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Regioselectivity of Arylation of 2,3'-Biquinolyl Dianion

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Abstract: The dianion of 2,3'-biquinolyl with aryl- and hetaryl halides forms the products of arylation to 4'-position, which on treatment with alkyl halides or water yield 1'-alkyl-1',4'dihydro-2,3'-biquinolyls or 4'-aryl-1',4'-dihydro-2,3'-biquinolyls respectively. The oxidation of the latter leads to 4'-aryl-2,3'-biquinolyls. The cation dependence of the arylation is shown.

Keywords: Regioselectivity, 2,3'-biquinolyl dianion.

Introduction

Recently [1] we have developed a procedure for the generation of the 2,3'-biquinolyl dianion (**1**) which has enabled us to study its properties. The present work is devoted to its arylation and heteroarylation.

The studied reactions of such species with aryl halides include, as a rule, the transfer of electrons from the dianion (anion-radical) to the halogenated derivative [2-4]. Thus the dianion of biphenyl reacts with halobenzenes yielding benzoic acid after treatment of the reaction mixture with carbon dioxide [2]. We supposed that the dianion **1** would also behave as an electron donor respective to aryl halides. However, we supposed that due to the greater affinity of **1** to electrons compared to that of biphenyl

there can be a one-electron transfer leading to the anion-radical (**2**). According to quantum chemical calculations the maximum spin density in **2** is at the 4'-position (see Figure 1.).

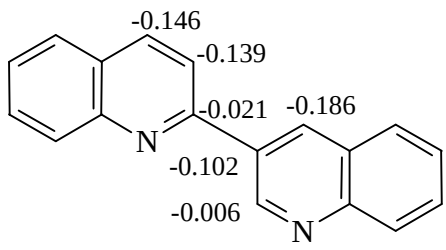
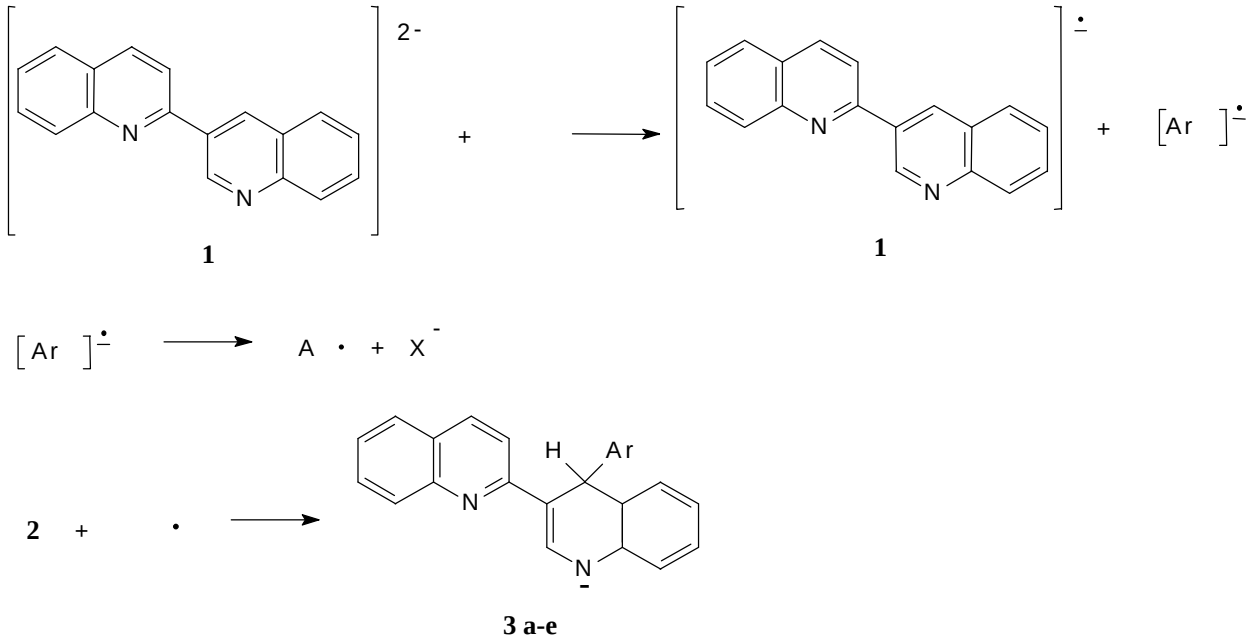


Figure 1. The distribution of the spin density in anion-radical **2** (MNDO calculations).

In this case, the aryl radical formed after the elimination of the halide ion would react with the anion radical (**2**) yielding the anion (**3**) (see Scheme 1).



