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# INVESTIGATIONS IN THE REGION OF 2,3′-BIQUINOLINE. 3.* SYNTHESIS OF 2′-ALKYL(ARYL)-1′,2′-DIHYDRO-2,3′-BIQUINOLINES AND 2′-ALKYL(ARYL)-2,3′-BIQUINOLINES

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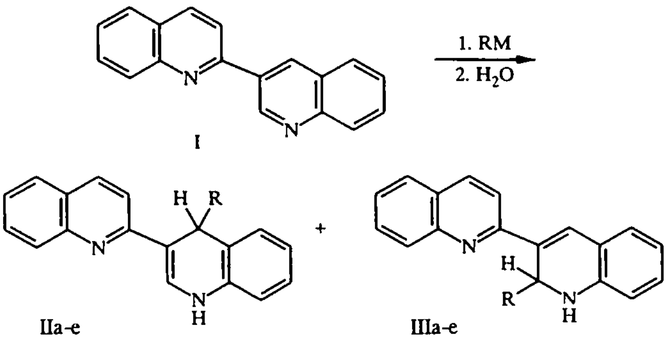
*A method was developed for the synthesis of 2′-alkyl(aryl)-1′,2′-dihydro-2,3′-biquinolines, based on the addition of organolithium compounds to 2,3′-biquinoline in the presence of tetramethylethylenediamine. Their oxidation with manganese dioxide led to 2′-alkyl(aryl)-2,3′-biquinolines.*

In the previous work [1] we investigated the reaction of 2,3′-biquinoline (I) with Grignard reagents, and this made it possible to develop a method for the synthesis of 4′-alkyl(aryl)-1′,4′-dihydro-2,3′-biquinolines (II). Unlike alkyl- and arylmagnesium halides, the more ionic allylmagnesium chloride adds to compound (I) at position 2′, and this is explained by a change in the mechanism. It seemed of interest, by varying the nature of the organometallic compound and the reaction conditions, to change the direction of alkylation (arylation) of the biquinoline (I) and to develop a method for the synthesis of the extremely difficultly obtainable 2′-alkyl(aryl)-1′,2′-dihydro-2,3′-biquinolines (III) and 2′-alkyl(aryl)-2,3′-biquinolines (IV).

On the basis of the foregoing we supposed that it would be possible to obtain the necessary change in regioselectivity of nucleophilic addition (substitution) by increasing the degree of ionicity of the C–metal bond with the organometallic compounds of elements less electronegative than magnesium.

In fact, the replacement of phenylmagnesium bromide by phenyllithium leads to the formation of significant amounts of compound (IIId) [the (IId):(IIId) ratio is practically 1:1), but in the case of other alkyl- and aryllithium reagents the fraction of compounds (III) does not exceed 15% (Table 1).



II, III a R = Me, b R = Pr, c R = Bu, d R = Ph, e R = *l*-$C_{10}H_7$

The use of the even more ionic organocalcium reagents leads to an increase in the fraction of (III) [in the case of BuCaI the (IIc):(IIIc) ratio amounts to 39:61], but the total yield does not exceed 55%.

On the other hand, changes in the direction of nucleophilic addition can be achieved by blocking the SET mechanism.

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*For Communication 2, see [1].

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TABLE 1. Results from the Addition of Organolithium Compounds to 2,3'-Biquinoline

| RLi | In the absence of TMEDA* | | In the presence of TMEDA | |
|---|---|---|---|---|
| | total yield, % | (II):(III) ratio | total yield, % | (II):(III) ratio |
| MeLi | 91 | 85 : 15 | 96 | 30 : 70 |
| PrLi | 84 | 86 : 14 | 86 | 43 : 57 |
| BuLi | 98 | 88 : 12 | 97 | 47 : 53 |
| PhLi | 95 | 52 : 48 | 98 | 26 : 74 |
| 1-$C_{10}H_7Li$ | 97 | 88 : 12 | 95 | 27 : 73 |

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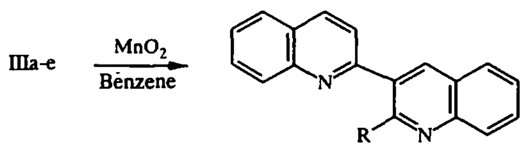
*Tetramethylethylenediamine.

