SYNTHESIS OF LUMINOPHORES BASED ON THIAZOLE DERIVATIVES OF PBD

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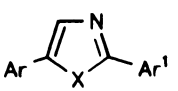
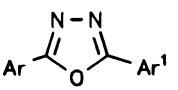
Received September 16, 1992
Accepted November 25, 1992

Organic luminophore 2-(biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (PBD, *III*) was converted by series of reactions into thioamide *VIII* which cyclized with substituted bromoacetylarenes *X* to give the bifluorophore system *XI*. The thiazole analog *XIII* was obtained by an analogous reaction of bromoacetyl derivative *V* with thiobenzamide. All the thus-prepared compounds exhibit pronounced fluorescence in solution as well as in the crystalline state.

Among organic luminophores, a very interesting group are the so-called bifluorophores[1]. These systems, arising by combination of two simple fluorophore fragments, have often very interesting photophysical properties, depending on how the parent fluorophores are linked together[2]. As known[1], very efficient fluorophores are diaryloxazoles or thiazoles (*I*) and diaryloxadiazoles (*II*). Since for a longer time we are studying the chemistry of the organic luminophore 2-(biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (PBD, *III*), it was of interest to investigate the use of this molecule in the synthesis of new bifluorophore systems based on thiazoles.



I



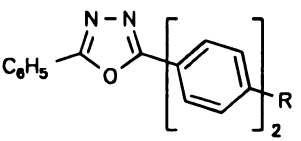
II

In formula *I* : X = O, S

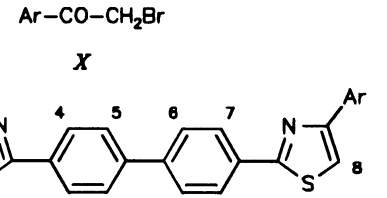
In formulae *I*, *II* : Ar, Ar^1 = C_6H_5, *p*-C_6H_5-C_6H_4

As the starting compound we made use of acetyl derivative *IV*, accessible by Friedel–Crafts acylation[3] of *III*. The compound *IV* was oxidized with sodium hypobromite and the obtained carboxylic acid *VI* was converted into amide *VII* by treatment with gaseous ammonia and carbonyldiimidazole. Reaction of the amide with P_4S_{10} or Lawesson reagent[4] in benzene afforded thioamide *VIII* which was used further as a precursor

in the preparation of thiazoles. However, the outcome of the reaction with Lawesson reagent much depends on the reaction temperature. Reaction of the reagent with amide *VII* in boiling toluene gave a 1 : 1 mixture of thioamide *VIII* and nitrile *IX* whereas in xylene the dehydration properties of the reagent already entirely predominated and the nitrile *IX* was isolated as the principal product. Thiazoles of the type *XI* were obtained by reaction of thioamide *VIII* with bromoacetyl derivatives *Xa* – *Xg* in boiling dioxane. In a similar manner, we synthesized compound *XIII* by reaction of bromoacetyl derivative *V* (ref.[5]) with thiobenzamide (*XII*). The basic physical data for compounds *XI* and *XIII* are summarized in Tables I and IV.



III – *IX*

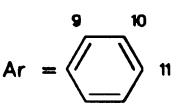


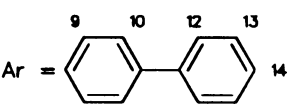
XI

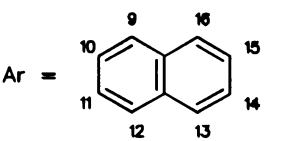
	R
III	H
IV	$COCH_3$
V	$COCH_2Br$
VI	COOH
VII	$CONH_2$
VIII	$CSNH_2$
IX	CN

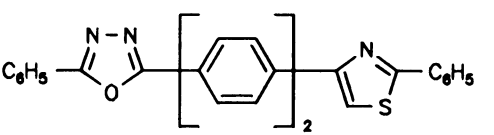
In formulae *X*, *XI* :

