position of tert-butyl peroxide was carried out in glass ampuls in a nitrogen atmosphere at 130°C for 20 h. Chlorobenzene was used as the solvent. Quantitative analysis was carried out with an LKhM-8MD chromatograph with a thermal-conductivity detector by means of previously constructed calibration dependences. The chromatographic-analysis conditions were as follows: The stationary phase was 10% polyethylene glycol sebacate on Chemosorb AW-HMDS, the column temperature was 80°C, the vaporizer temperature was 100°C, and the carrier-gas flow rate was 20 ml/min.

LITERATURE CITED

1. N. A. Batyrbaev, S. M. Kalashnikov, V. V. Zorin, S. S. Zlot-skii, U. B. Imashev, and D. L. Rakhmankulov, Zh. Prakt. Khim., 52, 174 (1979).
2. É. Kh. Kravets, S. S. Zlot-skii, V. S. Martem'yanov, and D. L. Rakhmankulov, Zh. Prakt. Khim., 49, 185 (1976).
3. V. V. Zorin, S. S. Zlot-skii, A. I. Gren', and D. L. Rakhmankulov, Zh. Prakt. Khim., 50, 1664 (1977).
4. E. T. Denisov, Rate Constants of Homolytic Liquid-Phase Reactions [in Russian], Nauka, Moscow (1971), p. 201.
5. K. Uneyama, H. Namba, and S. Oal, Bull. Soc. Chem. Jpn., 41, 1928 (1969).
6. D. L. Rakhmankulov, R. A. Karakhanov, S. S. Zlot-skii, E. A. Kantor, U. B. Imashev, and A. M. Syrkin, Progress in Science. Technology of Organic Substances [in Russian], Vol. 5 (1979), p. 153.
7. I. Apjok, M. Bartok, R. A. Karakhanov, and N. I. Shuikin, Usp. Khim., 38, 72 (1969).

LUMINOPHORES OF THE AZLACTONE SERIES WITH A DIFLUOROMETHYLSULFONYL GROUP

B. M. Krasovitskii, I. V. Lysova,
L. Sh. Afanasiadi, and Yu. N. Surov

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Organic luminophores of the azlactone series that contain a strong electron-acceptor substituent, viz., a difluoromethylsulfonyl group, were synthesized. The significant effect of the electronic nature of the substituents on the frequencies of the stretching vibrations of the CO and C=N groups was demonstrated, and the trans configuration of the investigated compounds was confirmed. The introduction of a difluoromethylsulfonyl group in the azlactone molecule promotes the development of intense fluorescence in solutions at room temperature. The character of the substituents and their mutual orientation have a substantial effect on the optical characteristics.

During a study of the spectral-luminescence properties of azlactone derivatives we noted intensification of the fluorescence of these compounds when electron-acceptor substituents are present in the arylidene fragment; this effect increased significantly as the acceptor properties of the substituents became more pronounced [1].

Continuing our search for effective organic luminophores among azlactone derivatives we synthesized I and II, which contain a difluoromethylsulfonyl group, which is a strong electron-acceptor substituent that surpasses the nitro group with respect to the strength of its electron-acceptor effect [2], in various structural fragments of the molecules.

The structures of the compounds obtained were identified by means of their IR spectra. A number of characteristic absorption bands are displayed distinctly in the 1580-1850 cm^{-1} region (Fig. 1). We assigned the high-frequency band at 1790-1800 cm^{-1} to the stretching vibrations of the carbonyl group.

All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Kharkov 310059. A. M. Gor'kii Kharkov State University, Kharkov 310077. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1600-1603, December, 1981. Original article submitted March 24, 1981.

