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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2,5-DIARYLOXAZOLES
THAT CONTAIN A DIFLUOROMETHYLSULFONYL GROUP

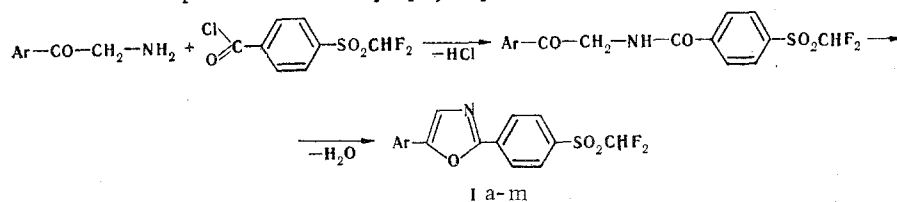
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UDC 547.787.2.07;535.542.953

A number of 2-(4-difluoromethylsulfonylphenyl)-5-aryloxazoles were synthesized by condensation of 4-difluoromethylsulfonylbenzoyl chloride with ω -aminomethyl aryl ketones and subsequent cyclodehydration of the resulting amides in sulfuric acid. The spectral-luminescence properties of these products were investigated. The introduction of a difluoromethylsulfonyl group in the 2-phenyl ring of 2,5-diphenyloxazole leads to significant bathochromic and bathofluoric effects and an increase in the quantum yields and photostabilities of the compounds obtained. Complication of the structure of the 5-phenyl ring is accompanied by a further long-wave shift of the absorption and fluorescence spectra without substantial changes in the fluorescence quantum yields. A positive solvatochromism effect is displayed distinctly in the fluorescence spectra of the compounds obtained on passing to polar solvents; this effect increases markedly as the polarity of the solvent increases.

Continuing our study of the effect of electron-acceptor substituents on the spectral-luminescence properties of 2,5-diaryloxazoles [1, 2], we synthesized and investigated compounds that contain a difluoromethylsulfonyl group in one of the aromatic rings (I).

The strong electron-acceptor effect of the SO_2CHF_2 group was established by one of us in an investigation of the chromaticity of organic compounds of various classes [3, 4]; in a number of cases the introduction of this grouping in organic dye molecules led to a substantial increase in their photostability [3, 5].



1a Ar=C₆H₅; b C₆H₅-C₆H₄; c 1-C₁₀H₇; d 2-C₁₀H₇; e 4-CH₃-C₆H₄; f 2,4,5-(CH₃)₃-C₆H₂;
g 4-CH₃O-C₆H₄; h 4-NH₂-C₆H₄; i 4-(CH₃)₂N-C₆H₄; j 4-CH₃COHN-C₆H₄; k 4-Cl-C₆H₄;
l 4-Br-C₆H₄; m 4-NO₂-C₆H₄

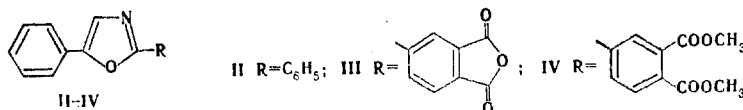
The introduction of a difluoromethylsulfonyl group in the 2-phenyl ring of 2,5-diphenyloxazole (II) leads to substantial bathochromic and bathofluoric effects with a simultaneous increase in the fluorescence quantum yield (for example, compare II and Ia in Table 1).

"Single Crystal Reagent" Scientific-Industrial Union, Kharkov 310141. Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 8, pp. 1042-1046, August, 1982. Original article submitted August 21, 1981; revision submitted February 17, 1982.

