2-(BIPHENYL-4-YL)-5-PHENYL-1,3,4-OXADIAZOLE (PBD): ELECTROPHILIC 4′-SUBSTITUTION AND FOLLOWING TRANSFORMATIONS

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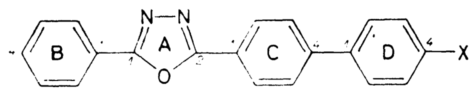
PBD was converted into 4′-substituted derivatives *I*–*XII* using usual electrophilic reagents. The decompositions of PBD, 4′-acetyl derivative *I* and 4′-nitro derivative *VI* with hydroiodic acid gave 4′-substituted 4-biphenylcarboxylic acids *XIIIa*–*XIIIc* and benzoic acid, respectively. The regioselectivity of the reactions was also proved by means of high resolution NMR spectroscopy.

2-(Biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (PBD) is a well known organic luminophore and an active component of various liquid scintillators[1,2]. The PBD residue in other bifluorophoric molecules may be expected to significantly support their luminiscence properties. In connection with our interest in the synthesis of such more compex molecular systems we have investigated some electrophilic reactions of PBD affording mainly 4′-substituted products suitable as intermediates for the mentioned purpose. No similar transformation of PBD has been published so far. The only nitration of similar 2,5-diphenyl-1,3,4-oxadiazole (DPD) has been reported[3,4] to yield all the six possible dinitro derivatives substituted in both phenyl groups.

All attempts to realize a Friedel–Crafts acylation of PBD by the addition of acylating agent to a substrate–catalyst mixture[6] have failed probably due to the chemical stability of a primary PBD–$AlCl_3$ complex towards the reagents. In agreement with this assumption 4′-acetyl deriative *I* was found to be formed after dropping of PBD solution to a mixture of the catalyst ($AlCl_3$), acetyl chloride and dichloromethane at elevated temperature. 4′-Bromoacetyl derivative *II* was then prepared in a similar way. Ketone *I* was further reduced with sodium borohydride into alcohol *III*, as well as converted into the corresponding hydrazone *IV* by treatment with aqueous hydrazine hydrate. The dehydration of *III* with P_2O_5 gave an interesting 4′-vinyl monomer *V*.

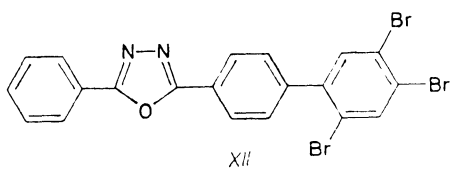


PBD, X = H
I, X = $COCH_3$
II, X = $COCH_2Br$
III, X = $CH(OH)CH_3$
IV, X = $C(CH_3)=N—NH_2$
V, X = $CH=CH_2$
VI, X = NO_2
VII, X = NH_2
VIII, X = $NHCOCH_3$
IX, X = SO_3H
X, X = SO_2Cl
XI, X = Br

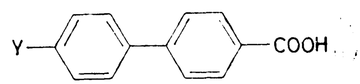
Nitration of PBD in the presence of sulfuric acid yielded 4′-nitroderivative *VI* which was further reduced to the corresponding amine *VII* by several methods (zinc-ammonium chloride, sodium sulfide under PTC conditions and with the reagent $NaBH_2S_3$ in THF). The 4′-amino group in *VII* could be easily acetylated with acetic anhydride in pyridine to give the corresponding acetamido derivative *VIII*.

Sulfonation of PBD with sulfuric or chlorosulfuric acid were found to proceed just at room temperature. 4′-Sulfonic acid *IX* arising in both cases could be converted to the corresponding sulfonyl choride *X* only by additional treatment with thionyl chloride.

Bromination of PBD with bromine was observed to be extremely slow at 20°C while a tribromo derivative *XII* could be only isolated at elevated temperatures. The expected 4′-bromo derivative *XI* was, however, obtained by the treatment of PBD with N-bromosuccinimide in diluted sulfuric acid at 60°C. Physico-chemical data of prepared compounds are given in Tables I and II.