Earlier [2] it was shown that the metal cation plays an important role in electron transfer. We supposed that the use of a strongly chelating solvent (cosolvent), such as tetramethylethylenediamine, would lead to an increase in the degree of ionicity of the C–metal bond and would also suppress complexation with compound (I) and thereby prevent realization of the SET mechanism.

In fact, the reaction of (I) with organolithium reagents in the presence of tetramethylethylenediamine leads to the preferential formation of 2'-R-1',2'-dihydro-2,3'-biquinolines (Table 1), and this is the only method for their synthesis.



IVa-e

IV a R = Me, b R = Pr, c R = Bu, d R = Ph, e R = *l*-$C_{10}H_7$

Compounds (IIIa-e) are easily oxidized by manganese dioxide with the formation of 2'-alkyl(aryl)-2,3'-biquinolines (IVa-e). The yields are close to quantitative.

The structure of the obtained compounds was confirmed by the PMR spectra and by experiments with 4'-D-2,3'-biquinoline. The PMR spectra of compounds (IVa-e) show a decrease in the intensity of the signal for the proton at position 4', corresponding to the degree of deuteroexchange in the initial biquinoline.

## EXPERIMENTAL

The PMR spectra were recorded on Bruker WP-200 and Bruker AM-300 instruments with TMS as internal standard. The reactions and the individuality of the products were monitored on Silufol UV-254 plates in the 1:1 ethyl acetate–hexane solvent system. Column chromatography was conducted on silica gel L 40/100. The THF was purified by distillation over lithium aluminum hydride and then over benzophenoneketyl. The diethyl ether was purified by distillation over benzophenoneketyl. The concentration of the organolithium compounds was determined by the method described in [3].

**General Procedure for the Alkylation (Arylation) of 2,3'-Biquinoline with Organolithium Compounds.** To a solution of 1.8 mmole of the organolithium compound in 5 ml of ether at 0°C we added 0.46 g (4 mmole) of tetramethylethylenediamine (TMEDA*). The mixture was stirred for 10 min, after which 0.32 g (1.25 mmole) of 2,3'-biquinoline in 10 ml of THF was carefully added. The reaction mixture was stirred in an atmosphere of argon at room temperature and was then boiled for a further 30 min. We then cautiously added 50 ml of water and extracted the product with 3 × 20 ml of benzene. The extracts were combined, dried over sodium sulfate, and evaporated. The residue was dissolved in 10 ml of benzene and chromatographed on a column. The first colored fraction was collected using the 10:1 benzene–ethyl acetate sol-

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*TMEDA was not used in the first series of experiments.

vent system. The solvent was evaporated, and compounds (IIIa-e) were obtained. The mixture was then eluted with ethyl acetate, and the second colored fraction was collected. After evaporation compounds (IIa-e) were obtained.

**4'-Methyl-1',4'-dihydro-2,3'-biquinoline (IIa) ($C_{19}H_{16}N_2$).** The yield was 0.10 g (29%) and without TMEDA 0.26 g (77%); mp 148-149°C (from benzene). Published data [1]: mp 148-149°C; $R_f$ 0.44 (Silufol UV-254, 1:1 ethyl acetate – hexane). A mixed melting test with an authentic sample did not give a melting point depression. The PMR spectrum was identical with the spectrum given in [1].

**4'-Propyl-1',4'-dihydro-2,3'-biquinoline (IIb) ($C_{21}H_{20}N_2$).** The yield was 0.14 g (37%) and without TMEDA 0.27 g (72%); mp 127-129°C (from benzene with hexane). Published data [1]: mp 127-129°C; $R_f$ 0.56 (Silufol UV-254, 1:1 ethyl acetate – hexane). A mixed melting test with an authentic sample did not give a melting depression. The PMR spectrum was identical with the spectrum given in [1].