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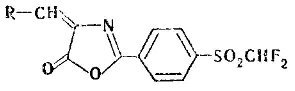
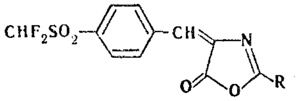
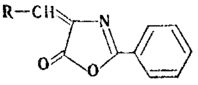


I a-h

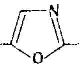


II a-d



III a, b

I–II a $R=C_6H_5$; b $R=4-C_6H_5-C_6H_4$; c $R=1-C_{10}H_7$; d $R=O_2N-C_6H_4$; Ie, IIIa $R=4-CH_3O-C_6H_4$;

If, III b $R=4-(CH_3)_2N-C_6H_4$; I g $R=4-F_2HCO_2S-C_6H_4$; h $R=4-C_6H_5-$  $-C_6H_4$

The high $\nu_{C=O}$ value (∿1800 cm^{-1}) for the investigated compounds is probably due to the effect of several factors: the negative inductive effect of the ester oxygen atom, the strain in the azlactone ring, the s-cis orientation of the C=C and C=O bonds, and the electron-acceptor effect of the C=N bond.

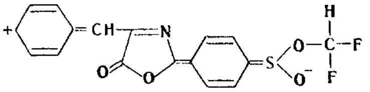
On passing from solutions in carbon tetrachloride to solutions in chloroform the $\nu_{C=O}$ values undergo a decrease of 5 cm^{-1} because of the formation of a hydrogen bond with the solvent. The low value of the $\nu_{C=O}$ shift attests to the low basicities of the azlactones; this is probably associated with the negative inductive effect of the ester oxygen atom on the carbonyl group. The low intensity and the high frequency of the band at 1769-1775 cm^{-1}, which is due to vibrations with the participation of the C=N bond, can be explained by the overall electron-acceptor effect of the ester oxygen atom and the carbonyl group.

In our opinion, the rather intense absorption at 1645-1660 cm^{-1} is due to the stretching vibrations of the exocyclic double bond. The high intensity of this band is explained by the s-cis orientation relative to the C=O bond and overlapping by a number of other bands. The latter evidently are bands of stretching vibrations of the azlactone ring, which also include a change in the length of the azomethine bond. Finally, the low-intensity band at ∿1600 cm^{-1} is associated with the absorption of aromatic rings.

The results of a study of the spectral-luminescence properties of I and II in toluene are presented in Table 1. Data for the previously described III [3] are presented for comparison.

The UV absorption spectra of I and II have vibrational structures. The nature of the long-wave band responsible for the fluorescence can be interpreted on the basis of concepts regarding localization of the electronic excitation in the arylideneazlactone fragment. We drew this conclusion on the basis of quantum-mechanical calculations for a number of azlactones and confirmed it experimentally by a study of the absorption spectra of these compounds [4, 5]. In the case of I and II the $S_0 \rightarrow S^*_1$ transition, which is localized in the arylideneazlactone fragment, is associated with redistribution of the electron density primarily in this fragment; the shift of the electron density is directed toward the arylidene grouping. It would seem that the introduction of a strong electron-acceptor substituent, viz., a difluoromethylsulfonyl group, in the 2-aryl grouping of the azlactones should to a certain extent hinder this shift and give rise to a hypsochromic shift of the absorption band as compared with II, in which this substituent is located in the 4-arylidene fragment. However, a difference in the position of the absorption maxima for these compounds is either almost absent, or a red shift of the long-wave absorption band is observed (Table 1).

The contribution to the mesomerism of the molecules with a quinoid form, in which the $S_0 \rightarrow S^*_1$ transition is determined by the length of the conjugation chain between the "transformed" benzylidene and arylazomethine groupings [3, 6], evidently increases when strong electron-acceptor substituents are introduced in the 2-aryl grouping. The bathochromic effect as compared with II is also a consequence of this.



In the interpretation of the nature of the long-wave absorption band for compounds that simultaneously contain electron-donor and electron-acceptor groupings in the same molecule (Ie, f) one should take into account the donor-acceptor interaction of the electron-donor group with both the carbonyl group of the azlactone ring and with the difluoromethylsulfonyl group. The interaction of these substituents with the "transformed" arylazomethine grouping, the acceptor properties of which are intensified owing to the

