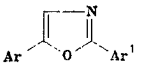
STERICALLY HINDERED MONO- AND BIS(2,5-DIARYLOXAZOLES) CONTAINING BIPHENYL SYSTEMS

B. M. Krasovitskii, S. G. Shapiro, and
É. G. Yushko

UDC 547.621:543.42

The condensation of hydrochloric salts of ω-aminomethyl aryl ketones with diphenic anhydride or with the diacid chloride of diphenic acid and subsequent cyclodehydration of the condensation products formed give sterically hindered mono- and bis(2, 5-diaryloxazoles) containing the biphenyl system. The spectroluminescent properties of these compounds were studied. Comparison of the absorption spectra of 2,2'-di(5-phenyloxazolyl-2)biphenyl and 2,5-diphenyloxazole indicates the complete lack of conjugation between the diphenyloxazole fragments, their independent behavior, and their retention of the spatial configuration of 2,5-diphenyloxazole. 2,2'-Di(5-phenyloxazolyl-2)biphenyl has a large Stokes shift. Steric hindrance is also found in 2-carboxy-2'-(5-phenyloxazolyl-2)biphenyl molecules.

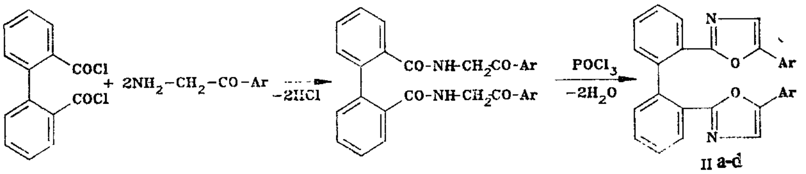
2,5-Diaryloxazoles (I) are efficient organic luminophores and commonly used in scintillation equipment [1] and quantum electronics [2]:



I

In the present work, we studied bisdiaryloxazoles (II) containing a biphenyl system substituted at C-2 and C-2' by aryloxazole groups.

These compounds were prepared by the acylation of ω-aminomethyl aryl ketones using the diacid chloride of diphenic acid and subsequent cyclization of the products obtained upon heating with $POCl_3$ as follows:



II a-d

II a Ar=C_6H_5; b Ar=p-C_6H_5—C_6H_4; c Ar=p-C_6H_4—OCH_3; d Ar=p-C_6H_4Cl; e Ar= =p-C_6H_4—NO_2

Previous studies of the structures of 2,2'-disubstituted biphenyls by various physical and chemical methods established that they are nonplanar. The benzene rings of the biphenyl group are twisted at a significant angle relative to each other; this angle depends on the size of the substituents [3-7]. The absorption spectra of solutions of 2,2'-disubstituted biphenyls are shifted toward shorter wavelengths relative to the 3,3'-disubsituted derivatives, which have more planar structure, due to a diminution of conjugation between the two halves of these molecules [8]. The same behavior was found in a study of the absorption spectra of 2,2-disubstituted benzidine dyes, in which the conjugation between the chromophores is diminished to an increasing extent with increasing size of the substituents introduced.

"Monokristallreaktiv" Scientific-Production Association, Kharkov 310141. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 184-188, February, 1985. Original article submitted May 22, 1984.

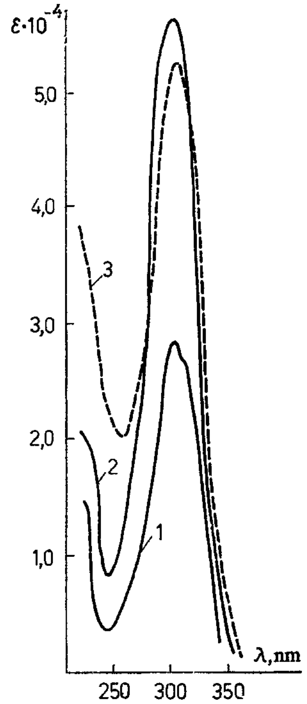
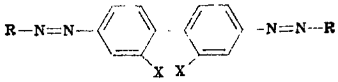


Fig. 1. Absorption spectra in ethanol for I (1), I in double concentration (2), and IIa (3).



III

III) R is the component and X represents functional substituents

The absorption spectra of these dyes are at longer wavelengths than the corresponding monoazo dyes obtained from meta-substituted aniline, which are "halves" of III [9]. On the other hand, bisazo dyes from 2,2',6,6,'-tetramethylbenzidine, in which the conjugation between the azo groups is completely eliminated due to large steric hindrance, absorb light in the same region as the corresponding monoazo dyes [10, 11].

The effect of 2,2'-substituents on the luminescence of biphenyl derivatives was studied for bisazomethine derivatives of benzidine and its derivatives which are analogous in structure to dyes III. The 2,2'-substituents produce a hyposofluoric effect and reduce the luminescence intensity [12].