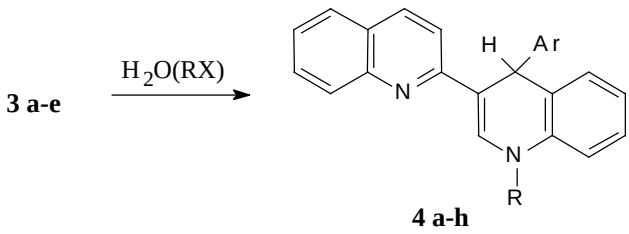
Scheme 1. 3 a Ar = Ph, X = Br; **3 b** Ar = 1-naphtyl, X = Br; **3 c** Ar = 2-pyridyl, X = F; **3 d** Ar = 1-methyl-2-benzimidazolyl, X = Cl; **3 e** Ar = 1-*iso*-propyl-2-benzimidazolyl, X = Br.

Results and Discussion

Indeed, the continuous addition of aryl or hetaryl halides to the dianion **1** obtained in the reaction of 2,3'-biquinolyl with metallic lithium in THF [1] with the subsequent treatment of the resulting mixture with water yielded 4'-aryl(hetaryl)-1',4'-dihydro-2,3'-biquinolyls (**4 a-e**) with yields ranging from 64 to 78%. The treatment of the reaction mixture with alkyl halides instead of water results in formation of N-alkylation products, i.e. 1'-alkyl-4'-aryl(hetaryl)-1',4'-dihydro-2,3'-biquinolyls (**4 f-h**) with yields in the

range 72-75% (Scheme 2).

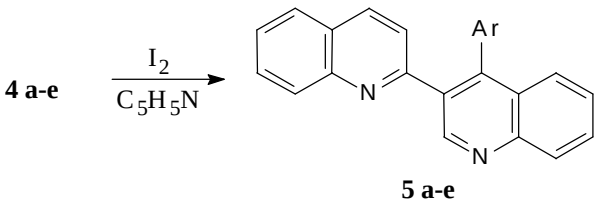
The same results were obtained when dianion **1** was generated using metallic potassium or potassium naphthalide, although their use is less convenient than that of lithium. Our investigations showed that the metal cation plays an important role in the electron transfer. Thus, 2,3'-biquinolyl does not react with potassium naphthalide in absolute THF in the presence of 1.2 molar excess of 18-crown-6 (on potassium) even during long stirring. The reaction begins only on addition of dry potassium iodide.



Scheme 2. 4 a Ar = Ph, R = H; **4 b** Ar = 1-naphtyl, R = H; **4 c** Ar = 2-pyridyl, R = H; **4 d** Ar = 1-methyl-2-benzimidazolyl, R = H; **4 e** Ar = 1-isopropyl-2-benzimidazolyl, R = H; **4 f** Ar = Ph, R = Me, X = I; **4 g** Ar = 1-naphtyl, R = Me, X = I; **4 h** Ar = 1-naphtyl, R = CH_2Ph, X = Cl.

The same results were obtained in the arylation reaction. Thus, dianion **1** obtained from 1.25 mmol 2,3'-biquinolyl and 2.7 mmol potassium does not react with bromobenzene in the presence of 3 mmol 18-crown-6 even after two hours reflux. On addition of 1.5 mmol KI the reaction proceeds in the usual way and results in formation of **4 a**.

Compounds **4 a-e** are readily oxidized by iodine in pyridine to 4'-aryl-2,3'-biquinolyls (**5 a-e**) with nearly quantitative yield (Scheme 3).



Scheme 3. 5 a Ar = Ph; **5 b** Ar = 1-naphtyl; **5 c** Ar = 2-pyridyl; **5 d** Ar = 1-methyl-2-benzimidazolyl; **5 e** Ar = 1-*iso*-propyl-2-benzimidazolyl.

The structure of these compounds was confirmed by ^{1}H NMR spectra. The characteristic feature of **5 a-e** spectra is the movement of the 3-H signal to the strong field region: **5 a** 6.97 ppm, **5 b** 6.83, **5 c** 7.08, **5 d** 7.32, **5 e** 7.43 compared with 8.04 in case of 2,3'-biquinolyl. In our opinion it is explained by the perpendicular position of the aryl substituent shielding the proton in the 3 position.

It is worth noting that protons of two methyl groups in **4 e** and **5 e** are not equivalent (**4 e** 1.73 (1H, d.), 1.85 (1H, d.); **5 e** 0.75 (1H, d.), 1.24 (1H d.) as these groups are diastereotopic. However if **4 e** posesses an asymmetric carbon atom in the 4' position, there is no such atom in **5 e**. Nevertheless, **5 e**

also has an asymmetric center due to the inhibited rotation about the C_4–C_2 bond of the imidazolic ring owing to the presence of bulky substituents in both quinolyl and benzimidazole fragments.