XII



XIIIa, Y = H
XIIIb, Y = CH_2CH_3
XIIIc, Y = $COCH_3$
XIIId, Y = NH_2

A chemical evidence supporting the expected 4′-regioselectivity in the electrophilic substitutions of PBD follows from the hydrolytic cleavage of the 1,3,4-oxadiazole ring A in PBD and its derivatives *I* and *VI* with hydroiodic or hydrochloric acids[5], respectively (Table III). In all cases benzoic acid was isolated from the reaction mixtures excluding so any substitution in the ring B. The second isolated component was 4-biphenylcarboxylic acid (*XIIIa*) from PBD and 4'-acetyl-4-biphenylcarboxylic acid (*XIIIc*) from *I* under hydrolytic conditions. If a mixture of hydroiodic acid and phosphorus was used to decompose PBD derivatives *I* and *VI* the reduction of acetyl

TABLE I

Analytical and IR data of compounds *I*—*XII*

Compound	Formula (M.w.)	Calculated/Found			IR $\tilde{\nu}$, cm^{-1}
		% C	% H	% N	
I (COCH$_3$)	$C_{22}H_{16}N_2O_2$ (340·4)	77·62 77·89	4·75 4·84	8·23 8·21	1 683 s (C=O)
II[a] (COCH$_2$Br)	$C_{22}H_{15}BrN_2O_2$ (419·29)	63·02 63·23	3·61 3·74	6·68 6·96	1 677 s (C=O)
III (CHOHCH$_3$)	$C_{22}H_{18}N_2O_2$ (342·42)	77·16 77·42	5·31 5·49	8·18 8·21	3 580 m 1 605 s
IV (C(=NNH$_2$)CH$_3$)	$C_{22}H_{18}N_4O$ (354·4)	74·55 74·23	5·13 5·28	15·81 15·98	3 360 s (N—H) 3 215 s
V (CH=CH$_2$)	$C_{22}H_{16}N_2O$ (324·4)	81·44 80·92	5·00 5·38	8·63 8·49	2 900 m 1 605 s
VI (NO$_2$)	$C_{20}H_{13}N_3O_3$ (343·2)	69·97 69·96	3·79 3·71	12·24 12·40	1 538 s (N=O) 1 340 s
VII (NH$_2$)	$C_{20}H_{15}N_3O$ (313·3)	76·68 76·09	4·79 4·93	13·42 13·39	3 400 s (N—H) 3 325 s
VIII (NHCOCH$_3$)	$C_{22}H_{17}N_3O_2$ (353·3)	74·32 74·26	4·79 4·98	11·82 11·37	1 658 s (C=O)
IX (SO$_3$H)	$C_{20}H_{14}N_2O_4S$ (378·3)	63·68 63·28	3·47 3·69	7·42 7·04	1 395 s (S=O) 1 150 s
X[b] (SO$_2$Cl)	$C_{20}H_{13}N_2O_3SCl$ (396·8)	60·51 60·54	3·28 3·40	7·06 6·96	1 470 s (S=O) 1 160 s
XI[c] (Br)	$C_{20}H_{13}N_2OBr$ (377·2)	63·68 63·28	3·47 3·69	7·42 7·04	— — — —
XII[d] (3 Br)	$C_{20}H_{11}N_2OBr_3$ (532·2)	44·86 44·97	2·02 2·11	5·23 4·86	— — — —

[a] Calculated: 19·06% Br, found: 19·16% Br; [b] calculated: 8·95% Cl, found 9·22% Cl; [c] calculated: 21·18% Br, found: 21·05% Br; [d] calculated: 44·86% Br, found: 44·40% Br.

and nitro groups took place affording 4'-ethyl-4-biphenylcarboxylic acid (*XIIIb*) or 4'-amino-4-biphenylcarboxylic acid (*XIIId*), respectively. Hence, both substituents $COCH_3$ and NO_2 must be at the *para*-position of the ring D.

