the substituents in the azomethine aromatic rings, which resulted in a coplanar molecular structure.

Investigation of the absorption spectra of compounds IX and X, which contained one or two trifluoromethyl groups in the meta-position of the "amine" ring respectively, demonstrated the bathochromic influence of the induction effect caused by this group; when a second CF_3 group was introduced, we observed both an intensification of the bathochromic effect and splitting of the absorption band. Compounds IX and X were analogous to compound VI in the character of the luminescence spectra and the positions of the maxima in them.

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