The direction of arylation was confirmed by experiments with 4'-D-2,3'-biquinolyl. In the ^{1}H NMR spectra of **4 a-e** we observed the lowering of the 4-H signal intensity corresponding to deuterium content in the starting biquinolyl. There is no "label" in **5 a-e**.

Experimental

General

Mass-spectra were registered on a Varian MAT 331 A mass-spectrometer, NMR spectra at Bruker WP-200 NMR spectrometer. The reactions were monitored by TLC on Silufol UV-254 plates, eluent ethyl acetate–hexane 2:1. THF was purified by distillation over $LiAlH_4$ and ketine radical, and 2,3'-biquinolyl was recrystallised from benzene and sublimed.

Syntheses of the compounds

*4'-Phenyl-1',4'-dihydro-2,3'-biquinolyl (**4 a**, $C_{24}H_{18}N_2$)*

A solution of 0.64 g (2.5 mmol) of 2,3'-biquinolyl and 0.05 g (7 mmol) of powdered lithium in 10 mL of THF is stirred for 3 h at ambient temperature under an Ar blanket. After that the solution of 0.71 g (4.5 mmol) bromobenzene in 4 mL THF is added dropwise. The reaction mixture is stirred for 1 hour at ambient temperature and refluxed for 1 h. After that 40 mL of water is added and the reaction mixture is extracted with benzene (3 × 30 mL). The organic solution is evaporated and the resulting yellow oil is crystallized on benzene addition. Yield 0.65 g (78%), m.p. 212-213 °C (bnz.). ^{1}H NMR spectrum ($CDCl_3$): 5.73 (1H, s, 4'-H); 6.36 (1H, d, $J_{NH-2'H}$= 5.5 Hz, NH); 6.70 (1H, d, $J_{7'8'}$ = 8.10 Hz, 8'-H); 6.88 (1H, d. d, $J_{5'6'}$ =7.64, $J_{6'7'}$= 7.82 Hz, 6'-H); 7.04 (1H, d. d, $J_{6'7'}$ = 7.82, $J_{7'8'}$ =8.12 Hz, 7'-H); 7.2 (3H, m, 3''-H, 4''-H, 5''-H); 7.23 (1H, d, $J_{5'6'}$ =7.64 Hz, 5'-H); 7.34 (1H, d. d, J_{56} = 8.02, J_{67} = 7.51 Hz, 6-H); 7.38 (1H, d, J_{34} = 8.91 Hz, 3-H); 7.46 (2H, d, J= 7,1 Hz, 2''-H, 6''-H); 7.61 (1H, d. d, J_{67}=7.51, J_{78} =8.61 Hz, 7-H); 7.62 (1H, d, J_{56} = 8.02 Hz, 5-H); 7.77 (1H, d, $J_{NH-2'H}$=5.5 Hz, 2'-H); 7.86 (1H, d, J_{34} = 8.91 Hz, 4-H); 7.98 (1H, d, J_{78} =8.61 Hz, 8-H); determined, % C 86.28; H 5.29; N 8.43. $C_{24}H_{18}N_2$, calculated, % C 86.19; H 5.43; N 8.38.

*4'-(1-Naphthyl)-1',4'-dihydro-2,3'-biquinolyl (**4 b**, $C_{28}H_{20}N_2$)*

Was obtained as above from 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li and 0.72 g (3.5 mmol) 1-bromonaphthalene. Yield 0.7 g (73%), m.p. 196-197 °C (bnz). ^{1}H NMR spectrum ($CDCl_3$): 6.38 (1H, d, $J_{NH-2'H}$= 5.7 Hz, NH); 6.64 (1H, s, 4'-H); 6.72 (1H, d. d, $J_{5'6'}$ =7.72, $J_{6'7'}$= 7.92 Hz, 6'-H); 6.74 (1H, d, $J_{7'8'}$ = 8.06 Hz, 8'-H); 7.01 (1H, d. d, $J_{6'7'}$ = 7.92, $J_{7'8'}$ =8.06 Hz, 7'-H); 7.23 (1H, d,

$J_{5'6'}$ =7.72 Hz, 5'-H); 7.27-7.33 (3H, m, 6'-H, 3''-H, 6''-H); 7.49 (1H, d, J_{34} = 8.83 Hz, 3-H); 7.51-7.8 (7H, m, arom.); 7.81 (1H, d, J_{34} = 8.83 Hz, 4-H); 7.86 (1H, d, $J_{NH-2'H}$=5.7 Hz, 2'-H); 9.01 (1H, d, J = 8.54, 8''-H or 8-H); determined, % C 87.71; H 5.12; N 7.17. $C_{28}H_{20}N_2$. Calculated, % C 87.46; H 5.25; N 7.29.

