SYNTHESIS OF ARYLAZOLES AND THEIR LUMINESCENT PROPERTIES

E. A. Andreeshchev, V. S. Viktorova, S. F. Kilin, K. A. Kovyrzina, L. N. Kosyakina, Yu. P. Kushakevich, I. M. Rozman, and Yu. G. Chkhikvadze UDC 547.793.4'789.6'759. 3.07:535.37:541.651

The luminescent spectral properties of aryl derivatives of indole, oxazole, thiazole, benzoxazole, benzothiazole, and oxadiazole have been studied.

Heterocyclic compounds with high quantum yields of luminescence and short lifetimes of excited state are known [1-3]. For the purpose of further shortening the duration of the excited state in luminescent molecules, quenchers, i.e., halogen atoms or a nitro group, are introduced. The present article describes a study of the luminescent spectral properties of aryl derivatives of indole, oxazole, thiazole, benzoxazole, benzothiazole, and oxadiazole, both previously described and newly synthesized by us (Table 1).

Of the aryl derivatives of indole (I) the N-butyl have the highest luminescent efficiency [2, 4]. 1-Butyl-2-phenyl- and 1-butyl-2-biphenylylindoles (II, III) were obtained by cyclization of the respective acetophenone and acetylbiphenyl phenylhydrazones in the presence of zinc chloride according to Fischer [5]. The newly synthesized 1-butyl-2-(p-iodobiphenyl)indole (IV) was obtained by cyclization of 4-acetyl-4'-iodobiphenyl phenylhydrazone in polyphosphoric acid [6] followed by alkylation with butyl bromide. To shift the arylindole fluorescence spectrum to the longer wave region we synthesized 1,4 bis[8-(1-butyl-2phenyl-3-indolyl)vinyl]benzene (V) by the Wittig reaction from 1-butyl-2-phenyl-3-indolecarbaldehyde.

The principal advantages of the aryl benzoxazoles are the high quantum yield of fluorescence and their synthetic availability. Condensation of o-aminophenol with cinnamic aldehyde, followed by oxidation of the resulting azomethine with lead tetraacetate under the conditions described for 2-phenylbenzoxazole (VII) and 2-styrylbenzoxazole (VIII) [7] yielded 1,4-bis(2-benzoxazolyl)benzene (IX). It turned out that IX has low solubility in the usual organic solvents. The shortening of the duration of the excited state of arylazoles by introducing bromine into the molecule was studied with the easily available compound 1,4-bis-(5-phenyl-2-oxazolyl)benzene (POPOP). Testing of known methods for introducing bromine [8] were unsuccessful; only perbromides were separated, which easily split off bromine and were converted back to POPOP. In [9, 10] a bromination of aromatic and heterocyclic compounds with elemental bromine is described that uses the latter as solvent. By brominating POPOP under the conditions of [9] we succeeded in introducing two bromine atoms into the end benzene rings, and two into the oxazole rings (compound X).

In order to study the effect of bromine location on the luminescent properties of arylazoles, POPOP containing two bromines in the end benzene rings (compound XI) was synthesized from bromophenacylamine and terephthaloyl dichloride. When the reaction product, di(bromophenacyl)terephthalamide, was heated with phosphorus oxychloride it was converted to 1,4bis[5-(p-bromophenyl)-2-oxazolyl]benzene (XI). p-Bromophenacylamine hydrochloride was prepared from α ,p-dibromoacetophenone by the Delepin method under conditions analogous to those of [11].

It is known [12] that replacement of oxazole rings by thiazole shortens the duration of the excited state in heterylpolyphenylenes. In order to compare the luminescent properties of oxazole and thiazole derivatives we synthesized the thiazole analog of compound XI (XII) by treating di(bromophenancyl)terephthalamide with phosphorus pentasulfide [13]. 1,4-Bis[5-(p-bromophenyl)-2-thiazolyl]benzene (XII) and 1,4-bis(benzothiazolyl-2)benzene (XIII) were brominated analogously to POPOP, and 1,4-bis[5-(p-bromophenyl)-4-bromo-2-thiazolyl)benzene

I. N. Veku Sukhumi Physicotechnical Institute, Sukhumi 384900. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1557-1562, November, 1986. Original article submitted March 29, 1985; revision submitted November 26, 1985.