**4'-Butyl-1',4'-dihydro-2,3'-biquinoline (IIc) ($C_{22}H_{22}N_2$).** The yield was 0.18 g (46%) and without TMEDA 0.34 g (86%). The product was a yellow oil; $R_f$ 0.62 (Silufol UV-254, 1:1 ethyl acetate – hexane). PMR spectrum (δ, ppm, deuterochloroform): 0.81 (3H, t, $J$ = 7.02 Hz, 4'-$CH_2CH_2CH_2\underline{CH_3}$); 1.28 (2H, m, 4'-$CH_2CH_2\underline{CH_2}CH_3$); 1.39 (2H, m, 4'-$CH_2\underline{CH_2}CH_2CH_3$); 1.64 (2H, m, 2'-$\underline{CH_2}CH_2CH_2CH_3$); 4.58 (1H, dd, $J_{cis}$ = 4.92, $J_{trans}$ = 6.45 Hz, 4'-H); 6.03 (1H, d, $J_{NH\text{-}2'H}$ = 5.71 Hz, NH); 6.70 (1H, dd, $J_{7'8'}$ = 7.78, $J_{6'8'}$ = 1.25 Hz, 8'-H); 6.97 (1H, dt, $J_{5'6'}$ = 7.65, $J_{6'7'}$ = 7.29, $J_{6'8'}$ = 1.25 Hz, 6'-H); 7.11 (1H, dt, $J_{6'7'}$ = 7.29, $J_{7'8'}$ = 7.78, $J_{5'7'}$ = 1.61 Hz, 7'-H); 7.22 (1H, dd, $J_{5'6'}$ = 7.65, $J_{5'7'}$ = 1.61 Hz, 5'-H); 7.38 (1H, dt, $J_{56}$ = 8.01, $J_{67}$ = 6.93, $J_{68}$ = 1.26, 6-H); 7.46 (1H, d, $J_{NH\text{-}2'H}$ = 5.71 Hz, 2'-H); 7.53 (1H, d, $J_{34}$ = 8.89 Hz, 3-H); 7.62 (1H, dt, $J_{67}$ = 6.93, $J_{78}$ = 8.54, $J_{57}$ = 1.62 Hz, 7-H); 7.71 (1H, dd, $J_{56}$ = 8.01, $J_{57}$ = 1.62 Hz, 5-H); 7.97 (1H, dd, $J_{78}$ = 8.54, $J_{68}$ = 1.26 Hz, 8-H); 7.98 (1H, d, $J_{34}$ = 8.89 Hz, 4-H). Found %: C 84.24; H 6.98; N 8.78. $C_{22}H_{22}N_2$. Calculated %: C 84.03; H 7.06; N 8.91.

**4'-Phenyl-1',4'-dihydro-2,3'-biquinoline (IId) ($C_{24}H_{18}N_2$).** The yield was 0.10 g (25%) and without TMEDA 0.21 g (49%); mp 213-214°C (from benzene). Published data [2]: mp 213-214°C; $R_f$ 0.32 (Silufol UV-254, 1:1 ethyl acetate – hexane). A mixed melting test with an authentic sample did not give a melting point depression. The PMR spectrum was identical with the spectrum given in [2].

**4'-(1-Naphthyl)-1',4'-dihydro-2,3'-biquinoline (IIe) ($C_{28}H_{20}N_2$).** The yield was 0.12 g (26%) and without TMEDA 0.41 g (85%); mp 196-197°C (from benzene). Published data [2]: mp 196-197°C. $R_f$ 0.27 (Silufol UV-254, 1:1 ethyl acetate – hexane). A mixed-melting test with an authentic sample did not give a melting point depression. The PMR spectrum was identical with the spectrum given in [2].