*4'-(2-Pyridyl)-1',4'-dihydro-2,3'-biquinolyl (***4 c***, $C_{23}H_{17}N_3$)*

As **4 a** from 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li and 0.34 g (3.5 mmol) 2-fluoropyridine. Yield 0.56 g (67%), m.p. 219-220° C (bnz). ^{1}H NMR spectrum ($CDCl_3$): 5.88 (1H, s, 4'-H); 6.60 (1H, d, $J_{NH-2'H}$= 5.3 Hz, NH); 6.72 (1H, d, $J_{7'8'}$ = 7.94 Hz, 8'-H); 6.88 (1H, d. d, $J_{5'6'}$ =7.68, $J_{6'7'}$= 7.79 Hz, 6'-H); 6.98 (1H, m, 5''-H); 7.07 (1H, d. d, $J_{6'7'}$ = 7.79, $J_{7'8'}$ =7.94 Hz, 7'-H); 7.34 (1H, d, $J_{5'6'}$ =7.68 1.63 Hz, 5'-H); 7.38 (1H, d. d., J_{56} = 7.98, J_{67} = 7.62 Hz, 6-H); 7.46 (1H, d, J_{34} = 8.96 Hz, 3-H); 7.5 (2H, m, 3''-H, 4''-H); 7.57 (1H, d. d., J_{67}=7.62, J_{78} =8.46 Hz, 7-H); 7.62 (1H, d, J_{56} = 7.98 Hz, 5-H); 7.88 (1H, d, J_{34} = 8.96 Hz, 4-H); 7.90 (1H, d, J_{78} =8.46, J_{68} = 1.1 Hz, 8-H); 7.92 (1H, d, $J_{NH-2'H}$=5.3 Hz, 2'-H); 8.51 (1H, d. d., $J_{5''6''}$ = 4.7, $J_{4''6''}$ = 1.7 Hz, 6''-H); determined, % C 82.64; H 4.98; N 12.38. $C_{23}H_{17}N_3$. Calculated, % C 82.36; H 5.11; N 12.53.

*4'-(1-Methyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (***4 d***, $C_{26}H_{20}N_4$)*

As **4 a** from 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li and 0.58 g (3.5 mmol) 1-methyl-2-chlorobenzimidazole. Yield 0.66 g (68%), m.p. 266-267 °C (bnz). ^{1}H NMR spectrum ($CDCl_3$): 4.44 (3H, s, Me); 6.36 (1H, s, 4'-H); 6.70 (1H, d, $J_{7'8'}$ = 8.05 Hz, 8'-H); 6.81 (1H, d. d., $J_{5'6'}$ =7.68, $J_{6'7'}$ = 7.34 Hz, 6'-H); 6.92 (1H, d. d., $J_{6'7'}$ = 7.34, $J_{7'8'}$ =8.05, 7'-H); 7.09 (1H, d, $J_{5'6'}$ =7.68 Hz, 5'-H); 7.13 (1H, d. t., $J_{4''5''}$ = 8.55, $J_{5''6''}$ = 7.38, $J_{5''7''}$ = 1.63 Hz, 5''-H); 7.21 (1H, d. t., $J_{5''6''}$ = 7.38, $J_{6''7''}$ = 7.67, $J_{4''6''}$ = 2.35 Hz, 6''-H); 7.29 (1H, d. d., J_{56} = 8.04, J_{67} = 7.31 Hz, 6-H); 7.38 (1H, d. d., $J_{6''7''}$ =7.67, $J_{5''7''}$ = 1.63 Hz, 7''-H); 7.41 (1H, d, $J_{NH-2'H}$=5.49 Hz, 2'-H); 7.43 (1H, d, J_{34} = 9.14 Hz, 3-H); 7.53 (1H, d. d., J_{67}=7.31, J_{78} =8.04 Hz, 7-H); 7.59 (1H, d. d., $J_{4''5''}$ =8.55, $J_{4''6''}$ = 2.35 Hz, 4''-H); 7.6 (1H, d., J_{56} = 8.04 Hz, 5-H); 7.78 (1H, d, J_{78} =8.04 Hz, 8-H); 7.80 (1H, d, J_{34} = 9.14 Hz, 4-H); 10.39 (1H, d, $J_{NH-2'H}$= 5.49 Hz, NH); determined, % C 80.63, H 5.11, N 14.26, $C_{26}H_{20}N_4$. Calculated C 80.39, H 5.19, N 14.42.