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	Absorption, λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)	Fluorescence			S found, %	Empirical formula	S calc., %	Yield, %
			λ_{max}, nm, at 293°K	λ_{max}, nm, at 77°K	η				
Ia	208—209	380 (3,38)	435	440, 475	—	8,8	$C_{17}H_{11}F_2NO_4S$	8,8	35
Ib	243—244	405 (2,92)	465	485	—	7,3	$C_{23}H_{15}F_2NO_4S$	7,3	30
Ic	293—294	425 (2,76)	505	485, 505	—	8,0	$C_{21}H_{13}F_2NO_4S$	8,0	25
Id	278—279	385 (3,24)	—	495	—	8,2	$C_{17}H_{10}F_2N_2O_5S$	8,2	35
Ie	198—199	385 (3,24)	485	495	—	8,4	$C_{18}H_{13}F_2NO_5S$	8,4	30
If	247—248	505 (5,60)	565	550, 570	—	7,9	$C_{19}H_{16}F_2N_2O_4S$	7,9	20
Ig	291—292	375 (3,80)	465	450, 470	0,35	13,5	$C_{18}H_{11}F_4NO_6S_2$	13,4	40
Ih	299—300	435 (4,35)	525	510, 535	0,30	6,3	$C_{26}H_{16}F_2N_2O_5S$	6,3	40
IIa	193—194	370 (5,05)	450	440, 465	0,23	8,9	$C_{17}H_{11}F_2NO_4S$	8,8	50
IIb	237—239	390 (3,76)	470	465	0,30	7,2	$C_{23}H_{15}F_2NO_4S$	7,3	42
IIc	267—268	400 (2,60)	480	470	0,42	7,9	$C_{21}H_{13}F_2NO_4S$	8,0	35
IIIa	—	380 (4,92)	460	455, 480	—	—	—	—	—
IIIb	—	470 (5,50)	510	560	—	—	—	—	—

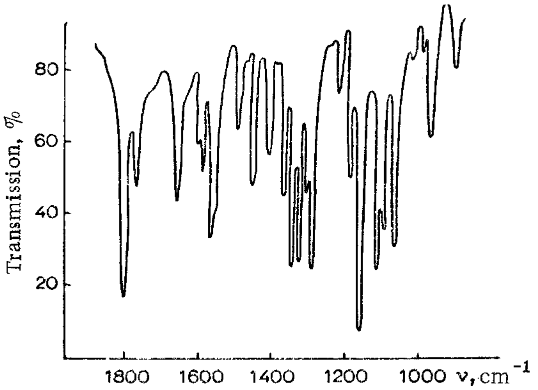


Fig. 1. IR spectrum of 2-phenyl-4-(4-difluoromethylsulfonylbenzylidene)-oxazole-5-one in KBr.

presence of a strong electron-acceptor grouping, is increased significantly under the influence of electron-donor substituents introduced in the arylidene fragment. The interaction of the electron-donor substituents with the carbonyl group of the azlactone ring is weakened correspondingly. The long-wave absorption band undergoes a bathochromic shift; the magnitude of this shift is determined to a considerable extent by the strongly expressed electron-donor properties of the substituent (Δλ for IIIa and Ie is 5 nm, as compared with 35 nm for IIIb and If).

In the case of compounds that simultaneously contain strong electron-acceptor groupings in both the 2-aryl and 4-arylidene groupings (Id and IId) there is virtually no difference between 2- and 4-substituted azlactones.

A long-wave shift of the absorption maxima is observed in the absorption spectra when the conjugation chain is lengthened in both the 2-aryl and 4-arylidene groupings. A compound with a 2,5-diphenyloxazole residue (Ie), the absorption maximum of which is determined not so much by the electron-acceptor properties of this structural grouping as by the lengthening of the conjugation chain of the arylidene fragment, is of interest in this respect.

When the chain of conjugated bonds in the 2-aryl grouping directly bonded to the azomethine grouping is increased, the role of this grouping in the $S_0 \rightarrow S^*_1$ transition increases; however, the effect of the carbonyl group on the absorption maxima of these compounds is very much weakened. As a result, a short-wave shift of the maxima as compared with the corresponding I is observed in the absorption spectra of II (compare Ia-c and IIa-c).