**2'-Methyl-1',2'-dihydro-2,3'-biquinoline (IIIa) ($C_{19}H_{16}N_2$).** The yield was 0.23 g (67%) and without TMEDA 0.048 g (14%); mp 138-139°C (from alcohol); $R_f$ 0.44 (Silufol UV-254, 1:1 ethyl acetate – hexane). PMR spectrum (δ, ppm, DMSO-$d_6$): 1.22 (3H, d, $J$ = 6.20 Hz, Me); 5.23 (1H, dq, $J_{2'H\text{-}Me}$ = 6.20, $J_{NH\text{-}2'H}$ = 2.23 Hz, 2'-H); 6.24 (1H, d, $J_{NH\text{-}2'H}$ = 2.23 Hz, NH); 6.54 (1H, dd, $J_{5'6'}$ = 7.41, $J_{6'7'}$ = 7.38 Hz, 6'-H); 6.60 (1H, d, $J_{7'8'}$ = 7.96 Hz, 8'-H); 7.00 (1H, dd, $J_{6'7'}$ = 7.38, $J_{7'8'}$ = 7.96 Hz, 7'-H); 7.10 (1H, d, $J_{5'6'}$ = 7.41 Hz, 5'-H); 7.49 (1H, s, 4'-H); 7.55 (1H, dd, $J_{56}$ = 8.23, $J_{67}$ = 7.08 Hz, 6-H); 7.74 (1H, dd, $H_{67}$ = 7.08, $J_{78}$ = 8.47 Hz, 7-H); 7.92 (1H, d, $J_{56}$ = 8.23 Hz, 5-H); 7.97 (1H, d, $J_{78}$ = 8.47 Hz, 8-H); 8.04 (1H, d, $J_{34}$ = 8.77 Hz, 3-H); 8.31 (1H, d, $J_{34}$ = 8.77 Hz, 4-H). Found %: C 84.04; H 5.81; N 10.15. $C_{19}H_{16}N_2$. Calculated %: C 83.78; H 5.93; N 10.29.

**2'-Propyl-1',2'-dihydro-2,3'-biquinoline (IIIb) ($C_{21}H_{20}N_2$).** The yield was 0.18 g (49%) and without TMEDA 0.045 g (12%); mp 131-132°C (from alcohol); $R_f$ 0.91 (Silufol UV-254, 1:1 ethyl acetate – hexane). PMR spectrum (δ, ppm, DMSO-$d_6$): 0.81 (3H, t, $J$ = 7.03 Hz, 2'-$CH_2CH_2\underline{CH_3}$); 1.29 (2H, m, 2'-$CH_2\underline{CH_2}CH_3$); 1.63 (2H, m, 2'-$\underline{CH_2}CH_2CH_3$); 5.15 (1H, m, 2'-H); 6.35 (1H, d, $J_{NH\text{-}2'H}$ = 2.70 Hz, NH); 6.53 (1H, dd, $J_{5'6'}$ = 7.38, $J_{6'7'}$ = 7.30 Hz, 6'-H); 6.64 (1H, d, $J_{7'8'}$ = 7.98 Hz, 8'-H); 7.00 (1H, dd, $J_{6'7'}$ = 7.30, $J_{7'8'}$ = 7.98 Hz, 7'-H); 7.06 (1H, d, $J_{5'6'}$ = 7.38 Hz, 5'-H); 7.45 (1H, s, 4'-H); 7.55 (1H, dd, $J_{56}$ = 8.10, $J_{67}$ = 7.32 Hz, 6-H); 7.75 (1H, dd, $J_{67}$ = 7.32, $J_{78}$ = 8.37 Hz, 7-H); 7.90 (1H, d, $J_{56}$ = 8.10 Hz, 5-H); 7.94 (1H, d, $J_{78}$ = 8.37 Hz, 8-H); 8.04 (1H, d, $J_{34}$ = 8.79 Hz, 3-H); 8.30 (1H, d, $J_{34}$ = 8.79 Hz, 4-H). Found %: C 84.26; H 6.62; N 9.12. $C_{21}H_{20}N_2$. Calculated %: C 83.95; H 6.72; N 9.33.