TABLE 1. Properties of New Arylazoles

Com- pound	mp [●] , ℃	Found, %				Empirical	Calculated, %				Yield,
		с	н	Br	N	tormula	с	н	Br	N	~/0
IV V XI XII XIII XIV XV XV XV XV XV XX XX XXI	$\begin{array}{c} 169 - 171 \\ 193 - 197 \\ 299 - 301 \\ 301 - 303 \\ 340 - 355 \\ 269 - 271 \\ 299 - 302 \\ 350 - 352 \\ 198 - 200 \\ 224 - 226 \\ 203 - 204 \\ 303 - 304 \end{array}$	66,5 88,2 55,2 51,7 69,6 40,0 47,1 63,6 52,3 58,5 58,9	5.0 6.7 1.8 3.3 2.6 3.8 1.4 2.7 3.6 2.5 3.5 3.7		3.0 5.2 4.7 5.0 5.0 4.9 4.9 5.8 14.2 16.3	$\begin{array}{c} C_{24}H_{22}IN\\ C_{46}H_{44}N\\ C_{24}H_{12}Br_4N_2O_2\\ C_{24}H_{14}Br_2N_2O_2\\ C_{24}H_{14}Br_2N_2S_2\\ C_{20}H_{12}N_2S_2\\ C_{20}H_{12}Br_4N_2S_2\\ C_{20}H_{12}Br_4N_2S_2\\ C_{20}H_{10}Br_2N_2O\\ C_{20}H_{12}Br_2N_2O\\ C_{20}H_{12}Br_2N_2O\\ C_{18}H_{12}N_4O_5\\ \end{array}$	66.8 88,5 42,4 55,2 52,0 69,8 40,5 47,8 63,7 52,6 59,3 59,3	4,8 7,0 1,8 2,7 2,5 3,5 1,7 2,0 3,5 2,6 3,4 3,3	47,1 30,6 28,9 44,9 31,9 21,2 35,0	$\begin{array}{c} 3,1\\ 4,5\\ 4,1\\ 5,4\\ 6,0\\ 8,1\\ 3,9\\ 5,6\\ 7,7\\ 6,1\\ 14,8\\ 15,3\end{array}$	51 30 38 10 16 10 23 15 69 30 32 30

*Purified by recrystallization: V from cyclohexane, X-XIV from toluene, XV from chlorobenzene, IV and XVIII-XX from ethyl acetate, XXI from DMFA. +Composition of XII-XV confirmed by sulfur determination, IV by iodine determination.

(XIV) and 1,4-bis(6-bromobenzothiazolyl-2)benzene (XV) were obtained. Compound XIII was synthesized by condensation of dianilino-p-xylylene with sulfur. The initial dianilino-p-xylylene was obtained by the reaction of aniline with xylylene dichloride [14].

Of the oxadiazole derivatives, 2,5-bis(p-bromophenyl)- (XVI) [15] and 2-phenyl-5-biphenylyl-1,3,4-oxidazole (XVII) [16] were prepared by cyclization of the respective dihydrazides in phosphorus oxychloride. Under analogous conditions [16], from p-bromobenzoic acid there was obtained 2-(p-bromophenyl)-5-biphenylyl-1,3,4-oxadiazole (XVIII); bromination of XVIII in bromine medium gave 2-(p-bromophenyl-5-(p-bromobiphenylyl)-1,3,4-oxadiazole (XIX). Cyclization of m-nitrocinnamic acid with furane-2-carboxylic hydrazide or with hydrazine hydrate in polyphosphoric acid gave 2-(m-nitrostyryl)-5-furyl-1,3,4-oxadiazole (XX) or 2,5-bis(m-nitrostyryl)-1,3,4-oxadiazole (XXI) respectively.

The properties of the new arylazoles are shown in Table 1, the luminescent spectral properties in Table 2.