Either cis or trans arrangement of the substituents relative to the interring bond is possible for 2,2'-disubstituted biphenyl. This question has not been studied in detail, but according to the data of Littlejohn and Smith [13], the configuration of some biphenyls with 2,2'-substituents corresponds to the cis form.

In contrast to simple functional substituents such as methyl groups or chlorine atoms, the aryloxazole groups in II form a single conjugated system in biphenyl systems. However, the introduction of such bulky groups may create considerable steric hindrance. For trans arrangement of these groups, the van der Waals radii of the heteroatoms of each of the oxazole rings overlap with the radius of the ortho-hydrogen atom of the benzene ring of the biphenyl system which is not directly bound to this heterocycle. For the cis configuration, the aryloxazole groups overlap each other, thereby, increasing the angle between the benzene rings of the biphenyl system. In this case, steric hindrance due to the presence of a bulky substituent in their phenylene chains ortho to the hetero rings (the second diaryloxazole group) is possible in each of the diaryloxazole groups. These features of II are reflected in their spectroluminescent properties.

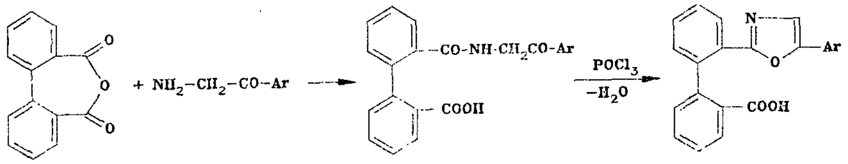
Comparison of the absorption spectra of ethanolic solutions of 2,2'-di(5-phenyloxazolyl-2)biphenyl (IIa) and 2,5-diphenyloxazole (I, Ar, Ar' = C_6H_5) taken in doubled concentrations shows that these compounds are analogous: Both solutions absorb in the same spectral region with similar optical density (Fig. 1). This similarity indicates the complete lack of conjugation between the diaryloxazole fragments of IIa, their independent behavior, and the retention of the structure of 2,5-diphenyloxazole in each fragment. The phenylene groups comprising the biphenyl groups are mutually perpendicular and apparently do not hinder the arrangement of the aromatic and heterocyclic rings in each of the diaryloxazole groups in a single plane or almost planar alignment.

The significant increase in the Stokes shift for IIa relative to 2,5-diphenyloxazole (7880 and 5450 cm^{-1}, respectively) is an important finding of the luminescence study. This effect is apparently a consequence of some flattening of IIa in going to the excited state. The conjugation which arises in this case between the aryloxazole fragments facilitates the displacement of the luminescence toward long wavelengths and increase in luminescence intensity.

Extension of the conjugation chain in the diaryloxazole fragments in II by replacement of the phenyl groups at C-5 by para-biphenyl groups (IIb), as expected, shifted the absorption and luminescence maxima toward longer wavelengths and significantly enhanced the absorption intensity and luminescence quantum yield (Table 1). Methoxyl groups in the para positions of the 5-phenyl groups (IIc) have a similar effect. The introduction of chlorine atoms (IId) has virtually no effect on the absorption and luminescence. A significant bathochromic effect was observed upon the introduction of nitro groups, but IIe does not luminesce due to the quenching effect of these groups.

The compounds synthesized have rather good solubility in aromatic solvents even at room temperature, and their solutions have scintillation properties. However, these compounds in toluene solution have significantly lower scintillation efficiency than that found for I. Thus, for example, the light yield of a solution of IIa (c = 5 g/liter) upon gamma irradiation in 32% of the light yield of a solution of 2,5-diphenyloxazole with the same concentration. The addition introduction of 0.1 g/liter 1,4-bis(5-phenyloxazolyl-2)benzene, which shifts the luminescence toward the region of maximum sensitivity of the FÉU-13 photomultiplier, to a solution of IIa does not have a significant effect on the light yield, which is enhanced only to 40%. Thus, the nonplanar configuration of doubled 2,5-diaryloxazole molecules has a negative effect on their scintillation properties.

Product IV, containing a carboxylic acid group which permits us to transfer the luminophore to a water-soluble state, was synthesized by using diphenic anhydride, which is readily obtained upon heating diphenic acid with acetic anhydride [14, 15], as the starting compound.



IVa-d

IVa Ar=C_6H_5; b Ar=p-C_6H_4—C_6H_5; c Ar=p-C_6H_4—OCH_3; d Ar=p-C_6H_4Cl

In contrast to II, compound IV contains only one fluorophore. These compounds may be considered as 2,5-diaryloxazoles containing a 2-carboxyphenyl group ortho to the 2-phenyl group and, concurrently, as 2,2'-disubstituted biphenyl derivatives. The formal conjugation chain in the 2-aryl groups of the 2,5-diaryloxazoles is lengthened and, thus, we could expect bathochromic and bathofluoric effects. However, IV are very similar in their spectroluminescent properties to unsubstituted 2,5-diaryloxazoles.