**2'-Butyl-1',2'-dihydro-2,3'-biquinoline (IIIc) ($C_{22}H_{22}N_2$).** The yield was 0.20 g (51%) and without TMEDA 0.047 g (12 %); mp 108-109°C (from alcohol); $R_f$ 0.94 (Silufol UV-254, 1:1 ethyl acetate – hexane). PMR spectrum (δ, ppm, DMSO-$d_6$): 0.82 (3H, t, $J$ = 7.02 Hz, 2'-$CH_2CH_2CH_2\underline{CH_3}$); 1.28 (2H, m, 2'-$CH_2CH_2\underline{CH_2}CH_3$); 1.39 (2H, m, 2'-$CH_2CH_2CH_2CH_3$); 1.61 (2H, m, 2'-$\underline{CH_2}CH_2CH_2CH_3$); 5.14 (1H, m, 2'-H); 6.36 (1H, d, $J_{NH\text{-}2'H}$ = 2.71 Hz, NH); 6.51 (1H, dd, $J_{5'6'}$ = 7.37, $J_{6'7'}$ = 7.31 Hz, 6'-H); 6.65 (1H, d, $J_{7'8'}$ = 7.96 Hz, 8'-H); 6.99 (1H, dd, $J_{6'7'}$ = 7.31, $J_{7'8'}$ = 7.96 Hz, 7'-H); 7.08 (1H, d, $J_{5'6'}$ = 7.37 Hz, 5'-H); 7.48 (1H, s, 4'-H); 7.54 (1H, dd, $J_{56}$ = 8.09, $J_{67}$ = 7.34 Hz, 6-H); 7.74 (1H, dd, $J_{67}$ = 7.34, $J_{78}$ = 8.39 Hz, 7-H); 7.92 (1H, d, $J_{56}$ = 8.09 Hz, 5-H); 7.93 (1H, d, $J_{78}$ = 8.39 Hz, 8-H); 8.03 (1H, d, $J_{34}$ = 8.76 Hz, 3-H); 8.29 (1H, d, $J_{34}$ = 8.76 Hz, 4-H). Found %: C 84.40; H 6.91; N 8.69. $C_{22}H_{22}N_2$. Calculated %: C 84.03; H 7.06; N 8.91.

**2'-Phenyl-1',2'-dihydro-2,3'-biquinoline (IIId) ($C_{24}H_{18}N_2$).** The yield was 0.30 g (73%) and without TMEDA 0.19 g (46%); mp 207-209°C (from alcohol); $R_f$ 0.90 (Silufol UV-254, 1:1 ethyl acetate–hexane). PMR spectrum (δ, ppm, acetone-$d_6$): 6.15 (1H, d, $J_{NH-2'H}$ = 2.13 Hz, NH); 6.51 (1H, d, $J_{NH-2'H}$ = 2.13 Hz, 2'-H); 6.60 (1H, dd, $J_{5'6'}$ = 7.41, $J_{6'7'}$ = 7.38 Hz, 6'-H); 6.62 (1H, d, $J_{7'8'}$ = 7.96 Hz, 8'-H); 7.01 ( 1H, dd, $J_{6'7'}$ = 7.38, $J_{7'8'}$ = 7.96 Hz, 7'-H); 7.15 (3H, m, 3"-H, 4"-H, 5"-H); 7.18 (1H, d, $J_{5'6'}$ = 7.41, 5'-H); 7.50 (1H, dd, $J_{56}$ = 8.23, $J_{67}$ = 7.08 Hz, 6-H); 7.52 (2H, d, $J$ = 8.23 Hz, 2"-H, 6"-H); 7.69 (1H, dd, $J_{67}$ = 7.08, $J_{78}$ = 8.47 Hz, 7-H); 7.74 (1H, s, 4'-H); 7.86 (1H, $J_{56}$ = 8.23 Hz, 5-H); 7.97 (1H, d, $J_{78}$ = 8.47 Hz, 8-H); 8.04 (1H, d, $J_{34}$ = 8.96 Hz, 3-H); 8.22 (1H, d, $J_{34}$ = 8.96 Hz, 4-H). Found %: C 86.31; H 5.31; N 8.38. $C_{24}H_{18}N_2$. Calculated %: C 86.19; H 5.43; H 8.38.