*4'-(1-iso-Propyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (***4 e***, $C_{28}H_{24}N_4$)*

As **4 a** from 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li and 0.68 g (3.5 mmol) 1-*iso*-propyl-2-chlorobenzimidazol. Yield 0.67 g (64%), m.p. 206-208° C (bnz).). ^{1}H NMR spectrum ($CDCl_3$): 1.73 (3H, d., J= 6.95, Me); 1.85 (3H, d, J= 6.95, Me); 5.86 (1H, m, CH); 6.58 (1H, s, 4'-H); 6.81 (1H, d, $J_{7'8'}$ = 7.98, Hz, 8'-H); 6.85 (1H, d. d., $J_{5'6'}$ =7.58, $J_{6'7'}$ = 7.42 Hz, 6'-H); 7.0 (1H, d. d., $J_{6'7'}$ = 7.42, $J_{7'8'}$ =7.98 Hz, 7'-H); 7.1 (2H, m, 5''-H, 6''H); 7.2 (1H, d, $J_{5'6'}$ = 7.58 Hz, 5'-H); 7.30

(1H, d. d., J_{56} = 8.08, J_{67} = 7.41 Hz, 6-H); 7.48 (1H, d, J_{34} = 9.05 Hz, 3-H); 7.5 (1H, d, $J_{NH-2'H}$=5.49 Hz, 2'-H); 7.54-7.61 (4H, m, 5-H, 7-H, 4''-H, 7''-H); 7.79 (1H, d, J_{34} = 9.05 Hz, 4-H); 7.88 (1H, d, J_{78} =8.34 Hz, 8-H); 10.33 (1H, d, $J_{NH-2'H}$= 5.49 Hz, NH); determined, % C 80.95; H 5.68; N 13.37. $C_{28}H_{24}N_4$. Calculated, % C 80.74; H 5.81; N 13.45.

*1'-Methyl-4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (***4 f***, $C_{25}H_{20}N_2$)*

The solution of 0.64 g (2.5 mmol) 2,3'-biquinolyl and 0.05 g (7 mmol) of powdered Li in 10 mL THF is stirred under an Ar blanket at ambient temperature for 3 h, then a solution of 0.71 g (4.5 mmol) of bromobenzene in 4 mL THF is added dropwise. The reaction mixture is stirred for 1 h at room temperature, than refluxed for 1 h. The mixture is cooled to room temperature 0.71 g MeI in 2 mL THF is added and mixture is stirred for 1 h. The mixture is poured into 50 ml of water and extracted with benzene (3 × 30 mL). The organic solution is evaporated and resulting yellow oil is crystallized from hexane addition. Yield 0.65 g (75%), m.p. 173-174 °C (EtOH). ^{1}H NMR spectrum ($CDCl_3$): 3.38 (3H, s, Me); 5.68 (1H, s, 4'-H); 6.84 (1H, d, $J_{7'8'}$ = 8.12 Hz, 8'-H); 6.89 (1H, d. d., $J_{5'6'}$ =7.61, $J_{6'7'}$= 7.76 Hz, 6'-H); 7.12 (1H, d. d., $J_{6'7'}$ = 7.76, $J_{7'8'}$ =8.12 Hz, 7'-H); 7.19 (3H, m, 3''-H, 4''-H, 5''-H); 7.27 (1H, d, $J_{5'6'}$ =7.61 Hz, 5'-H); 7.35 (1H, d. d., J_{56} = 7.99, J_{67} = 7.56 Hz, 6-H); 7.42 (1H, d, J_{34} = 9.01 Hz, 3-H); 7.48 (2H, d, J= 7.13 Hz, 2''-H, 6''-H); 7.64 (1H, d. d., J_{67}=7.56, J_{78} =8.53 Hz, 7-H); 7.67 (1H, d, J_{56} = 7.99 Hz, 5-H); 7.81 (1H, s, 2'-H); 7.91 (1H, d, J_{34} = 9.01 Hz, 4-H); 7.99 (1H, d, J_{78} =8.53 Hz, 8-H); determined, %,: C 86.44; H 5.67; N 7.89. .$C_{25}H_{20}N_2$. Calculated, % C 86.18; H 5.79; N 8.03.

