2-Amino-3-(2-furacyl)thiazolium bromide [1, 2] and its 4-methyl derivative were cyclized by being boiled with an aqueous solution of sodium bicarbonate, while for the cyclization of the thiazolium salts containing bromine or a nitro group in position 5 of the furan ring it was sufficient to boil them with water or ethanol.

The action of hydrobromic acid in acetone on the imidazolo[2, 1-b]thiazoles has given their hydrobromides.

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7 May 1967

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LUMINESCENCE OF SOME SULFUR-CONTAINING HETEROCYCLES AND THEIR SULFONES

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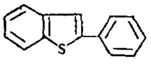
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 1, pp. 180–181, 1968

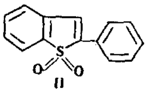
UDC 547.735.736:543.426

The luminescence spectra (of crystals and toluene solutions) and the absolute quantum yields of the fluorescence of thianaphtheno[3, 2-b]-thianaphthene, tetraphenylthiophene, 2-phenylthianaphthene, and their sulfones have been measured. The oxidation of the sulfur heterocycles to the corresponding sulfones leads to a marked decrease in the intensity of their luminescence.

Sulfur-containing heterocycles possess a smaller capacity for luminescence under irradiation with ultraviolet light than their oxygen and nitrogen analogs. This is clearly shown, in particular, with the 2, 5-diphenyl derivatives of thiophene, pyrrole, and furan [1].

A few years ago, it was reported [2] that toluene solutions of 2-phenylthianaphthene sulfone (II) luminesced more strongly than solutions of 2-phenylthianaphthene (I) itself.


I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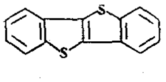
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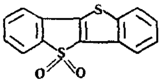
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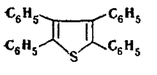
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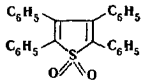
VI

It was interesting to ascertain whether this phenomenon was also observed for other sulfur-containing heterocycles and their sulfones.

For this purpose we have measured the luminescence spectra (of crystals and toluene solutions) and the absolute quantum yields (η_q) of the photoluminescence of the sulfur heterocycles I, III, V, and their sulfones (II), (IV), and (VI).

Both in the crystalline state and in solutions, the sulfone IV luminesced in a longer-wave region and more strongly than the unoxidized heterocycle III (Figs. 1 and 2). Thus, for a solution of III in toluene, λ_{max}

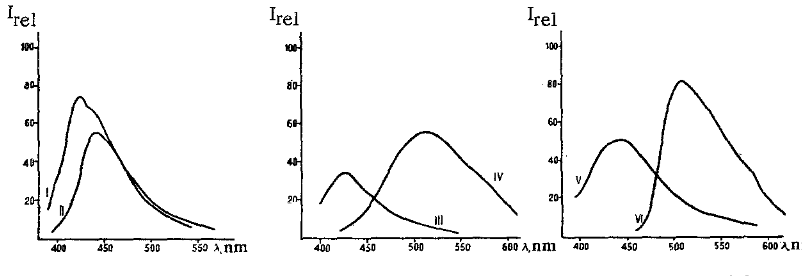

Fig. 1. Luminescence spectra of crystals of I–VI: I) 2-phenylthianaphthene; II) 2-phenylthianaphthene sulfone; III) thianaphtheno[3, 2-b]thianaphthene; IV) thianaphtheno[3, 2-b]thianaphthene monosulfone; V) tetraphenylthiophene; VI) tetraphenylthiophene sulfone.

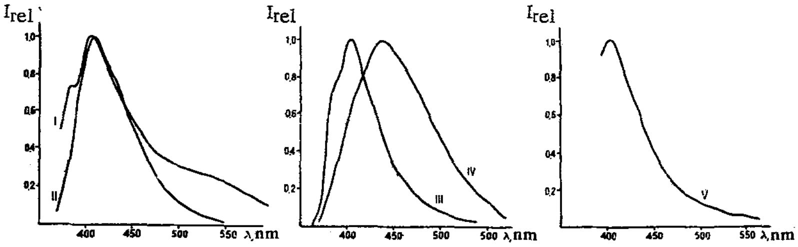

Fig. 2. Luminescence spectra of toluene solutions of I–VI: symbols as for Fig. 1. η_q = I 0.07; II 0.66; III 0.06; IV 0.38; V 0.198.

of the luminescence is 405 nm, and for crystals of III it is 425 nm; for solutions of IV in toluene λ_{max} = = 440 nm and for crystals of IV 510 nm. The absolute quantum yield of the toluene solution of III was 0.06 and that of IV 0.38 (according to our results, the absolute quantum yield of a toluene solution of II is 0.66 and of I 0.07).

We also observed visually a considerable increase in the intensity of the luminescence of the crystals on passing from V to its sulfone (VI). It is interesting, however, that VI does not fluoresce in toluene solution.

Thus, the exclusion from the conjugation of the unshared electrons of the sulfur atom in aromatic heterocycles by their conversion into the corresponding sulfones leads to a marked increase in the intensity of fluorescence.

This conclusion may be of practical importance in the production of new organic luminophores.

The compounds studied were synthesized as described previously [3]. The luminescence spectra were measured on an apparatus consisting of a SVDSh-500 quartz-mercury lamp from the spectrum of which the exciting line at 365 nm was isolated, a ZMR-3 mirror monochromator, and a FEU-18 [photoelectric multiplier].

The absolute quantum yields of the photoluminescence were determined by the equal absorption method [4].

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29 June 1967

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