**2'-(1-Naphthyl)-1',2'-dihydro-2,3'-biquinoline (IIIe) ($C_{28}H_{20}N_2$).** The yield was 0.33 g (69%) and without TMEDA 0.057 g (12%); mp 166-167°C (from alcohol); $R_f$ 0.86 (Silufol UV-254, 1:1 ethyl acetate–hexane). PMR spectrum (δ, ppm, DMSO-$d_6$): 6.48 (1H, d, $J_{7'8'}$ = 8.05 Hz, 8'-H); 6.55 (1H, dd, $J_{5'6'}$ = 7.41, $J_{6'7'}$ = 7.32 Hz, 6'-H); 6.70 (1H, d, $J_{NH-2'H}$ = 2.23 Hz, NH); 6.95 (1H, dd, $J_{6'7'}$ = 7.32, $J_{7'8'}$ = 8.05 Hz, 7'-H); 5.23 (1H, dq, $J_{2'H-Me}$ = 6.2, $J_{NH-2'H}$ = 2.23 Hz, 2'-H); 7.10 (1H, d, $J_{5'6'}$ = 7.41 Hz, 5'-H); 7.55 (1H, dd $J_{56}$ = 8.23, $J_{67}$ = 7.08 Hz, 6-H); 7.74 (1H, dd, $J_{67}$ = 7.08, $J_{78}$ = 8.47 Hz, 7-H); 7.92 (1H, d, $J_{56}$ = 8.23 Hz, 5-H); 7.97 (1H, d, $J_{78}$ = 8.47 Hz, 8-H); 7.95 (1H, s, 4'-H); 8.03 (1H, d, $J_{34}$ = 8.83 Hz, 3-H); 8.21 (1H, d, $J_{34}$ = 8.83 Hz, 4-H); 8.84 (1H, d, $J_{78}$ = 8.64 Hz, 8"-H). Found %: C 87.58; H 5.14; 7.28. $C_{28}H_{20}N_2$. Calculated %: C 87.46; H 5.25; N 7.29.

**General Procedure for the Synthesis of 2'-Alkyl(aryl)-2,3'-biquinolines (IVa-e).** A mixture of 0.75 mmole of 2'-alkyl(aryl)-1',2'-dihydro-2,3'-biquinolines (IIIa-e) and 0.33 g (3.75 mmole) manganese dioxide in 10 ml of benzene was boiled for an hour. The mixture was filtered without cooling, and the precipitate was washed with 2 × 10 ml of hot benzene. The obtained solutions were combined, cooled, and evaporated. We obtained a white oil, which in the case of compounds (IVa, d, e) crystallized after the addition of hexane.

**2'-Methyl-2,3'-biquinoline (IVa) ($C_{19}H_{14}N_2$).** The yield was 0.16 g (96%); mp 191-192°C (from hexane). Published data [4]: mp 191-193°C. PMR spectrum (δ, ppm, acetone-$d_6$): 2.83 (3H, s, 2'-$CH_3$); 7.59 (1H, dd, $J_{5'6'}$ = 8.26, $J_{6'7'}$ = 6.93 Hz, 6'-H); 7.67 (1H, dd, $J_{56}$ = 8.07, $J_{67}$ = 7.03 Hz, 6-H); 7.78 (1H, dd, $J_{6'7'}$ = 6.93, $J_{7'8'}$ = 8.36 Hz, 7'-H); 7.84 (1H, dd, $J_{67}$ = 7.03, $J_{78}$ = 8.39 Hz, 7-H); 7.88 (1H, d, $J_{34}$ = 8.51 Hz, 3-H); 8.02 (1H, d, $J_{5'6'}$ = 8.26 Hz, 5'-H); 8.05 (1H, d, $J_{8'7'}$ = 8.36 Hz, 8'-H); 8.05 (1H, d, $J_{56}$ = 8.07 Hz, 5-H); 8.13 (1H, d, $J_{78}$ = 8.39 Hz, 8-H); 8.44 (1H, s, 4'-H); 8.51 (1H, d, $J_{34}$ = 8.51 Hz, 4-H). Found %: C 84.71; H 5.16; N 10.13. $C_{19}H_{14}N_2$. Calculated %: C 84.41; H 5.22; N 10.37.