*1'-Methyl-4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (***4 g***, $C_{29}H_{22}N_2$)*

As **4 f** from 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li, 0.72 g (3.5 mmol) 1-bromonaphthalene and 0.71 g (5 mmol) MeI. Yield 0.73 g (73%), m.p. 151-153 °C (benzene-hexane). ^{1}H NMR spectrum ($CDCl_3$): 3.51 (3H, s, Me); 6.59 (1H, s, 4'-H); 6.77 (1H, d. d., $J_{5'6'}$ =7.78, $J_{6'7'}$= 7.62 Hz, 6'-H); 6.88 (1H, d, $J_{7'8'}$ = 8.04 Hz, 8'-H); 7.1 (1H, d. d., $J_{6'7'}$ = 7.62, $J_{7'8'}$ =8.04 Hz, 7'-H); 7.23-7.28 (4H, m, 5'-H, 6'-H, 3''-H, 6''-Í); 7.49 (1H, d, J_{34} = 8.79 Hz, 3-H); 7.51-7.8 (7H, m, arom.); 7.81 (1H, d, J_{34} = 8.88 Hz, 4-H); 7.83 (1H, s, 2'-H); 8.99 (1H, d, J = 8.54, 8''-H or 8-H); determined, %,: C 87.64; H 5.47; N 6.89. $C_{29}H_{22}N_2$. Calculated, %: C 87.41; H 5.56; N 7.03.

*1'-Benzyl-4'-(1'-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (***4 h***, $C_{35}H_{26}N_2$)*

As **4 f** from 0.64 g (2.5 mmol) 2,3'-biquinolyl, 0.05 g (7 mmol) Li, 0.72 g (3.5 mmol) 1-bromonaphthalene and 0.44 g (3.5 mmol) $PhCH_2Cl$. Yield 0.85 g (72%), m.p. 143-144 °C (EtOH). ^{1}H NMR spectrum ($CDCl_3$): 5.1 (2H, d, J = 4.38 Hz, CH_2); 6.69 (1H, s, 4'-H); 6.77 (1H, d. d., $J_{5'6'}$ =7.58, $J_{6'7'}$= 7.36 Hz, 6'-H); 6.78 (1H, d, $J_{7'8'}$ = 7.82 Hz, 8'-H); 6.95 (1H, d. d., $J_{6'7'}$ = 7.36, $J_{7'8'}$ = 7.82 Hz,

7'-H); 7.04 (1H, d, $J_{5'6'}$ =7.58 Hz, 5'-H); 7.29-7.59 (8H, m, arom.); 7.41 (1H, d, J_{34} = 8.91 Hz, 3-H); 7.42-7.8 (7H, m, arom.); 7.81 (1H, d, J_{34} = 8.91 Hz, 4-H); 7.93 (1H, s, 2'-H); 9.03 (1H, d, J = 8.56, 8''-H or 8-H); determined, %,: C 88.75; H 5.44; N 5.81 $C_{35}H_{26}N_2$. Calculated, %: C 88.58; H 5.52; N 5.90.

4'-Phenyl -2,3'-biquinolyl (**5 a**, *$C_{24}H_{16}N_2$)*

A solution of 0.42 g (1.25 mmol) 4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (**4 a**) and 0.33 g I_2 in 5 mL pyridine is refluxed for 10 min. The reaction mixture is poured into 100 mL of water containing 1 g $Na_2S_2O_3$ and 0.5 g NaOH, the white precipitate formed is filtered off and washed with water (3 × 30 mL). Yield 0.4 g (95%), m.p. 133-134 °C (bnz). ^{1}H NMR spectrum ($CDCl_3$): 6.97 (1H, d, J_{34} = 8.54 Hz, 3-H); 7.35 (5H, m, Ph); 7.52 (1H, d. d., $J_{5'6'}$ =8.11, $J_{6'7'}$= 6.95 Hz, 6'-H); 7.56 (1H, d. d., J_{56} = 8.04, J_{67} = 7.01 Hz, 6-H); 7.72 (1H, d. d., $J_{6'7'}$ = 6.95, $J_{7'8'}$ =8.38 Hz, 7'-H); 7.74 (1H, d. d., J_{67}=7.01, J_{78} =8.31 Hz, 7-H); 7.76 (1H, d., J_{56} = 8.04 Hz, 5-H); 7.79 (1H, d, $J_{5'6'}$ = 8.11 Hz, 5'-H); 7.84 (1H, d, J_{34} = 8.54 Hz, 4-H); 8.19 (1H, d, $J_{7'8'}$ = 8.38 Hz, 8'-H); 8.25 (1H, d, J_{78} =8.31 Hz, 8-H); 9.40 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 332 (M^+), determined, %,: C 86.92; H 4.75; N 8.33. $C_{24}H_{16}N_2$**.** Calculated, %: C 86.71; H 4.86; N 8.43.

