data for that compound, which should lie inside the values of the moments of its phenyl derivatives.

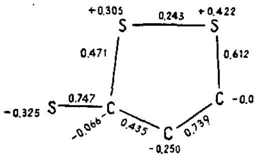

Fig. 3. Molecular diagram of 1, 2-dithiol-3-thione [10].

The dipole moment of 1, 2-dithiol-3-thione, calculated from the electron distribution of IV that we obtained, is 5.25 D. Thus the $\pi$-electron configurations of IV–VI correspond better to the actual electron density distribution in type I compounds than to the $\pi$-electron configuration shown in Fig. 2. The reason for this is obviously poor choice [10] of starting parameters.

Compounds V [14] and VI [15] were synthesized by methods previously described. The dipole moments were determined as described in [16]. The LCAO MO calculations were made on a EVM M-20 computer using the program of [17].

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# SYNTHESIS AND OPTICAL PROPERTIES OF β-ARYLETHYLENE DERIVATIVES OF 2, 5-DIPHENYLOXAZOLE

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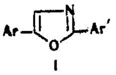
A series of arylethylene derivatives of 2,5-diphenyloxazole derivatives is synthesized, and the absorption and fluorescent spectra of their toluene solutions are investigated. Joining in one molecule of 2, 5-diphenyloxazole and arylethylene groups leads to long wave displacement of the absorption and fluorescence bands, and in most cases to greater intensity of absorption and increase in the photoluminescence quantum yield.

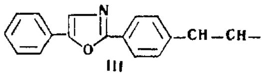
Many 2, 5-diaryloxazoles (I) and diarylethylenes (II) belong to the class of effective organic luminophors [1–3]. It was of interest to unite in one molecule the structural groups of 2, 5-diphenyloxazole and various diarylethylenes, and to investigate the absorption spectra and fluorescent properties of such compounds (III).



I

Ar—CH=CH—Ar′

II



III

Ar and Ar' are identical or different radicals.

Table 1

Optical Properties of β-Arylethylene Derivatives of 2, 5-Diphenyloxazole

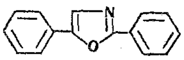
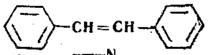
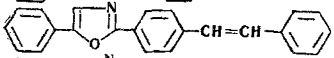
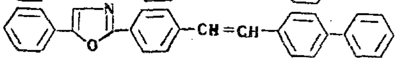
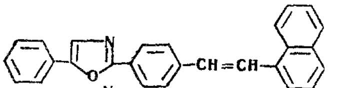
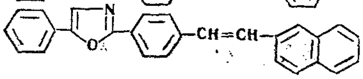
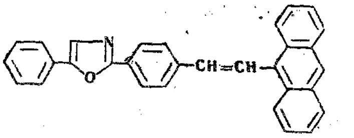
| Compound | Formula | $\lambda_{max}$, nm | $\varepsilon \cdot 10^{-4}$ | $\lambda_{max}$, fluorescence, nm | Y abs |
|---|---|---|---|---|---|
| IV |  | 308 | 3.06 | 365 | 0.51 |
| V |  | 300 | 2.92 | 355 | 0.04 |
| VI |  | 355 | 6.34 | 415 | 0.88 |
| VII |  | 368 | 7.11 | 430 | 0.83 |
| VIII |  | 360 | 4.66 | 435 | 0.75 |
| IX |  | 368 | 5.41 | 425 | 0.73 |
| X |  | 390 | 2.65 | 500 | 0.51 |

Table 2

β-Arylethylene Derivatives of 2,5-Diphenyloxazole

| Compound | Mp, °C | Formula | N, % | | Yield, % |
|---|---|---|---|---|---|
| | | | Found | Calculated | |
| VI | 153.5—154.5 | $C_{23}H_{17}ON$ | 4.43 | 4.33 | 30 |
| VII | 230 —231.5 | $C_{29}H_{21}ON$ | 3.75 | 3.50 | 30 |
| VIII | 167 —168 | $C_{27}H_{19}ON$ | 3.66 | 3.75 | 21 |
| IX | 213 —214 | $C_{27}H_{19}ON$ | 3.80 | 3.75 | 40 |
| X | 198 —199 | $C_{31}H_{21}ON$ | 3.28 | 3.30 | 50 |

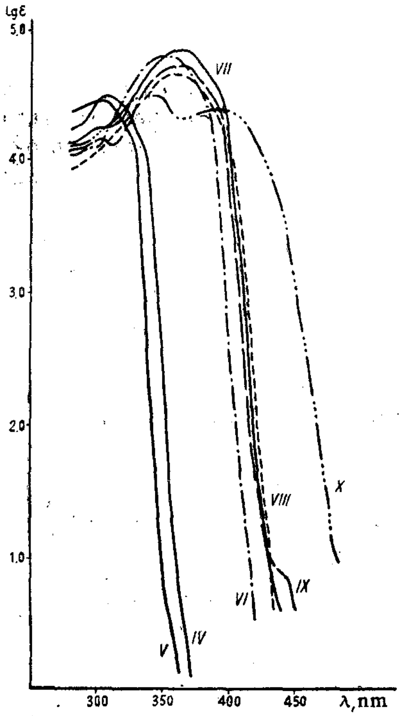


Fig. 1. UV spectra of toluene solutions of IV–X.