**2'-Propyl-2,3'-biquinoline (IVb) ($C_{21}H_{18}N_2$).** The yield was 0.17 g (93%). The product was a colorless oil. PMR spectrum (δ, ppm, acetone-$d_6$): 0.95 (3H, t, $J$ = 7.20 Hz, 2'-$CH_2CH_2\underline{CH_3}$); 1.70 (2H, m, 2'-$CH_2\underline{CH_2}CH_3$); 3.20 (2H, t, $J$ = 7.65 Hz, 2'-$\underline{CH_2}CH_2CH_3$); 7.60 (1H, dd, $J_{5'6'}$ = 8.38, $J_{6'7'}$ = 6.96 Hz, 6'-H); 7.67 (1H, dd, $J_{56}$ = 8.05, $J_{67}$ = 7.02 Hz, 6-H); 7.79 (1H, dd, $J_{6'7'}$ = 6.96, $J_{7'8'}$ = 8.35 Hz, 7'-H); 7.85 (1H, dd, $J_{67}$ = 7.02, $J_{78}$ = 8.31 Hz, 7-H); 7.87 (1H, d, $J_{34}$ = 8.54 Hz, 3-H); 8.02 (1H, d, $J_{5'6'}$ = 8.38 Hz, 5'-H); 8.07 (1H, d, $J_{8'7'}$ = 8.35 Hz, 8'-H); 8.06 (1H, d, $J_{56}$ = 8.05 Hz, 5-H); 8.12 (1H, d, $J_{78}$ = 8.31 Hz, 8-H); 8.43 (1H, s, 4'-H); 8.52 (1H, d, $J_{34}$ = 8.54 Hz, 4-H). Found %: C 84.81; H 6.02; N 9.17. $C_{21}H_{18}N_2$. Calculated %: C 84.52; H 6.08; N 9.39.

**2'-Butyl-2,3'-biquinoline (IVc) ($C_{22}H_{20}N_2$).** The yield was 0.18 g (92%). The product formed a colorless oil. PMR spectrum (δ, ppm, acetone-$d_6$): 0.80 (3H, t, $J$ = 7.17 Hz, 2'-$CH_2CH_2CH_2\underline{CH_3}$); 1.29 (2H, m, 2'-$CH_2CH_2\underline{CH_2}CH_3$); 1.75 (2H, m, 2'-$CH_2\underline{CH_2}CH_2CH_3$); 3.20 (2H, t, $J$ = 7.63 Hz, 2'-$\underline{CH_2}CH_2CH_2CH_3$); 7.60 (1H, dd, $J_{5'6'}$ = 8.15, $J_{6'7'}$ = 6.91 Hz, 6'-H); 7.67 (1H, dd, $J_{56}$ 8.09, $J_{67}$ = 7.14 Hz, 6-H); 7.79 (1H, dd, $J_{6'7'}$ = 6.91, $J_{7'8'}$ = 8.43 Hz, 7'-H); 7.85 (1H, dd, $J_{67}$ = 7.14, $J_{78}$ = 8.35 Hz, 7-H); 7.86 (1H, d, $J_{34}$ = 8.55 Hz, 3-H); 8.02 (1H, d, $J_{5'6'}$ = 8.15 Hz, 5'-H); 8.07 (1H, d, $J_{8'7'}$ = 8.43 Hz, 8'-H); 8.07 (1H, d, $J_{56}$ = 8.09 Hz, 5-H); 8.12 (1H, d, $J_{78}$ = 8.35 Hz, 8-H); 8.41 (1H, s, 4'-H); 8.52 (1H, d, $J_{34}$ = 8.55 Hz, 4-H). Found %: C 84.86; H 6.40; N 8.74. $C_{22}H_{20}N_2$. Calculated %: C 84.57; H 6.46; N 8.97.