*4'-(1-Naphthyl)2,3'-biquinolyl (***5 b**, *$C_{28}H_{18}N_2$)*

As 4'-phenyl-2,3'-biquinolyl (**5 a**), from 0.48 g (1.25 mmol) 4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (**4 b**) and 0.33 g (1.3 mmol) I_2. Yield 0.44 g (92%), m.p. 158-159 °C (benzene-hexane). ^{1}H NMR spectrum ($CDCl_3$): 6.83 (1H, d, J_{34} = 8.55 Hz, 3-H); 7.31 (3H, m, 2''-H, 3''-H, 6''-H); 7.39 (1H, d, J_{34} = 8.55 Hz, 4-H); 7.43-7.48 (3H, m, 7''-H, 8''-H, 6'-H); 7.63 (2H, d, J = 8.04 Hz, 4''-H, 5''-H); 7.68 (1H, d. d., J_{56} = 8.04, J_{67} = 7.03 Hz, 6-H); 7.71 (1H, d. d., $J_{6'7'}$ = 6.95, $J_{7'8'}$ =8.34 Hz, 7'-H); 7.73 (1H, d. d., J_{67}=7.03, J_{78} =8.28 Hz, 7-H); 7.89 (1H, d, J_{56} = 8.04 Hz, 5-H); 7.92 (1H, d, $J_{5'6'}$ = 8.11 Hz, 5'-H); 8.10 (1H, d, $J_{7'8'}$ = 8.34 Hz, 8'-H); 8.28 (1H, d, J_{78} =8.28 Hz, 8-H); 9.55 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 382 (M^+), determined, %,: C 88.17; H 4.53; N 7.3. $C_{28}H_{18}N_2$. Calculated, %: C 87.92; H 4.75; N 7.33.

*4'-(2-Pyridyl)-2,3'-biquinolyl (***5 c**, *$C_{23}H_{15}N_3$)*

As 4'-phenyl-2,3'-biquinolyl (**5 a**), from 0.42 g (1.25 mmol) 4'-(2-pyridyl)-1',4'-dihydro-2,3'-biquinolyl (**4 c**) and 0.33 g (1.3 mmol) I_2. Yield 0.4 g (94%), m.p. 93-94 °C (bnz). ^{1}H NMR spectrum ($CDCl_3$): 7.08 (1H, d, J_{34} = 8.54 Hz, 3-H); 7.18 (1H, d. d., $J_{3''4''}$ = 7.69, $J_{3''5''}$ = 1.28 Hz, 3''-H); 7.31 (1H, d. t., $J_{4''5''}$ = 7.54, $J_{5''6''}$ = 4.7, $J_{3''5''}$ = 1.28 Hz, 5''-H); 7.55 (1H, d. d., J_{56} = 8.04, J_{67} = 7.01 Hz, 6-H); 7.59 (1H, d. t., $J_{3''4''}$ = 7.69, $J_{4''5''}$ =7.54, $J_{4''6''}$ = 1.7 Hz, 4''-H); 7.71 (1H, d. d., $J_{6'7'}$ = 6.95, $J_{7'8'}$ =8.34 Hz, 7'-H); 7.73 (1H, d. d., $J_{5'6'}$ =8.11, $J_{6'7'}$= 6.95 Hz, 6'-H); 7.74 (1H, d. d.,

J_{67}=7.01, J_{78} =8.32 Hz, 7-H); 7.76 (1H, d, J_{56} = 8.04 Hz, 5-H); 7.79 (1H, d, $J_{5'6'}$ = 8.11 Hz, 5'-H); 7.91 (1H, d, J_{34} = 8.54 Hz, 4-H); 8.11 (1H, d, $J_{7'8'}$ = 8.34 Hz, 8'-H); 8.26 (1H, d, J_{78} =8.32 Hz, 8-H); 8.81 (1H, d. d., $J_{5''6''}$ = 4.7, $J_{4''6''}$ = 1.7 Hz, 6''-H); 9.43 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 333 (M^+), determined, %,: C 82.89; H 4.47; N 12.64. $C_{23}H_{15}N_3$. Calculated, %: C 82.85; H 4.54; N 12.61.