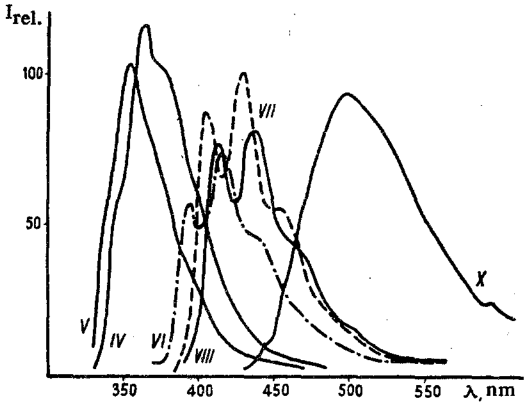


Fig. 2. Fluorescent spectra of toluene solutions of IV–IX.

For this purpose using the Wittig reaction and the phosphonate obtained by Arbuzov's method, we synthesized a series of compounds according to the equations

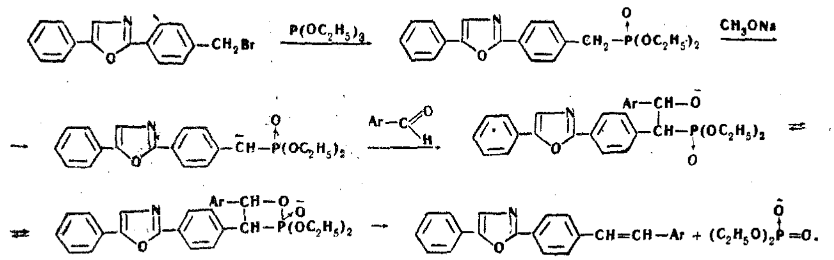


Table 1 gives absorption maxima and molar extinction coefficients of K bands of toluene solutions of compounds III, their fluorescent maxima, and the absolute quantum yields.

Transition from 2, 5-diphenyloxazole (IV) and stilbene (V) and VI is accompanied by shift of the absorption and fluorescence bands towards the long wave region; the intensity of absorption increases substantially, the absolute quantum yield is sharply increased, the fluorescence spectrum acquires a clearly exhibited vibration structure. Obviously the basic structural factor giving rise to these effects is the considerable increase in the chain of conjugated double bonds with VI as compared with IV and V.

Further increasing the degree of conjugation by making the structures of the aromatic radicals in the diarylethylene part of the molecule more complicated does not, in most cases, alter the character, but gives rise to bathochromic shift of the absorption (Fig. 1) and fluorescence (Fig. 2) bands. The exception is an anthryl derivative, for which splitting of an absorption band is found in the spectrum. Along with a K band which is less intense, but bathochromically shifted as compared with VI, a shorter wave band appears, lying in the region where anthracene itself absorbs. Possibly this is due to steric factors weakening conjugation between the anthryl radical and the rest of the molecule. The fluorescent spectrum of this compound, unlike that of other compounds in the same series, has no vibration structure.

The quantum yields with VII–X, despite the lengthening of the conjugated chain in their molecules compared with VI, were lower than for the latter. The anthryl derivative gives the lowest quantum yield.

## EXPERIMENTAL

**1-Phenyl-2-(2, 5-diphenyloxazolyl-4)ethylenes.** A mixture of equimolar quantities (0.01 mole) 2-(4-bromomethylphenyl)-5-phenyloxazole and triethylphosphite in 20 ml zylene, was refluxed in an oil bath for 4–5 hr. The xylene was distilled off, and the phosphonate, a yellow oil, formed in almost quantitative yield and solidified on cooling. It was dissolved in dimethylformamide (30 ml), a small excess of aldehyde (0.011 mole) added, along with a solution of Na(0.23 g) in 2–3 ml MeOH. The whole was kept for 2–3 hr at room temperature, neutralized with 50% AcOH, and 15 ml water added. The solid was filtered off, dried, and purified by chromatographing a benzene solution of it on alumina, followed by recrystallizing from acetone, or acetone–dioxane, using decolorizing carbon. Trans isomers of diarylethylenes are generally obtained under these conditions [5].

Analyses, melting points, and yields of the compounds prepared are given in Table 2.

The absorption spectra were investigated with a SF-4 spectrophotometer, the fluorescent spectra with a setup comprising ZMR-3 monochromator, M-59 and FEU-18 microammeters; the exciting source was a DPSh-500 lamp, from whose spectrum the DMP-4 monochromator isolated the exciting line 365 nm.

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