	R
a	C_6H_5
b	*p*-$C_6H_5C_6H_4$
c	*p*-BrC_6H_4
d	*p*-$CH_3C_6H_4$
e	*p*-$CH_3OC_6H_4$
f	α-naphthyl
g	β-naphthyl









XIII

NMR spectra of the compounds *XI* and *XIII* (Table II) exhibit signals of the AA'BB' or AA'XX' subspectra due two *p*-phenylene nuclei (H4 – H7) in the PBD residue. For the sake of simplicity, the signals were interpreted as doublets because of free rotation of the phenyl rings under the conditions of the measurement ($CDCl_3$, 20 °C). The protons of the terminal phenyl ring (H1, H2 and H3) are far from the substitution site and therefore their chemical shifts (ca 7.55 and 8.17 ppm) are practically independent of the kind of the substituent. In addition to the signals mentioned, the spectrum exhibits a singlet of thiazole proton at about 7.40 – 7.60 ppm. Its chemical shift does not depend on the position of substituent attached to PBD and has practically the same value for the analogous derivatives *XIa* and *XIII*. In case of compound *XIa*, replacement of $CDCl_3$ by $(CD_3)_2NCOD$ leads to a marked downfield shift of the H8 signal (Δ = 0.64 ppm), probably due to different solvation of the thiazole nucleus.

All the new thiazole derivatives prepared in this study exhibit fluorescence in the solid state as well as in solution. Their spectral characteristics are summarized in Table III, the elemental analyses and infrared spectra are given in Table IV.

EXPERIMENTAL

The melting points were determined on a Boetius block and are uncorrected. Infrared spectra were measured in KBr on a Perkin–Elmer 325 spectrometer, ^1H NMR spectra in $CDCl_3$ at 20 °C on a Bruker AM 400 instrument (400 MHz) with tetramethylsilane as internal standard. Electron absorption spectra were taken on a Perkin–Elmer 330 spectrophotometer, fluorescence excitation and emission spectra on a spectrofluorimeter Perkin–Elmer MPF-448. Mass spectra were obtained with a JEOL DX 303/DA 5000 instrument, using the "field desorption" method.

TABLE I
Preparation of bifluorophores *XI* and *XIII*

Compound	Starting bromo derivative	Reaction time, h	Yield, %	M. p., °C
XIa	*Xa*	7.5	62	226 – 227[a]
XIb	*Xb*	9	26	294 – 296[b]
XIc	*Xc*	5	28	276 – 277[b]
XId	*Xd*	7	41	261 – 263[b]
XIe	*Xe*	4	42	258 – 261[b]
XIf	*Xf*	4.5	30	223 – 224[c]
XIg	*Xg*	7	33	261 – 263[d]
XIII	*V*	24	40	225 – 226.5[e]

[a] Acetone–$CHCl_3$; [b] $CHCl_3$; [c] CH_2Cl_2–ethyl acetate; [d] CH_2Cl_2; [e] dioxane.

TABLE II
^{1}H NMR spectra of compounds *XIa* – *XIg* and *XIII*

Compound	δ, ppm / *J*, Hz						
	1,2	3	4	5	6	7	8
XIa[a]	7.57 m	8.18 m	8.25 d	7.83 d	7.77 d	8.17 d	7.52 s
	–	–	8.58	8.57	8.55	8.47	–
XIa[b]	7.65 m	8.17 m	8.25 d	8.03 d	7.96 d	8.17 m	8.16 s
	–	–	8.47	8.56	8.52	–	–
XIb[c]	7.55 m	8.17 m	8.24 d	7.83 d	7.76 d	8.18 d	7.55 s
	–	–	8.45	8.46	8.40	8.39	–
XIc[d]	7.55 m	8.16 m	8.24 d	7.81 d	7.75 d	8.14 d	7.50 s
	–	–	8.58	8.61	8.45	8.50	–
XId[e]	7.55 m	8.16 m	8.23 d	7.81 d	7.74 d	8.15 d	7.44 s
	–	–	8.52	8.54	8.44	8.32	–
XIe[f]	7.57 m	8.18 m	8.25 d	7.83 d	7.76 d	8.16 d	7.38 s
	–	–	8.43	8.43	8.34	8.40	–
XIf[g]	7.54 m	8.17 m	8.24 d	7.82 d	7.76 d	8.19 m	7.48 s
	–	–	8.38	8.30	8.09	–	–
XIg[h]	7.51 m	8.18 m	8.26 d	7.84 d	7.80 d	8.22 d	7.64 s
	–	–	7.96	8.17	7.23	7.89	–
XIII[i]	7.56 m	8.18 m	8.24 d	7.83 d	7.76 d	8.13 d	7.56 m
	–	–	8.53	8.51	8.45	8.45	–

