SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF AZOLE ANALOGS OF 1,4-DISTYRYLBENZENE AND ISOMERIC DISTYRYLNAPHTHALENES

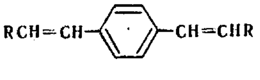
E. M. Vernigor, V. K. Shalaev,
L. P. Novosel'tseva, E. A. Luk'yanets,
A. A. Ustenko, V. P. Zvolinskii,
and V. F. Zakharov

UDC 547.78.07:542.953:535.37

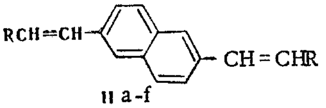
Azole analogs of 1,4-distyrylbenzene and the isomeric 2,6-, 1,5-, and 2,7-distyrylnaphthalenes were obtained by condensation of 2-methylazoles with terephthalaldehyde or the corresponding isomeric diformylnaphthalenes in dimethylformamide (DMF) in the presence of KOH. The electronic absorption and luminescence spectra of the synthesized compounds were recorded, and the dependence of the spectral-luminescence properties on their structures was studied.

Some azole analogs of 1,4-distyrylbenzene such as 1,4-bis[β-(2-benzoxazolyl)vinyl]-benzene (Ia) have intense luminescence in the blue-green region of the spectrum and find application as optical bleaches for synthetic fibers [1]. It was also recently found that they are highly effective as generating compounds in quantum electronics [2]. Nevertheless, the relationship between the spectral-luminescence properties of the indicated compounds and the structural peculiarities of their molecules has not been investigated.

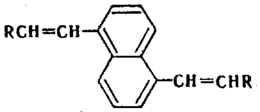
The aim of the present research was to synthesize and study the spectral properties of symmetrical azole analogs of 1,4-distyrylbenzene and isomeric distyrylnaphthalenes with subsequent structural changes in the Ia molecule, viz., replacement of the benzoxazole fragments by naphthoxazole, 5-phenyloxazole, benzothiazole, and naphthothiazole fragments (Ib-h) and replacement of the central 1,4-phenylene fragment by 2,6-, 1,5-, and 2,7-naphthylene fragments (IIa-f, IIIa-c, and IVa-d).



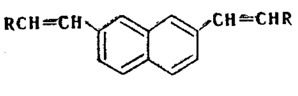
I a-h



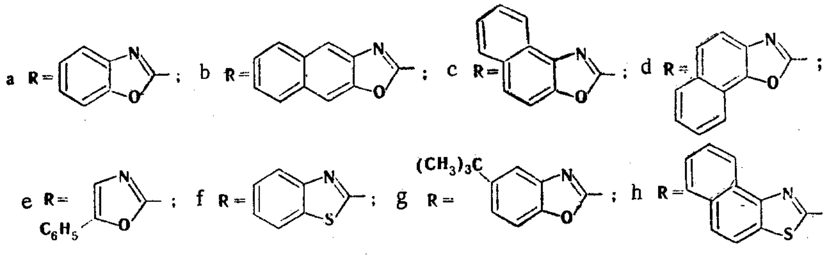
II a-f



III a-c



IV a-d



The known methods for the synthesis of azole analogs of 1,4-distyrylbenzene are based on the condensation of p-phenylenediacrylic acid or its dichloride with o-aminophenols [3] or α-amino ketones [4] or on the condensation of terephthalaldehyde with the corresponding 2-methyl-substitued azoles[5-10]. A single azole analog of 2,6-distyrylnaphthalene IIa, which was obtained by the Wittig—Horner reaction from 2,6-diformylnaphthalene and diethyl (2-benzoxazolyl)methylphosphonate [11], has been described [11]. The disadvantages of the

---

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 203787.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 604-608, May, 1980. Original article submitted August 14, 1979.