TABLE 1. Spectral-Luminescence Properties of 2-(4-Difluoromethylsulfonylphenyl)-5-aryloxazoles

Compound	Absorption			Fluorescence		
	toluene		ethanol	toluene		ethanol
	λ_{\max} , nm	$\epsilon \cdot 10^{-3}$	λ_{\max} , nm	λ_{\max} , nm	φ	λ_{\max} , nm
II	307	25,8	307	365	0,51	365
III	364	18,7	—	455	0,61	—
Ia	340	27,4	335	405	0,78	430
Ib	352	32,2	350	425	0,76	450
Ic	347	19,0	345	440	0,61	465
Id	355	25,3	350	425	0,79	450
Ie	347	25,0	345	415	0,67	444
If	345	18,0	343	425	0,76	495
Ig	357	25,4	350	445	0,78	550
Ih	360	24,6	360	487	0,40	620
Ii	398	18,8	398	505	0,52	640
Ij	355	—	—	440	0,77	—
Ik	345	27,7	331	410	0,61	430
Il	342	42,0	—	415	0,32	—
Im	357	39,0	—	Does not luminesce		

However, the absorption and emission spectra of 2-(4-difluoromethylsulfonylphenyl)-5-phenyloxazole (Ia) in toluene lie in a shorter-wave region than the spectra of our previously described 4-(5-phenyloxazol-2-yl)phthalic anhydride (III) (Table 1) [2], in which the anhydride grouping acts as a strong electron-acceptor substituent. At the same time, the basicity of Ia (pK_a 4.06) is lower than that of III (pK_a 4.72), i.e., the difluoromethylsulfonyl group has a stronger acceptor effect on the oxazole ring than the anhydride grouping.



From our point of view, this nonconformity is associated with the fact that the difluoromethylsulfonyl group, which has a strong negative inductive effect, decreases the basicity of the nitrogen atom of the oxazole ring to a greater degree than the anhydride grouping in III.

The weaker acceptor effect of the difluoromethylsulfonyl group on the absorption and emission spectra as compared with the anhydride grouping is evidently due to the fact that the sulfur atom in the SO_2CHF_2 group, as in the case of sulfonyl chloride, exists in the first valence state (sp^3 hybridization), which is responsible for its nonplanar structure. This in turn leads to weakening of the conjugation of the SO_2CHF_2 group with the π -electron system of Ia as compared with III, the two carbonyl groups of which are rigidly fixed in the plane of the molecule.

Complication of the structure of the aryl grouping in I by replacement of the phenyl ring by a 4-biphenyl or 2-naphthyl grouping leads to a further shift in the absorption and fluorescence to the long-wave region without a substantial change in the fluorescence quantum yield (Table 1).

The absorption maximum of the compound with a 1-naphthyl group (Ic) is shifted to the short-wave region not only with respect to the 2-substituted isomer but also as compared with Ib, which contains a biphenyl grouping. The intensity of the absorption band of Ic decreases markedly as compared with Ia, b, d. At the same time, when we compare the fluorescence spectra of Ib-d, we observe the opposite pattern — the compound that contains a 1-naphthyl grouping has the longest-wave fluorescence (Table 1). A significant increase in the Stokesian shifts is observed for this compound.

Compound Ic in the ground state evidently has a nonplanar structure; in particular, the 1-naphthyl grouping is turned at a significant angle with respect to the plane of the molecule.

This sort of anomaly in the behavior of the compound with a 1-naphthyl grouping is not observed for similar compounds that do not contain a SO_2CHF_2 group. It may be assumed that

TABLE 2. Spectral-Luminescence Properties of 2-(4-Difluoromethylsulfonylphenyl)-5-(4-dimethylamino-phenyl)oxazole in Various Solvents

Solvent	E_T (25°C), kcal/mole [9]	Absorption λ_{max} , nm	Fluorescence λ_{max} , nm
n-Octane	31,9	394	480
Toluene	33,9	398	505
Dioxane	36,0	385	550
Chlorobenzene	37,5	400	564
Acetone	42,5	393	630
Benzyl alcohol	50,8	405	635
Ethanol	51,9	288, 398	640
Dimethylformamide	53,9	398	655

the interaction of the difluoromethylsulfonyl group with the π -electron system of Ic increases to a considerable extent in the excited state, and, owing to this, the molecule emits light, inasmuch as it exists in a more planar configuration.

The spectra of Ie-m (Table 1) are sensitive to the electronic nature of the substituents introduced into the phenyl ring. The methyl group, owing to its interaction with the strong electron-acceptor difluoromethylsulfonyl group, gives rise to a small long-wave shift of the absorption and fluorescence maxima. The bathofluoric effect is intensified when three methyl groups (If), two of which are included in the conjugation chain, are introduced. The steric hindrance in this compound due to the 2-methyl group is probably overcome in the same way as in the compound with the n-naphthyl grouping.