**2'-Phenyl-2,3'-biquinoline (IVd) ($C_{24}H_{16}N_2$).** The yield was 0.20 g (94%); mp 131-133°C (from hexane with acetone). PMR spectrum (δ, ppm, acetone-$d_6$): 7.14 (1H, d, $J_{34}$ = 8.54 Hz, 3-H); 7.15 (3H, m, 3"-H, 4"-H, 5"-H); 7.50 (1H, dd, $J_{5'6'}$ = 8.36, $J_{6'7'}$ = 6.90 Hz, 6'-H); 7.52 (2H, d, $J$ = 8.23 Hz, 2"-H, 6"-H); 7.56 (1H, dd, $J_{56}$ = 8.06, $J_{67}$ = 7.06 Hz, 6-H); 7.72 (1H, dd, $J_{6'7'}$ = 6.90, $J_{7'8'}$ = 8.47 Hz, 7'-H); 7.74 (1H, dd, $J_{67}$ = 7.06, $J_{78}$ = 8.24 Hz, 7-H); 7.76 (1H, d, $J_{56}$ = 8.06 Hz, 5-H); 7.79 (1H, d, $J_{5'6'}$ = 8.36 Hz, 5'-H); 7.80 (1H, d, $J_{34}$ = 8.54 Hz, 4-H); 8.19 (1H, d, $J_{7'8'}$ = 8.47 Hz, 8'-H); 8.24 (1H, d, $J_{78}$ = 8.24 Hz, 8-H); 8.72 (1H, s, 4'-H). Found %: C 86.88; H 4.79; N 8.33. $C_{24}H_{16}N_2$. Calculated %: C 86.71; H 4.86; N 8.43.

**2′-(1-Naphthyl)-2,3′-biquinoline (IVe) ($C_{28}H_{18}N_2$).** The yield was 0.23 g (95%); mp 81-82°C (from hexane with acetone). PMR spectrum (δ, ppm, acetone-$d_6$): 7.08 (1H, d, $J_{34}$ = 8.55 Hz, 3-H); 7.33 (3H, m, 2″-H, 3″-H, 6″-H); 7.45 (3H, m, 7″-H, 8″-H, 6′-H); 7.52 (1H, dd, $J_{56}$ = 8.06, $J_{67}$ = 7.11 Hz, 6-H); 7.63 (2H, d, $J$ = 8.04 Hz, 4″-H, 5″-H); 7.72 (1H, dd, $J_{6'7'}$ = 7.00, $J_{7'8'}$ = 8.45 Hz, 7′-H); 7.74 (1H, dd, $J_{67}$ = 7.11, $J_{78}$ = 8.24 Hz, 7-H); 7.87 (1H, d, $J_{34}$ = 8.55 Hz, 4-H); 7.89 (1H, d, $J_{56}$ = 8.06 Hz, 5-H); 7.92 (1H, d, $J_{5'6'}$ = 8.29 Hz, 5′-H); 8.16 (1H, d, $J_{7'8'}$ = 8.45 Hz, 8′-H); 8.24 (1H, d, $J_{78}$ = 8.24 Hz, 8-H); 8.91 (1H, s, 4′-H). Found %: C 88.14; H 4.54; N 7.32. $C_{28}H_{18}N_2$. Calculated %: C 87.92; H 4.75; N 7.33.

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