[a] 8.03 d, *J* = 7.75 (H-9); 7.46 t, *J* = 7.69 (H-10); 7.38 t, *J* = 7.40 (H-11). [b] Measured in $(CD_3)_2SO$: 8.07 d, *J* = 7.76 (H-9); 7.49 t, *J* = 7.73 (H-10); 7.39 t, *J* = 7.42 (H-11). [c] 8.09 d, *J* = 8.39 (H-9); 7.70 d, *J* = 8.40 (H-10); 7.65 d, *J* = 7.78 (H-12); 7.46 t, *J* = 7.89 (H-13); 7.36 t, *J* = 7.46 (H-14). [d] 7.89 d, *J* = 8.49 (H-9); 7.58 d, *J* = 8.50 (H-10). [e] 7.90 d, *J* = 8.13 (H-9); 7.26 d, *J* = 8.12 (H-10); 2.43 s (CH_3). [f] 7.96 d, *J* = 8.75 (H-9); 7.00 d, *J* = 8.82 (H-10); 3.87 s (OCH_3). [g] 8.38 m, (H-10); 7.92 m, (H-12, H-16); 7.54 m (H-11,14,15);7.78 m (H-13). [h] 8.56 s (H-9); 8.09 d, *J* = 8.26 (H-11); 7.93 d, *J* = 8.21 (H-12); 7.86 m (H-13); 7.51 m (H-14,15); 7.96 m (H-16). [i] 8.07 dd, *J* = 8.03, *J* = 1.70 (H-9); 7.47 m (H-10).

Purity of the synthesized compounds and the reaction course were followed by TLC on Silufol and Alufol sheets (Kavalier, The Czech Republic), detection by iodine vapours or UV light.

The PBD derivatives *IV*, *V* and *VI* were prepared according to the published procedures[5,6]. The starting bromoacetyl derivatives *Xa* – *Xg* were obtained by bromination of the corresponding acetylarenes with bromine in ether or dioxane at room temperature and their melting points corresponded to the published values[7 – 13].

2-(4′-Aminocarbonylbiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*VII*)

A solution of carbonyldiimidazole (0.55 g) in anhydrous tetrahydrofuran (50 ml) was added under nitrogen to a suspension of compound *VI* (8.8 g) in anhydrous dichloromethane (50 ml) and the mixture was refluxed under stirring to homogeneity (0.5 h). Then dry ammonia was introduced into the boiling reaction mixture for 0.5 h and the stirring was continued for another 45 min. After cooling in a refrigerator, the precipitate was collected on a filter and washed with methanol. Yield 6.60 g (75%) of the product which on crystallization from dioxane afforded compound *VII* melting at 284 – 285 °C (reported[5] m.p. 283.5 – 285 °C).

2-(4′-Aminothiocarbonylbiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*VIII*)

A mixture of compound *VII* (0.25 g) and Lawesson reagent (0.32 g) in benzene (30 ml) was boiled for 2 h and then filtered through a short column of silica gel while hot. Evaporation of the solvent and crystallization of the solid portion from dioxane afforded 0.20 g (76%) of the product, m.p. 270 – 272 °C (reported[5] m.p. 272 – 274 °C).