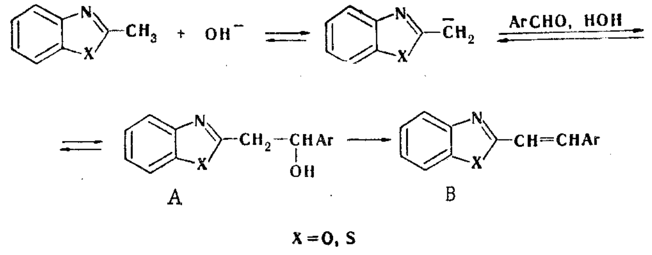
0009-3122/80/1605-0464$07.50

TABLE 1. Yields and Constants of the Azole Analogs of 1,4-Distyrylbenzene and Isomeric Distyrylnaphthalenes

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
Ia	335 [15]								95
Ib	364	82,8	4,2	6,1	$C_{32}H_{20}N_2O_2$	82,7	4,3	6,0	54
Ic	262 [6]								64
Id	297	82,6	4,6	5,7	$C_{32}H_{20}N_2O_2$	82,7	4,3	6,0	62
Ie	263 [4]								75
If	287 [9]								97
Ig	285 [15]								94
Ih	316 [15]								77
IIa	322 [11]								89
IIb	368	84,3	4,5	5,4	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	85
IIc	336	83,9	4,5	5,7	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	74
IId	320	83,7	4,7	5,2	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	78
IIe	296	82,4	4,9	5,8	$C_{32}H_{22}N_2O_2$	82,4	4,8	6,0	31
IIf	296	75,6	4,4	6,3	$C_{28}H_{18}N_2S_2$	75,3	4,1	6,3	56
IIIa	287	80,7	4,6	6,8	$C_{28}H_{18}N_2O_2$	81,1	4,4	6,8	88
IIIb	354	84,4	4,4	5,5	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	58
IIIc	308	84,3	4,4	5,4	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	90
IVa	292	81,4	4,7	6,8	$C_{28}H_{18}N_2O_2$	81,1	4,4	6,8	79
IVb	370	84,1	4,7	5,4	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	84
IVc	306	84,3	4,5	5,3	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	91
IVd	320	84,1	4,5	5,3	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	76

enumerated methods are the severe reaction conditions or the difficulties involved in obtaining the starting compounds and the low yields of the reaction products. From our point of view, the condensation of terephthalaldehyde with 2-methyl-substituted azoles under the influence of acidic ($ZnCl_2$ [5], p-toluenesulfonic acid [6], or acetic anhydride [7]) or basic (pyridine [8] or potassium methoxide [9]) catalysts has the greatest synthetic possibilities. Under basic catalysis conditions the reaction may proceed under milder conditions; however, the reaction products in this case are formed in low yields. Thus, Ia was obtained from terephthalaldehyde and 2-methylbenzoxazole in refluxing methanol in the presence of potassium methoxide in a yield of only 6.5% [9].

The reaction of 2-methylbenzazoles with aromatic aldehydes under the influence of bases proceeds via a mechanism of the aldol condensation type [12]. Depending on the conditions under which the condensation is carried out, the products are either hydroxy compounds (A) or unsaturated compounds (B); the latter are formed in a more basic medium than the intermediate hydroxy compounds [13].



We carried out the reaction of 2-methyl-substituted azoles with terephthalaldehyde in the presence of KOH in dipolar aprotic solvents [dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexametapol], which markedly increase the basicity of the hydroxide ion due to its desolvation [14]. We have shown that the condensation of 2-methylbenzoxazole with terephthalaldehyde (in a molar ratio of 3:1) in the presence of KOH in DMF (DMSO or hexametapol) for 1 h with subsequent acidification of the reaction mixture with dilute hydrochloric acid leads to virtually pure Ia in 95% yield [15]. Compounds Ib-h were obtained under similar conditions by condensation of the corresponding 2-methyl-substituted azoles with terephthalaldehyde, while IIa-f, IIIa-c, and IVa-d were obtained from the isomeric diformylnaphthalenes (Table 1).