The bathochromic and bathofluoric effects are manifested to a considerably greater extent under the influence of methoxy, amino, acetamido, and dimethylamino groups. The electronic interaction of these substituents along the chain of conjugated bonds that includes the oxazole ring leads to a substantial shift of the absorption and fluorescence of 2,5-diaxyloxazoles to the long-wave region and imparts a visible color to them.

The spectral-luminescence characteristics of chloro-substituted Ik are virtually the same as those of unsubstituted Ia; the introduction of a bromine atom in the 4 position of the phenyl ring, although it does not have an appreciable effect on the positions of the absorption and fluorescence maxima, markedly decreases the quantum yield; this is associated with the quenching effect of the heavy bromine atom. The introduction of a nitro group quenches the fluorescence completely.

It should be noted that the fluorescence spectra of I, in contrast to the absorption spectra, for which positive solvatochromism is manifested to only a slight degree, are extremely sensitive to a change in the polarity of the solvent (Tables 1 and 2). Thus a pronounced shift in the fluorescence of I to the long-wave region is observed on passing from toluene to the more polar ethanol (Table 1). This is particularly graphically apparent for Ii, which contains a dimethylamino group (Table 2). Molecules of this compound, in which a strong electron donor and a strong electron acceptor are found at the ends of the conjugated system, are analogs of 4-dimethylamino-4'-nitrostilbene [6], for which the same principles are observed.

It is apparent from Table 2 that the position of the fluorescence maximum of Ii is symbatic to the Dimroth E_T value — one of the most important empirical parameters of the polarity of a solvent — and may range from 480 to 655 nm. This indicates a substantial increase in the dipole moment of Ii in the excited state, as a result of which, the positive solvatochromism effect increases.

Considering the photostabilizing effect of some fluorine-containing substituents [3,5], we investigated the resistance to the effect of UV radiation of toluene solutions of some 2-(4-difluoromethylsulfonylphenyl)-5-aryloxazoles as compared with unsubstituted analog II. In order to ascertain how important the electron-acceptor character of the substituent is for photostability we simultaneously investigated the resistance to UV radiation of analogous compounds with anhydride (III) and ester (IV) groupings. Irradiation was carried out with the unfiltered light of a PRK-2 mercury-quartz lamp. The photostability was characterized by the change in the intensity of the fluorescence of the samples at the luminescence maximum with respect to the fluorescence intensity of nonirradiated samples at the luminescence maximum, which was taken to be 100%.

TABLE 3. Photo-stabilities of Ia, b, g-IV

Compound	I, * %
II	25
Ia	58
Ib	61
Ig	88
III	90
IV	75

*Symbol I is the fluorescence intensity after irradiation with UV light.

TABLE 4. 2-(4-Difluoromethylsulfonylphenyl)-5-aryloxazoles (Ia-m)

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		N	S		N	S	
Ia	185—185,5	4,2	9,6	C ₁₆ H ₁₁ F ₂ NO ₃ S	4,2	9,6	74
Ib	177—178	3,3	7,8	C ₂₂ H ₁₅ F ₂ NO ₃ S	3,4	7,8	80
Ic	144—145	3,7	8,2	C ₂₀ H ₁₃ F ₂ NO ₃ S	3,6	8,3	91
Id	177—178	3,4	8,6	C ₂₀ H ₁₃ F ₂ NO ₃ S	3,6	8,3	83
Ie	159—160	3,9	9,6	C ₁₇ H ₁₃ F ₂ NO ₃ S	4,0	9,3	90
If	182—183	3,8	8,7	C ₁₉ H ₁₇ F ₂ NO ₃ S	3,7	8,5	80
Ig	174—175	3,6	8,9	C ₁₇ H ₁₃ F ₂ NO ₄ S	3,8	8,8	92
Ih	165—166	7,9	9,2	C ₁₆ H ₁₂ F ₂ N ₂ O ₅ S	8,0	9,2	58
Ii	180—180,5	7,3	8,6	C ₁₈ H ₁₆ F ₂ N ₂ O ₃ S	7,4	8,5	53
Ij	214—215	7,1	8,3	C ₁₈ H ₁₄ F ₂ N ₂ O ₄ S	7,1	8,2	58
Ik	189—190	3,9	8,7	C ₁₆ H ₁₀ ClF ₂ NO ₃ S	3,8	8,3	94
Il	186—187	3,5	7,8	C ₁₆ H ₁₀ BrF ₂ NO ₃ S	3,4	7,7	84
I _m	218—219	7,6	8,5	C ₁₆ H ₁₀ F ₂ N ₂ O ₅ S	7,4	8,4	72