The carboxylic acid group is a substituent producing only slight steric hindrance [16] and, for trans arrangement of substituents, which may be predominant in this case, is capable of producing only a slight rotation of the benzene rings of the biphenyl group relative to each other. This rotation, however, is sufficient to compensate for the bathochromic effect of extension of the conjugation chain. In this case, the slight difference in the spectra of 2,5-diphenyloxazole and IVa (Table 1) is apparently a result of the failure of the ortho-carboxyphenyl group found in a position close to perpendicular to the conjugation system of the diaryloxazole system in the case of a large angle of rotation to extrude the heterocycle from the plane of the attached aryl groups.

TABLE 1. Characterization of the Compounds Synthesized

Compound	mp, deg C	Absorption λ_{max}, nm ($\epsilon \cdot 10^{-4}$)	Luminescence λ_{max}, nm (η)	Found N, %	Chemical formula*	Calc. N, %	Yield, %
I†	—	305 (2,84)	365 (0,50)	—	—	—	—
IIa	153—154	307 (5,25)	405 (0,41)	6,3	$C_{30}H_{20}N_2O_2$	6,4	20
IIb	176—177	320 (6,08)	420 (0,70)	4,9	$C_{42}H_{28}N_2O_2$	4,7	28
IIc	177—178	320 (5,33)	420 (0,45)	5,8	$C_{32}H_{24}N_2O_4$	5,6	12
IId	267—269	310 (5,30)	403 (0,44)	5,6	$C_{30}H_{18}Cl_2N_2O_2$	5,5	36
IIe	114—115	350‡	—	10,6	$C_{30}H_{18}N_4O_6$	10,6	36
IVa	180—181	310 (1,92)	385 (0,33)	4,0	$C_{22}H_{15}NO_3$	4,1	34
IVb	173—174	322 (2,17)	395 (0,60)	3,3	$C_{28}H_{19}NO_3$	3,4	16
IVc	193	315 (2,07)	400 (0,40)	4,0	$C_{23}H_{17}NO_4$	3,8	10
IVd	239—240	310 (2,14)	385 (0,40)	3,8	$C_{22}H_{14}ClNO_3$	3,7	25

*The compositions of IId and IVd were also confirmed by determination of the halogen content.

†2,5-Diphenyloxazole.

‡Poor solubility.

Products IV have rather high luminescence intensity. The quantum yield of these compounds is in the range from 0.3 to 0.6. They have a lower Stokes shift than that found for II. This finding is likely a result of the participation of a shorter conjugation system in the flattened excited molecule in conjugation with the diaryloxazole fragment than in II upon conversion to the excited state.

The sodium salts of IV are soluble in water and luminesce at longer wavelengths and lower intensity than in ethanolic solutions of the acids from which they were obtained. Thus, for example, the luminescence maximum for an aqueous solution of the sodium salt of IVb lies at 405 nm and the quantum yield is 0.2.

EXPERIMENTAL

The absorption spectra of the ethanolic solutions were taken on an SF-4 spectrophotometer, while the luminescence spectra were taken on a system consisting of ZMR-3 mirror monochromator, FÉU-18 light detector, and M-95 microamperometer. The photoluminescence was excited by an SVDSh-500 lamp. Light at 365 nm was separated from the spectrum of this lamp using a DMR-4 quartz monochromator. The absolute luminescence quantum yields of the ethanolic solutions were determined by the equal absorption method.

The characteristics of the compounds synthesized are given in Table 1.

2,2'-Di(aryloxazolyl-2)biphenyls. A saturated solution of sodium carbonate was added with vigorous stirring to a mixture of solutions of 0.01 mole diacid chloride of diphenic acid [14, 15] in 100 ml benzene and 0.02 mole hydrochloride salt of ω-aminomethyl aryl ketone in 150 ml water until the pH was brought to ~9 and then stirred for 1 h. The precipitate was filtered off, washed with water, and dried. A 1:5 mixture of this precipitate and $POCl_3$ was prepared and heated at reflux for 3 h. The solution was cooled and poured onto ice. The precipitate formed was filtered off and washed with water until the wash water was neutral to litmus, dried, and crystallized from ethanol.

2-Carboxy-2'- 5-aryloxazolyl-2)biphenyls. A mixture of equimolar amounts of diphenic anhydride [14, 15] and the hydrochloride salt of ω-aminomethyl aryl ketone in a 10-fold amount of chlorobenzene was heated at reflux until no further hydrogen chloride was liberated. Two-thirds of the chlorobenzene was distilled off and $POCl_3$ was added to the residue. The reaction mass was heated at reflux for 1 h, cooled, and poured onto ice. The precipitate formed was filtered off, washed with water until the wash water was neutral to litmus, dissolved in 5% aqueous sodium carbonate, and filtered. The product was isolated by the addition of hydrochloric acid and subsequent recrystallization from ethanol.