The simplicity and convenience of the proposed synthetic method — the mild conditions, the simplicity of isolation, the high yields, and the individuality of the compounds formed, monitoring of which was realized by thin-layer chromatography (TLC) — should be noted. The structures of the synthesized compounds were confirmed by their IR and UV spectra. Their

TABLE 2. Electronic Absorption Spectra and Luminescence Spectra of Azole Analogs of 1,4-Distyrylbenzene and Isomeric Distyrylnaphthalenes

Compound	Absorption in chloroform		Luminescence in chloroform	
	λ_{max}, nm	lg ε	λ_{max}, nm	η, %
Ia	366, 382, 401^{a}	4,72; 4,78; 4,49	425, 448^{b}, 475^{a}	43
Ib	390	4,48	500	46
Ic	392, 412, 434^{a}	4,84; 4,89; 4,69	462, 488^{b}, 520^{a}	78
Id	394, 406, 426^{a}	4,79; 4,90; 4,70	454, 482^{b}, 505^{a}	77
Ie	382, 397, 420^{a}	4,74; 4,75; 4,53	448, 475^{b}, 503^{a}	73
If	373, 391, 409^{a}	4,62; 4,61; 4,37	435, 460^{b}, 490^{a}	50
Ig	373, 388, 406^{a}	4,88; 4,91; 4,70	430, 455^{b}, 485^{a}	62
Ih	400, 418, 440^{a}	4,65; 4,72; 4,55	472, 500^{b}, 533^{a}	74
IIa	369^{a}, 384, 404	4,81; 4,88; 4,79	425^{a}, 447^{b}, 475^{a}	48
IIb	404	4,85	515	58
IIc	388^{a}, 407, 430	4,82; 4,93; 4,80	450, 480^{b}, 503^{a}	76
IId	384^{a}, 403, 426	4,54; 4,67; 4,55	454, 475^{b}, 503^{a}	74
IIe	377^{a}, 396, 415^{a}	4,77; 4,86; 4,66	440^{a}, 465^{b}, 503^{a}	66
IIf	376^{a}, 392, 414	4,74; 4,85; 4,71	437, 458^{b}, 485^{a}	50
IIIa	366	4,51	465^{a}, 485^{b}	16
IIIb	375	4,62	518	25
IIIc	389	4,66	495	49
IVa	349	4,75	400^{b}, 425, 452	8
IVb	362	4,50	518	30
IVc	363^{a}, 379, 398^{a}	4,76; 4,83; 4,68	482	50
IVd	356^{a}, 373, 390^{a}	4,59; 4,77; 4,64	480	37

^{a}Shoulder. ^{b}Principal luminescence maximum.

IR spectra contain absorption bands at 970-990 cm^{-1}, which are characteristic for trans-disubstituted alkenes [16]. Two doublets of an AB spin system with chemical shifts at δ 7.50 and 8.33 ppm, which belong to vinyl protons, are observed in the PMR spectrum of Ia. The J_{AB} spin–spin coupling constant (SSCC) of 16.0 Hz constitutes evidence for a trans, trans configuration for this compound.

The electronic absorption spectra of solutions of the synthesized compounds in chloroform at 300-500 nm were recorded (Table 2). The position and character of the long-wave bands depend on the structures of both the central and terminal fragments. In the case of compounds with identical central fragments the position of the absorption bands is determined by the length of the effective conjugation chain, and compounds with terminal naphthoxazole (Ib-d, IIb-d, IIIb,c, and IVb-d), 5-phenyloxazole (Ie and IIe), and naphthothiazole (Ih) fragments therefore absorb in a longer-wave region than compounds with benzoxazole (Ia, IIa, IIIa, and IVa) and benzothiazole (If and IIf) fragments. Compounds Ib, IIb, IIIb, and IVb with linear naphthoxazole fragments display a hypsochromic shift of the absorption as compared with Ic,d, IIc,d, IIIc, and IVc,d, which contain fragments of angular naphthoxazoles; this was also noted in the 2-arylnaphthoxazole series [17].

Replacement of the central 1,4-phenylene fragment in Ia-f by a 2,6-naphthylene fragment (IIa-f) has virtually no effect on the spectra (except for IIb); this is also observed on passing from 1,4-distyrylbenzene to 2,6-distyrylnaphthalene (λ_{max} 356 and 360 nm in DMF, respectively [18]). In the series of oxazole analogs of distyrylnaphthalenes the long-wave absorption bands of 1,5 isomers IIIa-c are shifted hypsochromically 15-23 nm relative to the analogous absorption bands of 2,6 isomers IIa-c, and the hypsochromic shift is displayed to an even greater extent (28-33 nm) in the case of the 2,7 isomers IVa-d. The absorption bands of the oxazole analogs of 1,4-distyrylbenzene and the isomeric distyrylnaphthalenes display a vibrational structure, except for the compounds with terminal linear naphthoxazole fragments (I-IVb) or with a central 1,5-naphthylene fragment (IIIa-c).