TABLE II

^{1}H NMR spectra of compounds *I*–*XII* (δ, ppm; *J*, Hz[a])

Compound (Subst.)	Position					
	Ring B 3, 4, 5	Ring B 2, 6	Ring C 2, 6	Ring C 3, 5	Ring D 2, 6	Ring D 3, 5
I[b] ($COCH_3$)	7·65 m	8·18 m	8·27 d	8·01 d *J* = 8·5	7·93 d	8·11 d *J* = 8·5
II[c] ($COCH_2Br$)	7·65 m	8·18 m	8·29 d	8·03 d *J* = 8·4	7·97 d	8·18 d *J* = 8·3
III[d] ($CHOHCH_3$)	7·69 m	8·22 m	8·28 d	7·99 d *J* = 8·5	7·79 d	7·57 d *J* = 8·2
IV[e] ($C(=NNH_2)CH_3$)	7·64 m	8·18 m	8·23 d	7·95 d *J* = 8·3	7·82 d	7·75 d *J* = 8·4
V[f,i] ($CH=CH_2$)	7·55 m	8·16 m	8·20 d	7·76 d *J* = 8·4	7·63 d	7·52 d *J* = 8·3
VI (NO_2)	7·65 m	8·19 m	8·31 d	8·06 d *J* = 8·5	8·09 d	8·36 d *J* = 8·4
VII[g] (NH_2)	7·68 m	8·22 m	8·19 d	7·88 d *J* = 8·4	7·58 d	6·83 d *J* = 8·4
VIII[h,i] ($NHCOCH_3$)	7·56 m	8·17 m	8·20 d	7·74 d *J* = 8·4	7·64 s	7·64 s
IX (SO_3H)	7·69 m	8·23 m	8·30 d	8·02 d *J* = 8·4	7·85 d	7·95 d *J* = 8·1
X[i] (SO_2Cl)	7·57 m	8·17 m	8·28 d	7·80 d *J* = 8·4	7·88 d	8·15 d *J* = 8·5
XI (Br)	7·57 m	8·14 m	8·19 d	7·73 d *J* = 8·5	7·61 d	7·52 d *J* = 8·6
XII (Br_3)	7·66 m	8·20 m	8·28 d	7·79 d *J* = 8·3	8·15 s	7·85 s

[a] Approximative doublets of two center multiplets; [b] 2·64 s (CH_3); [c] 4·86 s (CH_2); [d] 1·46 d (CH_3, $J = 6·4$), 4·92 q (CH, $J = 6·4$), 5·26 s (OH); [e] 2·17 s (CH_3); [f] 6·77 q (CH=), 5·83 d (=CH—H, $J_{trans} = 17·6$), 5·31 d (—CH=H, $J_{cis} = 10·9$); [g] 5·54 s (NH_2); [h] 2·23 s (CH_3), 7·30 s (NH); [i] $CDCl_3$ was used as a solvent.

TABLE III

4′-Substituted 4-biphenylcarboxylic acids *XIIa*—*XIIId*

Comp.	Start. comp.	Y	Agent	Formula (M.w.)	Yield, % M.p., °C	Calculated/Found		IR, cm^{-1}	^{1}H NMR (δ, ppm)			
						% C	% H		3	2	3′	2′
XIIIa	PBD	H	HI, HCl	$C_{13}H_{10}O_2$ (198·2)	90 225—226[a]	78·76 78·62	5·09 5·01	1 680 (C=O)				
XIIIb[c]	I	Et	HI[b]	$C_{15}H_{14}O_2$ (258·3)	90 228—230	79·61 79·42	6·24 6·19	2 980 (C—H)	8·11 d	7·83 d	7·38 d	7·72
									J = 8·3 Hz		J = 8·1 Hz	
XIIIc[d]	I	Ac	HI	$C_{15}H_{12}O_3$ (240·3)	29 281—284	74·98 74·68	5·04 5·36	1 670 (C=O)	8·08 d	7·90 d	8·06 d	7·88 d
									J = 8·3 Hz		J = 8·2 Hz	
XIIId[e]	*VI*	NH_2	HI[b]	$C_{13}H_{11}NO_2$ (213·2)	21 243—245	73·21 [f]	5·21	3 450 (N—H) 3 340	7·91 d	7·48 d	6·68 d	7·31 d
									J = 8·37 Hz		J = 8·51 Hz	

[a] Ref.[7]: m.p. 226—228°C; [b] 0·6 g of red phosphorus was added to the reaction mixture; [c] 1·25 t (CH_3), 2·72 q ($-CH_2-$); [d] ^{1}H NMR measured in $(CD_3)_2SO$: 2·54 s (CH_3); [e] ^{1}H NMR measured in CD_3CD_2OD; [f] from MS: calculated 213·2354, found 213·2342.