TABLE III
UV-VIS and fluorescence spectra of compounds *XIa* – *XIg* and *XIII*

Compound	UV-VIS[a] λ, nm (log ε)	Fluorescence; λ, nm			
		ex.[a]	em.[a]	ex.[b]	em.[b]
XIa	298 (4.40), 339 (4.54)	355	413	382	448
XIb	308 (4.79), 342 (4.67)	365	415	397	450
XIc	303 (4.60); 339 (4.67)	360	407	393	448
XId	302 (4.14), 342 (4.19)	366	420	394	448
XIe	307 (4.22), 344 (4.09)	370	428	393	456
XIf	335 (4.70)	368	411	376	415, 436
XIg	307 (4.78), 335 (4.70)	355	417	391	454
XIII	324 (4.80)	358	397	–	–

[a] Dichloromethane solution. [b] Solid state.

2-(4′-Cyanobiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*IX*)

A mixture of amide *VII* (0.3 g), Lawesson reagent (0.36 g) and xylene (20 ml) was refluxed for 3 h. The precipitate was filtered and crystallized from dioxane to give 0.18 g (64%) of compound *IX*, m.p. 192 – 195 °C (reported[5] m.p. 186 – 187 °C).

General Procedure for Preparation of Thiazoles *XIa – XIg* and *XIII*

A mixture of thioamide *VIII* (0.6 mmol), the corresponding bromoacetyl derivative *Xa – Xg* (0.65 mmol) and dioxane (40 ml) was refluxed to disappearance of the thioamide TLC spot. After evaporation to dryness, the residue was dissolved in chloroform and subjected to chromatography on silica gel (50 g). Crystallization from an appropriate solvent gave the product *XI*. Thiazole *XIII* was prepared analogously from bromoacetyl derivative *V* and thiobenzamide *XII*.

TABLE IV
Elemental analyses and IR characteristics of the newly prepared compounds

Compound	Formula (M. w.)	IR $\tilde{\nu}$, cm^{-1}	Calculated/Found		
			% C	% H	% N
XIa[a]	$C_{29}H_{19}N_3OS$	1 548s, 1 488s	76.12	4.19	9.19
	(457.6)	1 472s, 1 398s	75.98	4.44	8.92
XIb	$C_{35}H_{23}N_3OS$	1 608s, 1 544s	78.77	4.35	7.88
	(533.7)	1 490s, 1 474s			
XIc	$C_{29}H_{18}N_3OSBr$	1 538s, 1 488s		537[f] $(M + 1)^+$	
	(536.5)	1 466s, 1 400s			
XId	$C_{30}H_{21}N_3OS$	1 610m, 1 540s		470[f] $(M - 1)^+$	
	(471.6)	1 500s, 1 400s			
XIe[b]	$C_{30}H_{21}N_3O_2S$	1 610s, 1 528s	73.89	4.35	6.58
	(487.6)	1 472s, 1 250s	73.57	4.47	8.57
XIf[c]	$C_{33}H_{23}N_3OS$	1 610s, 1 558s	77.77	4.56	8.25
	(509.6)	1 488s, 1 400m	77.96	4.52	8.33
XIg[d]	$C_{33}H_{23}N_3OS$	1 610s, 1 558s	77.77	4.56	8.25
	(509.6)	1 488s, 1 400s	77.62	4.45	8.11
XIII[e]	$C_{29}H_{19}N_3OS$	1 610m, 1 548s	76.12	4.19	9.19
	(457.6)	1 470s, 1 400m	76.44	4.45	8.94

[a] % S calculated/found: 7.01/6.95; [b] % S calculated/found: 6.58/6.78; [c] % S calculated/found: 6.29/6.61; [d] % S calculated/found: 6.29/6.29; [e] % S calculated/found: 7.01/6.75; [f] determined by mass spectrometry.

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Translated by M. Tichý.