From a comparison of the effect of the SO₂CHF₂ group and the phthalanhydride and ester groupings on the photostability of 2,5-diaryloxazoles (Table 3) it may be concluded that it is associated to a considerable degree with their electron-acceptor properties. The introduction of strong electron-acceptor substituents in the 2-phenyl ring leads to delocalization of the unshared pair of electrons of the nitrogen atom of the heteroring, which in turn leads to stabilization of the oxazole ring and hence the entire molecule.

EXPERIMENTAL

The absorption spectra were recorded with an SF-4 spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, and FEU-18 optical emission detector, and an M-95 microammeter. Photoluminescence was excited with an SVDSH-500 lamp, from the spectrum of which the light with a wavelength of 365 nm was isolated by means of a DMR-4 quartz monochromator. The absolute luminescence quantum yields were determined by the equal-absorption method [7]. The photostability was characterized by the change in the fluorescence intensity of the luminophores at the luminescence maximum with respect to the fluorescence intensity of nonirradiated samples during irradiation with the unfiltered light of a PRK-2 mercury-quartz lamp. The power of the lamp was 378 W, the distance from the lamp to the sample was 12 cm, and the temperature of the illuminated field was 26°C.

4-Difluoromethylsulfonylbenzoyl Chloride. A 25.5-g (0.1 mole) sample of 4-difluoromethylsulfonylbenzoic acid [8] was refluxed in 100 ml of thionyl chloride for 2 h, after which the excess thionyl chloride was removed by vacuum distillation, and the residue was recrystallized from benzene to give 23 g (90%) of a product with mp 85–86°C. Found: F 14.6; S 12.3%. C₈H₅ClF₂SO₃. Calculated: F 14.9; S 12.2%.

2-(4-Difluoromethylsulfonylphenyl)-5-aryloxazoles (Ia-g, i, k-m, Table 4). A 10% solution of sodium carbonate was added with vigorous stirring at 20-25°C to a mixture of solutions of equimolar amounts (0.01 mole) of 4-difluoromethylsulfonylbenzoyl chloride in 250 ml of benzene and ω -aminomethyl aryl ketone hydrochloride in 400-500 ml of water until the mixture was alkaline with respect to litmus, and the mixture was stirred at 20°C for 30 min. The precipitate was removed by filtration, washed with water, dried, and dissolved in a tenfold (by mass) amount of concentrated H₂SO₄. The resulting dark-brown solution was maintained at 40-45°C for 2 h, after which it was poured over ice. The precipitate was removed by filtration, washed with water, and dried.

2-(4-Difluoromethylsulfonylphenyl)-5-(4-aminophenyl)oxazole (Ih, Table 4). A 3.8-g (0.01 mole) sample of 2-(4-difluoromethylsulfonylphenyl)-5-(4-nitrophenyl)oxazole was dissolved in 50 ml of acetic acid, 5 g of iron filings was added, and the mixture was refluxed for 1 h and poured into 10% ammonium hydroxide. The precipitate was removed by filtration, washed with water, and dried.

A similar procedure was used to synthesize 2-(4-difluoromethylsulfonylphenyl)-5-(4-acetamidophenyl)oxazole (Ij, Table 4), for the preparation of which reduction was carried out in a mixture of acetic anhydride and acetic acid (1:10).

The purification of the 2-(4-difluoromethylsulfonylphenyl)-5-aryloxazoles was carried out by chromatography of benzene solutions on aluminum oxide in a continuous-operation column.

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