Further, ^1H and ^{13}C NMR spectra were measured to confirm molecular structures of all other prepared PBD derivatives on the basis of comparison of their spectral patterns.

The main arguments in favour of the presence of introduced substituents X in position 4 (ring D) may be drawn from the following findings: Two AA'XX' or AA'BB' systems ($J_{HH} \cong 8\cdot2$ to $8\cdot5$ Hz) in ^1H NMR spectra of compounds *I*–*XI* (Table II) indicate the occurence of two para-disubstituted benzenoic rings C and D in the same molecule. In addition, some proton chemical shifts of the both spin systems are influenced by the nature of the substituents X. This is most conspicuous in the comparison of the couple of the π-electron releasing substituent $X = NH_2$ (compound *VII*, δ 6·83 to 8·19) and the electron withdrawing substituent $X = NO_2$ (compound *VI*, δ 7·68, 8·22 and δ 7·65, 8·19, respectively). No such effects might be expected for alternative structures possessing the substituents X in position 4 of the ring B.

Similar substituent effects may be recognized for several ^{13}C signals (Table IV). For example, signals of C-1, C-3 and C-5 carbons were found to be up-field and those of C-2, C-4 and C-6 carbons down-field shifted on changing the nitro group by the amino residue in position 4 (ring D).

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. Infrared spectra were measured by the KBr technique on a Perkin Elmer 325 spectrometer and are given in cm^{-1}, ^1H NMR spectra as well as ^{13}C NMR were measured on a Bruker AM 400 (400 MHz) instrument in heptadeuterodimethylformamide at 20°C using tetramethylsilane as internal standard. Samples for elemental analyses were dried over P_4O_{10}. The purity of the compounds and course of the reactions were followed by means of TLC on Silufol or Alufol foils (Lachema Brno).

2-(4'-Acetylbiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*I*)

Solution of 5 g PBD in 50 ml of dichloromethane was added dropwise to a boiling suspension of 22·35 g aluminium trichloride and 13·2 g acetyl chloride in 20 ml dichloromethane for 1·5 h. After 5 h of boiling the reaction mixture was cooled and treated with water. The organic layer was separated, washed with water and dried over $MgSO_4$. The solvent was distilled off and the raw product recrystallized from acetone to give 4·55 g (80%) of compound *I*, m.p. 183·5–184·5°C.

2-(4'-Bromoacetylbiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*II*)

Solution of 2 g PBD in 35 ml dichloromethane was added dropwise to a suspension of 3·91 g $AlCl_3$ and 5·93 g bromoacetyl bromide in 20 ml dichloromethane over 1 h. After 3 h of boiling, the reaction mixture was treated with water and the precipitate was collected by suction. Organic layer was diluted with 300 ml of dichloromethane, washed with water, dried over $MgSO_4$, and evaporated. The residue was collected with the precipitate and crystallized from the acetone–dichloromethane mixture. Yield 1·91 g (68%) of compound *II*, m.p. 232–235°C.