As Table 2 shows, introduction of iodine into an indole derivative (IV) reduces the duration of the excited state 2.5-fold, but the quantum yield is disproportionately reduced 10-fold. Increasing the conjugation chain by introducing a second indole residue (V) reduces only the quantum fluorescence yield. Introduction of each two bromines into POPOP decreases the duration of the excited state by 0.4 nsec (X, XI). The picture is analogous when the oxazole ring is replaced by thiazole (XII-XV). Introduction of bromine into oxadiazole derivatives (XVI, XVIII, XIX) decreases the quantum fluorescence 2-fold, whereas the duration of the excited state is shortened only 1.5-fold, while introduction of a nitro group quenches the luminescence practically completely (XX, XXI). Introduction of a styryl group into a benzoxazole derivative (VIII) shortens the excited state almost 5-fold and decreases the quantum fluorescence yield 12-fold. Increasing the conjugation chain by introducing a second benzoxazole residue (IX), in contrast to indole (V), increases the quantum fluorescence yield and shortens the excited state. The luminescent spectral properties of compound IX agree with the data of [3].

EXPERIMENTAL

Absorption and fluorescence spectra, quantum fluorescence yield (n), and duration of excited state (τ_s) were measured in solution at 24-26° and concentrations of 2.10⁻³ to 2.5.10⁻⁴ mole/liter. Solvents were additionally purified by distillation from aluminum oxide. Air was not removed from the solution.

UV spectra were obtained with a SF-26 spectrophotometer. Fluorescence spectra were measured in a unit of known spectral sensitivity [17]. Fluorescence was excited from the measurement side through a DMR-4 monochromator by individual mercury wavelengths from a PRK-8 lamp. Quantum fluorescence yield was determined by comparison of luminescence

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Compound	Absor	rption	Fluorescence					
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		λ_{\max} , nm	cm ² /mmole	mmole/liter	λ _{max} , nm	n	τ_s , nsec		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	I II [5] IV V VI [21] VII [7] VII [7] VII [7] X XI XII XII XIV XV XVI [15] XVII [16] XXIX XXI XXI	266 297 316 396 271 286 318 343 372 365 380 352 330 352 330 352 330 352 330 352 330 330 330 330 330 330 330 330 330 33	$\begin{array}{c} 0,7\\ 2,0\\ -2.9\\ 4,4\\ 0,5\\ 1,5\\ 3,6\\ 6,7\\ 5,8\\ 5,9\\ 4,6\\ 5,1\\ 6,4\\ 4,2\\ -4,4\\ 5,4\\ 2,2\\ 2,9\end{array}$	1,0 2,0 1,0 1,0 1,0 1,0 1,0 1,0 0,1 0,3 0,1 0,5 0,1 0,01 1,0 0,1 1,0 0,1 1,0 0,1 1,0 0,1	300 368 419 460 288 332 387 390 451 423 451 402 459 416 367 363 370 not lumine 386	0,115 0,44 0,97 0,095 0,115 0,23 0,70 0,034 0,90 0,61 0,68 0,584 0,223 0,166 0,08 0,255 0,80 0,71 0,435 tsce 0,002	2,67 1,92 1,80 0,80 1,89 1,52 0,30 1,30 1,30 1,30 1,43 1,04 0,81 0,82 0,56 0,65 1,19 1,03 0,80		

TABLE 2. Luminescent Spectral Properties of Arylazoles

*Compounds I, II, VIII in hexane; VI, VII in heptane; IX, XIV, XV in chlorobenzene; others in dioxane.

intensity of a test solution with that of a solution of 1,3,5-triphenyl- Δ^2 -pyrazoline in dioxane for which n = 0.76 [18]. Corrections were made for reabsorption, secondary fluorescence, and the spectral sensitivity of the unit. Duration of excited state was determined with a phase fluorimeter [19].

4-Acetyl-4'-iodobiphenyl Phenylhydrazone. A mixture of 11.3 g (34 mmole) of 4-acetyl-4'-iodobiphenyl [20] and 100 ml of glacial acetic acid was heated until homogeneous and 4 g (36 mmole) of phenylhydrazine was added. Within several minutes a bright yellow precipitate formed. The mixture was stirred for another hour and cooled, and the precipitate was filtered off. Yield 11 g (80%), mp 194-200° (decomposes). The material was used without further purification.