*4'-(1-Methyl-2-benzimidazolyl)-2,3'-biquinolyl (***5 d***, $C_{26}H_{18}N_4$)*

As 4'-phenyl-2,3'-biquinolyl (**5 a**), from 0.48 g (1.25 mmol) 4'-(1-methyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (**4 d**), and 0.33 g (1.3 mmol) I_2. Yield 0.46 g (95%), m.p. 338-340 °C (EtOH). ^{1}H NMR spectrum ($CDCl_3$): 3.25 (1H, s, Me); 7.31 (1H, d, $J_{5'6'}$ = 8.1 Hz, 5'-H); 7.32 (1H, d, J_{34} = 8.4 Hz, 3-H); 7.38 (1H, d. t., $J_{4''5''}$ = 8.52, $J_{5''6''}$ = 7.41, $J_{5''7''}$ = 1.61 Hz, 5''-H); 7.51 (1H, d. d., $J_{5'6'}$ =8.1, $J_{6'7'}$= 6.94 Hz, 6'-H); 7.53 (1H, d. d., $J_{6''7''}$ =7.65, $J_{5''7''}$ = 1.61 Hz, 7''-H); 7.55 (1H, d. d., J_{56} = 8.06, J_{67} = 7.14 Hz, 6-H); 7.58 (1H, d. t., $J_{5''6''}$ = 7.41, $J_{6''7''}$ = 7.61, $J_{4''6''}$ = 2.23 Hz, 6''-H); 7.68 (1H, d. d., $J_{6'7'}$ = 6.94, $J_{7'8'}$ =8.32 Hz, 7'-H); 7.73 (1H, d, J_{56} = 8.06 Hz, 5-H); 7.82 (1H, d. d., J_{67}=7.14, J_{78} =8.21 Hz, 7-H); 7.87 (1H, d. d., $J_{4''5''}$ =8.52, $J_{4''6''}$ = 2.23 Hz, 4''-H); 7.93 (1H, d, $J_{7'8'}$ = 8.32 Hz, 8'-H); 7.94 (1H, d, J_{34} = 8.4 Hz, 4-H); 8.29 (1H, d, J_{78} =8.21 Hz, 8-H); 9.61 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 386 (M^+), determined, %,: C 80.94; H 4.59; N 14.47. $C_{26}H_{18}N_4$. Calculated, %: C 80.81; H 4.69; N 14.5.

*4'-(1-iso-Propyl-2-benzimidazolyl)-2,3'-biquinolyl (***5 e***, $C_{28}H_{22}N_4$)*

As 4'-phenyl-2,3'-biquinolyl (**5 a**), from 0.52 g (1.25 mmol) 4'-(1-*iso*-propyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl (**4 e**) and 0.33 g (1.3 mmol) I_2. Yield 0.47 g (91%), m.p. 221-222 °C (bnz). ^{1}H NMR spectrum ($CDCl_3$): 0.72 (3H, d, J= 6.83, Me); 1.24 (3H, d, J= 6.83, Me); 4.16 (1H, m, CH); 7.31 (1H, d, $J_{5'6'}$ = 8.14 Hz, 5'-H); 7.36 (1H, d. t., $J_{4''5''}$ = 8.55, $J_{5''6''}$ = 7.38, $J_{5''7''}$ = 1.63 Hz, 5''-H); 7.43 (1H, d, J_{34} = 8.78 Hz, 3-H); 7.5 (1H, d. d., $J_{6''7''}$ =7.67, $J_{5''7''}$ = 1.63 Hz, 7''-H); 7.52 (1H, d. d., $J_{5'6'}$ =8.14, $J_{6'7'}$= 6.97 Hz, 6'-H); 7.55 (1H, d. d., J_{56} = 8.04, J_{67} = 7.11 Hz, 6-H); 7.59 (1H, d. t., $J_{5''6''}$ = 7.38, $J_{6''7''}$ = 7.67, $J_{4''6''}$ = 2.25 Hz, 6''-H); 7.7 (1H, d. d., $J_{6'7'}$ = 6.97, $J_{7'8'}$ =8.31 Hz, 7'-H); 7.74 (1H, d, J_{56} = 8.04 Hz, 5-H); 7.81 (1H, d. d., J_{67}=7.11, J_{78} =8.21 Hz, 7-H); 7.92 (1H, d. d., $J_{4''5''}$ =8.55, $J_{4''6''}$ = 2.25 Hz, 4''-H); 7.93 (1H, d, J_{34} = 8.78 Hz, 4-H); 8.06 (1H, d, $J_{7'8'}$ = 8.31 Hz, 8'-H); 8.28 (1H, d, J_{78} =8.21 Hz, 8-H); 9.57 (1H, s, 2'-H); mass spectrum (m/z 70 eV) 414 (M^+), determined, %,: C 81.24; H 5.27; N 13.49. $C_{28}H_{22}N_4$. Calculated, %: C 81.13; H 5.35; N 13.52.

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References and Notes

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Samples Availability: Available from the authors.