TABLE IV

^{13}C NMR spectra of compounds PBD, *I*–*III*, *VI* and *VII*

Comp.	Ring A		Ring B				Ring C				Ring D			
	2[a]	1[a]	1	2,6	3,5	4	1	2,6	3,5	4	1	2,6	3,5	4
PBD	165·1	165·0	124·6	127·4	130·1	132·6	123·4	128·0	128·4	144·6	140·0	127·7	129·8	129·0
I	165·2	164·9	125·0	127·5	130·0	132·6	124·7	127·9	128·7	148·4	146·4	128·1	129·6	142·2
II	165·4	165·0	124·7	127·6	130·0	132·6	124·5	128·1	128·8	145·1	143·2	128·3	127·6	134·6
III	165·1	165·1	124·6	127·4	130·1	132·6	123·2	128·0	128·2	148·7	144·7	127·4	126·8	138·4
VI	165·4	164·9	124·6	127·5	130·1	132·7	124·3	124·8	130·0	144·2	143·3	129·0	128·2	137·5
VII	165·3	164·9	124·7	127·4	130·0	132·5	121·5	127·9	126·7	145·3	127·1	128·3	115·1	150·5
X	165·2	165·0	124·5	127·4	130·1	132·7	123·6	128·0	128·5	148·4	144·1	127·3	127·3	140·5
$\delta_{VI} - \delta_{VII}$	0·1	0·0	−0·1	0·1	0·1	0·2	2·8	−3·1	3·3	−1·1	16·2	0·7	13·1	−13·0

[a] These signals could be interchanged.

2-(4'-(1-Hydroxyethyl)biphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*III*)

$NaBH_4$ (0·33 g) was added to a solution of 2 g PBD in 150 ml of benzene–ethanol mixture (2 : 1). After 2 h stirring the solvent was distilled off and the solid residue was crystallized from ethanol to yield 1·74 g of derivative *III* (87%), m.p. 175—178°C.

2-(4'-Acetylbiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole Hydrazone (*IV*)

A mixture of 1·5 g compound *I*, 1·7 g 80% hydrazine hydrate and 0·5 ml glacial acetic acid in 30 ml dichloroethane was refluxed for 10 h. After cooling the precipitate was separated by suction and recrystallized from toluene. The yield of hydrazone *IV* was 1·2 g (77%), m.p. 314—315°C.

2-(4'-Vinylbiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*V*)

A mixture of 1 g alcohol *III* and 0·5 g P_4O_{10} in 50 ml benzene was refluxed for 10 h. Then 1 g of P_4O_{10} was added and the mixture was repeatedly refluxed for 30 h. The solid was filtered off and the filtrate was evaporated in vacuum. The raw product was recrystallized three times from ethanol to give 0·4 g (42%) of compound *V*, m.p. 132—134°C.

2-(4'-Nitrobiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*VI*)

A mixture of 10 ml 63% HNO_3 and 12 ml 96% H_2SO_4 was dropped to a stirred ice cooled solution of 2 g PBD in 40 ml dichloromethane during 1 h. The mixture was continuously stirred 2 h at room temperature and poured into 100 ml of ice-water. The precipitated product was extracted three times with 50 ml chloroform, the combined organic layers were washed twice with 50 ml water and dried over calcium chloride. The solvent was evaporated and the residue was crystallized from dioxane. The yield of the nitro derivative *VI* was 1·5 g (65%), m.p. 224 to 226°C.

2-(4'-Aminobiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*VII*)

a) Dry THF (5 ml) was dropped to 0·34 g natrium borohydride and 1 g sulfur under vigorous stirring and ice cooling. After 15 min, the solution of 1 g of the nitro compound *VI* in 60 ml THF was dropped in. The mixture was stirred under reflux for 16 h, then treated with 150 ml water and the forming suspension was immediately extracted twice with 50 ml chloroform. Collected organic layers were dried over magnesium sulfate and the solvent was distilled off in vacuum. After recrystallization from benzene (charcoal) the yield of amino derivative *VII* was 0·8 g (55%), m.p. 224—26°C.

b) A solution of 5·5 g $Na_2S.9\,H_2O$ in 5 ml of water was added to a stirred suspension of 1 g compound *VI* in 80 ml of benzene. Concentrated hydrochloric acid (2·1 ml) was then dropped to the mixture. After addition of 0·05 g benzyldodecyldimethylammonium bromide, the reaction mixture was repeatedly stirred for 30 h at 40°C. The aqueous layer was twice washed with 50 ml chloroform, combined organic layers were dried over magnesium sulfate and evaporated in vacuum. The raw product was purified by column chromatography (eluent chloroform–acetone 15 : 1, adsorbent silica gel) and crystallized from toluene. Yield 0·4 g of compound *VII*, m.p. 225—226°C (45%)

c) A solution of 0·5 g nitro derivative *VI* in 8 ml DMF was added to a stirred solution of 0·72 g ammonium chloride in 3 ml of water. Then 1 g of zinc dust was added at 65°C. The resulting mixture was stirred at the same temperature for 30 min and filtered. Precipitated crystals were filtered off and washed with 20 ml methanol and 20 ml ether. The yield of the amino derivative *VII* was 0·15 g (45%), m.p. 224—26°C.