Solutions of all of the investigated compounds luminesce intensely in the blue-green region of the spectrum (425-530 nm, Table 2). The luminescence spectra of the corresponding azole analogs of 2,6-distyrylnaphthalene (IIa-f) and 1,4-distyrylbenzene (Ia-f) are analogous both with respect to the character of the bands and the magnitude of the Stokesian shift, except for Ib and IIb. The Stokesian shifts increase when the central 2,6-naphthylene fragment is replaced by a 1,5-naphthylene fragment, such that the azole analogs of 1,5-distyrylnaphthalene (IIIa-c), which absorb in a shorter-wave region, have longer-wave luminescence than the corresponding 2,6 isomers IIa-c. In the case of compounds with linear naphthoxazole fragments the Stokesian shift increases appreciably, reaching a value of 150 nm in the case of 2,7-bis[β-(naphth[2,3-d]oxazol-2-yl)vinyl]naphthalene IVb.

The absolute luminescence quantum yields (η) of Ia-f and IIa-f with identical terminal groups are close to one another. The η values for IIIa-c and IVa-c are also close to one another but are substantially lower than in the case of the corresponding IIa-c. The luminescence quantum yields of the benz- and naphthoxazole analogs of 1,4-distyrylbenzene and the isomeric distyrylnaphthalenes increase in the order a < b < d ⩽ c.

A study of the generation properties of the synthesized compounds showed that they are effective converters of laser radiation that generate with high efficiency over the 410-500 nm spectral range [2, 19].

EXPERIMENTAL

The electronic absorption spectra of solutions of the compounds in chloroform were recorded with a Hitachi-356 spectrophotometer. The luminescence spectra were recorded with a setup based on an MDR-3 monochromator. The luminescence was excited with the light from a DKSSh-200 lamp isolated by filters. The absolute luminescence quantum yields were determined by a relative method. An ethanol solution of 3-aminophthalimide with a known quantum yield (η = 60% [20]) was used as the standard. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrophotometer. The PMR spectrum of a solution of Ia in CF_3CO_2H [with tetramethylsilane (TMS) as the internal standard] was recorded with a Hitachi-Perkin-Elmer apparatus with an operating frequency of 90 MHz. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates.

The starting 2-methylnaphthoxazoles and isomeric diformylnaphthalenes were obtained by known methods [21, 22].

General Method for the Condensation of 2-Methyl-Substituted Azoles with Aromatic Dialdehydes. A solution of 0.01 mole of aromatic dialdehyde in the necessary amount of DMF (20 ml for terephthalaldehyde and 2,6-diformylnaphthalene, 70 ml for 2,7-diformylnaphthalene, and 170 ml for 1,5-diformylnaphthalene) was added dropwise to a stirred mixture of 0.03 mole of the 2-methyl-substituted azole and 4.5 g of powdered KOH in 30 ml of DMF, and the mixture was stirred at room temperature for 1 h. It was then cooled with ice and treated with 10% HCl until it was slightly acidic, and the resulting precipitate was removed by filtration, washed to neutrality with water, washed with 10 ml of methanol, and dried. The compounds were recrystallized from DMF to obtain analytical samples.