LITERATURE CITED

1. Luminescent Materials and Chemicals. NIITÉKhim Catalog [in Russian], Cherkassy (1975), p. 180.
2. G. A. Abakumov, V. V. Fadeev, R. V. Khokhlov, and A. P. Simonov, Spectrosc. Lett., 8, 651 (1975).
3. B. Williamson and W. Rodebush, J. Am. Chem. Soc., 63, 3018 (1941).

4. O. Bastiansen, Acta Chem. Scand., 3, 408 (1949); 4, 926 (1950).
5. L. M. Litvinenko and A. P. Grekov, Ukr. Khim. Zh., 20, 194 (1954).
6. A. G. London and R. Z. Mazengo, Org. Mass Spectrom., 8, 179 (1974).
7. E. D. Schmid and R. D. Tomsom, J. Am. Chem. Soc., 103, 1628 (1981).
8. G. H. Beaven and D. M. Hall, J. Chem. Soc., 4637 (1956).
9. B. M. Krasovitskii and D. G. Pereyaslova, Dokl. Akad. Nauk SSSR, 98, 71 (1957).
10. R. J. Morris and W. R. Brode, J. Am. Chem. Soc., 70, 2485 (1948).
11. W. R. Brode and R. J. Morris, J. Org. Chem., 13, 200 (1948).
12. B. M. Krasovitskii, V. B. Smelyakova, and R. N. Nurmukhametov, Opt. Spektrosk., 17, 558 (1964).
13. A. C. Littlejohn and J. W. Smith, J. Chem. Soc., 2552 (1954).
14. R. Roberts and T. Johnson, J. Am. Chem. Soc., 47, 1396 (1925).
15. C. Graebe and C. Aube, Ann., 247, 257 (1888).
16. F. Bell and P. H. Robinson, J. Chem. Soc., 1695 (1927).

SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES.

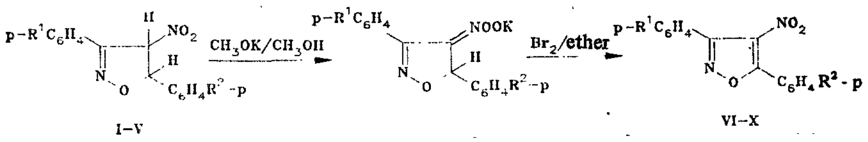
10.* SYNTHESIS OF 3,5-DIARYL-4-NITROISOXAZOLES

A. Barański

UDC 547.786.1.07:541.634

A method was proposed for the synthesis of 3,5-diaryl-4-nitroisoxazoles entailing the bromination of potassium salts of the corresponding 3,5-diaryl-Δ^2-isoxazolinyl-4-nitronic acids. The method may be used for the conversions of both the trans and cis isomers of 3,5-disubstituted 4-nitro-Δ^2-isoxazolines.

In a continuation of a study of the reactivity of nitro-Δ^2-isoxazolines [2, 3], we investigated the conversion of 3,5-diaryl-4-nitro-Δ^2-isoxazolines (I-V) to the corresponding 3,5-diaryl-4-nitroisoxazoles (VI-X), which hold interest as potentially biologically active compounds. The potassium salts of 3,5-diaryl-Δ^2-isoxazolinyl-4-nitronic acids undergo bromination by molecular bromine and are readily converted to 4-nitroisoxazoles VI-X. The proposed reaction, in contrast to the reported methods for the aromatization of 4-nitro-Δ^2-isoxazoline derivatives [4, 5], proceeds under relatively mild conditions and may be used for either trans or cis isomers of 4-nitro-Δ^2-isoxazolines.



The potassium salts of 3,5-diaryl-Δ^2-isoxazolinyl-4-nitronic acids were obtained by the action of potassium methylate on trans and cis isomers of I-V at −5°C. The salts formed were treated with ethereal bromine without isolation at from −15° to −20°C to yield 3,5-diaryl-4-nitroisoxazoles VI-X in 70-80% yields.

Thin-layer chromatographic analysis indicated that the reaction mixtures contained other possible reaction products in addition to VI-X. We should note that this method cannot be used for the aromatization of 5-nitro-Δ^2-isoxazolines since, according to our previous results [2], these derivatives are unstable in alkaline media.

---

*Communication 9, See [1].

T. Kostushko Cracow Polytechnical University. Cracow 31-155, Poland. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 189-192, February, 1985. Original article submitted April 10, 1984.

0009-3122/85/2102-0153$09.50