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

Acetyl chloride (1 ml) was added to a solution of 0·2 g amine *VII*, in 1 ml dry pyridine and 70 ml benzene under reflux. The mixture was continuously refluxed for 40 min and then 70 ml water was added. The liquid phases were separated and the aqueous layer was extracted with two portions of 30 ml chloroform. The combined organic layers were dried over potassium carbonate and the solvent was distilled off in vacuum. The yield of compound *VIII* after recrystallization from benzene was 0·15 g (66%), m.p. 227—229°C.

4-(5-Phenyl-1,3,4-oxadiazole-2-yl)-biphenyl-4′-yl Sulfonic Acid (*IX*)

a) Chlorosulfonic acid (8 ml) was dropped to a stirred solution of 2 g PBD in 20 ml dichloromethane at 20°C. The mixture was heated to gentle reflux for 2 h and then decomposed by pouring on 200 g ice. The solid was filtered off, washed with 10 ml water and crystallized from dioxane–water (1 : 3). The yield of the sulfonic acid *IX* was 2·0 g (96%), m.p. >360°C.

b) PBD (2 g) in 12 ml of conc. sulfuric acid was stirred at room temperature for 2 h. The mixture was decomposed by pouring on 200 g of ice, the solid was filtered off, washed with 10 ml water and crystallized from dioxane–water (1 : 3). The yield of the sulfonic acid *IX* was 1·8 g (87%), m.p. >360°C.

4-(5-Phenyl-1,3,4-oxadiazole-2-yl)-biphenyl-4′-yl Sulfonyl Chloride (*X*)

A mixture of 8 g sulfonic acid *IX*, 150 ml thionyl chloride and 1 ml DMF was heated for 3 h. The excessive thionyl chloride was distilled off and the residue was recrystallized from toluene (charcoal). The yield of the obtained sulfonyl chloride *X* was 6 g (72%), m.p. 204—206°C.

2-(4′-Bromobiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*XI*)

PBD (2 g) was dissolved in 21 ml of diluted sulfuric acid (H_2SO_4–H_2O 7 : 1). N-Bromosuccinimide (1·2 g) was added in small portions under vigorous stirring at 60°C. The mixture was continuously stirred at the same temperature for 4 h and then poured into 200 ml of ice-water mixture. The precipitate was filtered off and crystalized from ethanol. Yield 1·6 g (63%) of compound *XI*, m.p. 180—181°C.

2-(2′,4′,5′-Tribromobiphenyl-4-yl)-5-phenyl-1,3,4-oxadiazole (*XII*)

A solution of 1 g PBD in 50 ml carbon disulfide was added to a stirred boiling suspension of 0·3 g iron powder and 1 ml bromine in 10 ml of the same solvent. The reaction mixture was repeatedly stirred and refluxed for 4 h and finally treated with a solution of 10 g sodium sulfite in 80 ml of water. The precipitate was dissolved by addition of 50 ml of chloroform and the separated aqueous layer was washed twice with the same solvent. The combined organic layers were dried over calcium chloride and the solvent was distilled off. After crystallization from toluene the yield of the compound *XII* was 1 g (79%), m.p. 225—227°C.

Hydrolysis of PBD, *I* and *VI*

A mixture of the given derivative (0·0017 mol), 50 ml of acetic acid and 5 ml hydrohalogenic acid was refluxed for 15 h. After dilution with 100 ml water the precipitate was filtered off and washed with 15 ml 10% aqueous Na_2SO_4 and twice with 15 ml of water. After crystallization from ethanol, the yields of Y-substituted carboxylic acids *XIII* were 0·1—0·6 g. Benzoic acid, as the second component, was isolated by extraction of the filtrate with ether, drying over calcium chloride and evaporating the solvent. The results are summarized in Table III.

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