<u>2-(p-Iodobiphenylyl)indole.</u> A mixture of 4 g (10 mmole) of 4-acetyl-4'-iodobiophenyl hydrazone and 30 g of polyphosphoric acid (made from 60 ml of 85% H₃PO₄ and 90 g of P₂O₅) was heated slowly to 125°, held there for 30 min, and then poured into water. The precipitate was filtered off and washed with water. Yield 3.5 g (81%), mp 320-325° (sublimes). The material was used without further purification.

<u>l-Butyl-2-(p-iodobiphenylyl)indole (IV).</u> A mixture of 5.25 g (13 mmole) of 2-(p-iodobiphenylyl)indole, 1.1 g (18 mmole) of potassium hydroxide, and 20 ml of DMSO was heated at 100° in a nitrogen stream for 1 h. Then 1.5 ml (15 mmole) of butyl bromide was added slowly and the mixture was left overnight. It was then heated at 80° for 2 h, and poured into water. The precipitate was filtered off, washed with water, dissolved in ether, and boiled with aluminum oxide that had been treated with hydrogen chloride. The ether was evaporated, and the residue was sublimed at 150° and 10^{-1} Pa residual pressure. Yield 3.52 g.

1,4-bis[β (1-Buty1-2-pheny1-3-indoly1)viny1]benzene (V). To a mixture of 5.98 g (21 mmole) of 1-buty1-2-pheny1-3-indolecarbaldehyde and 6.98 g (10 mmole) of p-phenylenebis(meth-ylenetriphenylphosphonium bromide) in 70 ml of absolute alcohol was added a solution of 0.6 g (26 mmole) of sodium in 20 ml of absolute alcohol at 20° dropwise. The mixture was stirred at 20° for 2 h and at 80° for 1 h. The precipitate was filtered off, washed with alcohol, and sublimed at 270-280° at 10⁻¹ Pa residual pressure. There was obtained 3.5 g of yellowish green crystals.

1,4-bis[5-(p-Bromopheny1)-4-bromo-2-oxazoly1]benzene (X). A mixture of 7 g (20 mmole) of POPOP and 50 ml (1000 mmole) of bromine was boiled for 7 h, then cooled, and excess bromine was blown off in a current of air. To the residue was added 400 ml of alcohol, the

mixture was boiled and filtered hot. The residue was sublimed at 260-265° at 10⁻¹ Pa residual pressure. Yield 4.9 g, yellow needles.

<u>p-Bromophenacylamine Hydrochloride</u>. To a solution of 27.8 g (100 mmole) of α ,p-dibromoacetophenone in 200 ml of chloroform was added a solution of 14.2 g (100 mmole) of hexamethylene tetramine in 100 ml of chloroform. The mixture was stirred and left overnight. The precipitate was filtered off and washed with chloroform to give 38.7 g (92%) of quaternary salt, mp.135-140° (decomposes). A mixture of 26.5 g (63 mmole) of quaternary salt and 20 ml of 38% hydrochloric acid in 200 ml of alcohol was left at 20° for 3-4 days with recurrent stirring. The precipitate was filtered off and washed with water and alcohol. Yield 14 g (90%), mp 260-265°.

<u>N,N'-Di(p-bromophenancyl)terephthalamide.</u> To a solution of 6 g (29 mmole) of terephthaloyl dichloride in 100 ml of dry pyridine was added 14 g (65 mmole) of bromophenacylamine hydrochloride portionwise with stirring. The mixture was boiled for 20 min, cooled, and poured into water. The precipitate was filtered off, boiled in 60 ml of alcohol, and filtered hot. Recrystallization from pyridine gave a colorless powder, mp 290-310° (decomposes) Yield 83%. Found, %: C 52.1, H 3.8, Br 28.7, N 5.2. $C_{24}H_{18}Br_2N_2O_4$. Calculated, %: C 51.6, H 3.2, Br 28.7, N 5.0.