LITERATURE CITED

1. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Leningrad (1976), p. 230.
2. E. M. Bernigor, L. A. Lavrovskii, E. A. Luk'yanets, Yu. F. Morgun, M. A. Muravitskii, S. A. Ryzhechkin, and V. K. Shalaev, Summaries of Papers Presented at the First All-Union Conference on Laser Optics [in Russian], Leningrad (1977), p. 100.
3. T. Tanaka, Japanese Patent No. 3510; Chem. Abstr., 65, 7328 (1966).
4. M. Matsuo, T. Sakaguchi, and T. Akamatsu, US Patent No. 3843632; Ref. Zh. Khim., 1N237P (1976).
5. I. Okubo and M. Tsujimoto, Japanese Patent No. 18913; Chem. Abstr., 78, 5407 (1973).
6. H. G. Thompson and M. B. Bacher, Belgian Patent No. 659424; Chem. Abstr., 64, 2090 (1966).
7. T. Maruyama, N. Kuroki, and K. Konishi, Bull. Univ. Osaka Prefect., Ser. A, 13, 75 (1964).
8. K. Tonegawa, S. Jono, and J. Fujino, Japanese Patent No. 29177; Chem. Abstr., 64, 12857 (1966).
9. W. Ried and S. Hinsching, Lieb. Ann., 600, 47 (1956).
10. H. Pommer and W. Sarnecki, German Offen., 1903191 (1970); Chem. Abstr., 73, 77068 (1970).
11. K. Konishi, M. Matsuoka, and T. Kitao, Japan Kokai, 50020 (1974); Chem. Abstr., 83, 61734 (1975).
12. V. Dryanska and C. Ivanov, Tetrahedron Lett., No. 41, 3519 (1975).
13. V. Dryanska and C. Ivanov, Synthesis, No. 1, p. 37 (1976).
14. K. Bowden, Chem. Rev., 66, 119 (1966).
15. E. A. Luk'yanets and E. M. Vernigor, USSR Inventor's Certificate No. 568645; Byul. Izobr., No. 54, 56 (1977).
16. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen, London (1958).

17. I. Ya. Postovskii and L. N. Pushkina, Zh. Obshch. Khim., 34, 424 (1964).
18. A. E. Siegrist, P. Liechti, H. R. Meyer, and K. Weber, Helv. Chim. Acta, 52, 2521 (1969).
19. E. M. Vernigor, L. S. Loiko, Yu. F. Morgun, et al., Summaries of Papers Presented at the Second All-Union Conference on Lasers Based on Complex Organic Compounds and their Application [in Russian], Dushanbe (1977), p. 63.
20. J. N. Demas and G. A. Grosby, J. Phys. Chem., 75, 991 (1971).
21. K. Fries, R. Walter, and K. Schilling, Ann., 516, 248 (1935).
22. W. Ried, H. Bodem, U. Ludwig, and H. Neidhardt, Chem. Ber., 91, 2479 (1958).

QUANTUM-CHEMICAL STUDY OF THE ELECTRONIC STRUCTURES AND SPECTRAL PROPERTIES OF OXAZOLE ANALOGS OF 1,4-DISTYRYLBENZENE AND THE ISOMERIC DISTYRYLNAPHTHALENES

A. A. Ustenko, V. P. Zvolinskii,
E. M. Vernigor, V. K. Shalaev,
and E. A. Luk'yanets

UDC 547.787.3:541.651:543.422.6

The electronic structures and spectral properties of a number of oxazole analogs of 1,4-distyrylbenzene and the isomeric 2,6-, 1,5-, and 2,7-distyrylnaphthalenes were studied within the framework of the Pariser—Parr—Pople method. The long-wave band of the electronic spectra of these compounds is formed by the $S_0 \rightarrow S_1$ lower electron transition, which has general molecular character and is accompanied by intramolecular charge transfer. Intense electron transitions from fluorescent level S_1 to higher electron-excitation levels are absent over the range of the absorption and fluorescence bands.

In our preceding communication [1] we described the synthesis and spectral-luminescence properties of azole analogs of 1,4-distyrylbenzene and the isomeric distyrylnaphthalenes. The synthesized compounds have intense fluorescence, and some of them are efficient converters of laser radiation. For a more profound study of the observed fluorescence and generation properties one must ascertain the nature of the electron-excitation states and the electron transitions in these compounds. The literature does not contain information regarding a theoretical study of the electronic spectra of such systems, and the available data are restricted to a few diaryl-, styryl-, and stilbenyl-substituted oxazoles [2, 3].

The aim of the present research was to make a quantum-chemical study of the electron structures and electronic absorption spectra of oxazole analogs of 1,4-distyrylbenzene and

TABLE 1. Effect of the Conformation on the Wavelength (λ) and Oscillator Force (f) of the $S_0 \rightarrow S_1$ Transition in the I Molecule

Conformation	λ, nm	f
syn-cis	360,8	2,33
syn-trans	360,1	2,46
anti-cis	360,7	2,34
anti-trans	359,9	2,53

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 609-615, May, 1980. Original article submitted August 14, 1979.

0009-3122/80/1605-0468$07.50