It should be noted that the $\nu_{C=O}$ value in the IR spectra of the investigated compounds is sensitive to the effect of the substituents introduced in the molecule, although this effect is appreciably weaker than in the UV spectra. As expected, electron-donor substituents give rise to a decrease, whereas electron-acceptor substituents give rise to an in-

increase in the $\nu_{C=O}$ values (the $\nu_{C=O}$ values for Ia, If, and Id are 1792, 1790, and 1798 cm^{-1}, respectively). The substituents have a smaller effect on the other bands.

Compounds I and II have intense fluorescence in solutions at room temperature and at the temperature of liquid nitrogen. The fluorescence spectra of frozen solutions are characterized by a broad curve with two distinctly expressed maxima, which are shifted only slightly to the long-wave region relative to the fluorescence spectra of toluene solutions at room temperature. The Stokesian shift ranges from 2000 to 5500 cm^{-1}.

Owing to its strong acceptor effect, the difluoromethylsulfonyl group intensifies the polarization of the azlactone molecules in the first excited state, as a consequence of which they acquire a more rigid structure. The probability of nonradiating degradation of the energy of the electronic excitation decreases, and the fluorescence quantum yields for these compounds increase correspondingly.

Different changes in the energies of the $\pi \rightarrow \pi^*$ energies and $p \rightarrow \pi^*$ transitions occur when the length of the conjugation chain is increased in both the 2-aryl and 4-arylidene groupings: The energies of the $\pi\pi^*$ states are lowered considerably more markedly than the energies of the $p\pi^*$ states. This leads to a change in the nature of the long-wave transitions and to the development of intense fluorescence. The fluorescence quantum yields increase regularly as a consquence of an increase in the difference in the energies of the $p\pi^*$ and $\pi\pi^*$singlet and triplet states.

Thus our studies open up possibilities for the directed synthesis of luminophores of the azlactone series; the introduction of a difluoromethylsulfonyl group in both the 2-aryl and 4-arylidene groupings leads to the development of fluorescence in solutions at room temperature; the intensity of the luminescence of compounds that contain this group in the 4-arylidene grouping is higher than in the case of the corresponding compounds that contain a difluoromethylsulfonyl group in the 2-aryl grouping.

EXPERIMENTAL

The fluorescence spectra were measured with an apparatus consisting of a ZMR-3 monochromator, an FÉU-18 optical radiation detector, and an M-95 microammeter. Photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated by means of a DMR-4 quartz monochromator. The absorption spectra of solutions of the compounds (c $3 \cdot 10^{-3}$ mole/liter) were measured with an SF-4 spectrophotometer. The absolute fluorescence quantum yields were determined by the equal-absorption method [7]. The IR spectra were measured with a UR-20 spectrometer.

The azlactones were obtained by the method described in [4]. The products were recrystallized from suitable solvents: Ia, g, h from acetic acid, Ib, d, f and IIb, d from benzene, Ic from chlorobenzene, and Ie and IIa, c from benzene—heptane (1:1). The characteristics of the synthesized compounds are presented in Table 1.

LITERATURE CITED

1. B. M. Krasovitskii, M. B. Stryukov, B. Ya. Simkin, I. V. Lysova, V. I. Minkin, S. E. Kovalev, and L. Sh. Afanasiadi, Izv. Akad. Nauk SSSR, Ser. Fiz., 44, 812 (1980).
2. L. M. Yagupol'skii, A. Ya. Il'chenko, and N. V. Kondratenko, Usp. Khim., 43, 64 (1974).
3. B. M. Krasovitskii, I. V. Lysova, and L. Sh. Afanasiadi, Khim. Geterotsikl. Soedin., No. 7, 909 (1980).
4. B. M. Krasovitskii, I. V. Lysova, and L. Sh. Afanasiadi, Khim. Geterotsikl. Soedin., No. 2, 158 (1978).
5. B. M. Krasovitskii, A. V. Yudashkin, I. V. Lysova, L. Sh. Afanasiadi, and A. E. Lipkin, Khim. Geterotsikl. Soedin., No. 12, 1624 (1979).
6. D. Bassi, V. Deulofen, and F. Ortega, J. Am. Chem. Soc., 75, 171 (1953).
7. A. S. Cherkasov, Zh. Fiz. Khim., 29, 2209 (1955).