<u>1,4-bis[5-(p-Bromopheny1)-2-oxazoly1]benzene (XI).</u> A mixture of 3.5 g (6 mmole) of di(bromophenacy1)terephthalamide and 100 ml of phosphorus oxychloride was boiled for 24 h. Most of the phosphorus oxychloride was boiled off, and the residue was cooled and carefully poured into ice water. The precipitate was filtered off, washed with water and alcohol, and dissolved in 400 ml of boiling toluene. The mixture was filtered hot and treated with 70 ml of alcohol. Yield 0.35 g.

<u>1,4-bis[5-(p-Bromopheny1)-2-thiazoly1]benzene (XII)</u>. A mixture of 3 g (5 mmole) of di(bromophenacy1)terephthalamide and 15 g (33.8 mmole) of phosphorus pentasulfide in 100 ml of dry chloroform was boiled for 20 h, cooled, and treated with 500 ml of water. The mixture was agitated vigorously and filtered after 1 h, and the precipitate was washed with alcohol. Then it was boiled with 100 ml of DMFA, and after cooling the precipitate was filtered off. Yield, 0.47 g, lemon yellow needles.

<u>Dianilino-p-xylylene</u>. To a mixture of 100 g (1.08 mole) of freshly distilled aniline, 17 g (200 mmole) of sodium bicarbonate, and 17 ml of water at 90-95° was added 14 g (80 mmole) of xylylene dichloride portionwise over 3 h with vigorous stirring. The mixture was heated another 2 h. Then it was cooled and the precipitate was filtered off and washed with water and alcohol. The filtrate was washed with saturated sodium chloride solution and water, and 250 ml of alcohol was added. The precipitates were combined and recrystallized from cyclohexane. Yield 13.4 g (58%), mp 126-129°. Found, %: C 83.6, H 6.7, N 9.5. $C_{20}H_{20}N_2$. Calculated, %: C 83.3, H 6.9, N 9.7.

 $\frac{1,4-\text{bis}(\text{Benzothiazolyl-2})\text{benzene}(\text{XIII})}{g}$. A mixture of 8 g (250 mmole) of sulfur and 5.5 g (19.1 mmole) of dianilino-p-xylylene was heated at 190-250° for 8 h. After cooling the mixture was pulverized and sublimed at 10⁻¹ Pa residual pressure, and the fraction subliming at 200-230° was removed. Yield 0.66 g.

1,4-bis[5-(p-Bromophenyl)-4-bromo-2-thiazolyl]benzene (XIV). A mixture of 1 g (1.8 mmole) of compound XII and 10.ml (200 mmole) of bromine was boiled for 7 h. After cooling, the bromine was blown off with air, and the residue was washed with hot alcohol (150 ml). Yield 0.3 g.

<u>1,4-bis(6-Bromobenzothiazoly1-2)benzene XV).</u> A mixture of 0.7 g (2 mmole) of compound XIII and 5 ml (100 mmole) of bromine was boiled for 7 h. After cooling the bromine was blown off with air, and the residue was washed with 150 ml of hot alcohol. Yield 0.15 g.

1-(p-Bromobenzoy1)-2-(p-biphenylcarbonyl)hydrazine. To a solution of 31 g (14 mmole) of 4-biphenylcarboxyl chloride in 300 ml of dry pyridine was added 31 g (14 mmole) of p-bro-mobenzhydrazide portionwise. The mixture was boiled 20-30 min, cooled, and poured into water. The precipitate was filtered off and washed with water. Yield, 45 g (85%), mp 280-286°.

2-(p-Bromophenyl)-5-biphenylyl-1,3,4-oxadiazole (XVIII). A mixture of 20 go (5 mmole) of 1-(p-bromobenzoyl)-2-(p-biphenylcarbonyl)hydrazine in 100 ml of phosphorus oxychloride was boiled for 4 h. Most of the phosphorus oxychloride was distilled off, and the residue

was cooled and poured carefully into ice water. The precipitate was filtered off, washed with water until the washings were neutral, and sublimed at 180° and 10⁻¹ Pa residual pressure. Yield 10.6 g.

2-(p-Bromopheny1)-5-(p-bromobipheny1y1)-1,3,4-oxadiazole (XIX). A mixture of 1.85 g (5 mmole) of compound XVIII, 1 ml (19 mmole) of bromine, and 5 ml of glacial acetic acid was stirred for 6 h at 20°. Then excess bromine was blown off with compressed air. The precipitate was filtered off and washed with hot alcohol (50 ml). Yield 0.5 g.

2-(m-Nitrostyry1)-5-(2-fury1)-1,3,4-oxadiazole (XX). A mixture of 3.86 g (2 mmole) of m-nitrocinnamic acid and 2.52 g (2 mmole) of furane-2-carboxylic hydrazide in 60 g of polyphosphoric acid (made from 90 g of P_2O_5 and 60 ml of 85% H_3PO_4) was heated for 30 min to 120°, held at 120-130° for 30 min, cooled, and poured into water. The precipitate was filtered off and sublimed at $180-190^{\circ}$ and 10^{-1} Pa residual pressure. Yield 1.8 g.

2,5-bis(m-Nitrostyryl)-1,3,4-oxadiazole (XXI). A mixture of 3.86 g (2 mmole) of m-nitro-cinnamic acid, 1.3 g (1 mmole) of hydrazine hydrate, and 45 g of polyphosphoric acid was heated at 140-145° for 2 h, cooled, and poured into water. The precipitate was filtered off and washed with water. Sublimation at 300° and 10⁻¹ Pa residual pressure gave 1 g of lemoncolored compound.

LITERATURE CITED

- 1. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Khimiya, Moscow (1984).
- I. B. Berlman, Spectrochim. Acta, 27A, 473 (1971). 2.
- A. Reiser, L. J. Leyshon, D. Saunders, M. V. Mijovic, A. Bright, and J. Bogie, J. Am. 3. Chem. Soc., 94, 2414 (1972).
- D. L. Horrocks and H. O. Wirth, US Patent No. 3,478,208; Ref. Zh. Khim., 2A511P (1971). 4.
- E. Fischer, J. Chem. Soc., <u>236</u>, 142 (1886).
 M. K. Shah and K. H. Shah, Indian J. Chem., <u>12</u>, 357 (1974).
- 7. F. F. Stephen and J. D. Bower, J. Chem. Soc., No. 3, 1722 (1950).
- A. N. Grinev, S. A. Zotava, and T. F. Vlasova, Khim. Geterotsikl. Soedin., No. 3, 311 8. (1976).
- R. Macarovici and M. Ionescu, Rev. Roum. Chim., 21, 881 (1976). 9.
- I. Noguti, E. Noda, K. Sasakawa, and K. Tanab, Japanese Patent Application 53-127,428; 10. Ref. Zh. Khim., 24N148P (1979).
- N. A. Adrova, M. M. Koton, and F. S. Florinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 11. No. 3, 385 (1957).
- S. Schoof and H. Güsten, Fed. Repub. Germany Patent No. 2,232,260; Ref. Zh. Khim., 12. 20N214P (1975).
- J. Heince and H. Baumgärtel, Chem. Ber., 103, 1572 (1970). 13.
- Synthetic Organic Preparations [in Russian], Vol. 1 (1949), p. 85. 14.
- 15. Ya. I. Levin and M. S. Skorobogatova, Khim. Geterotsikl. Soedin., No. 2, 1114 (1967).
- 16. A. P. Grekov, Metody Poluchen. Khim. Reaktiv. Prepar., No. 2, 65 (1961).
- 17. E. A. Andreeshchev and I. M. Rozman, Opt. Spektrosk., 2, 488 (1957).
- I. M. Rozman, Opt. Spektrosk., 2, 480 (1957). 18.
- S. F. Kalin, Yu. P. Kushakevich, and I. M. Rozman, Zh. Prikl. Spektrosk., 10, No. 2, 19. 341 (1969).
- 20. D. J. Byron and G. W. Gray, J. Chem. Soc., No. 2, 840 (1966).
- 21. F. Ladenburg, Chem. Ber., 9, 1524 (1976).