

STUDIES IN THE AREA OF 2,3'-BIQUINOLYL.

1. ARYLATION AND HETARYLATION OF 2,3'-BIQUINOLYL DIANION

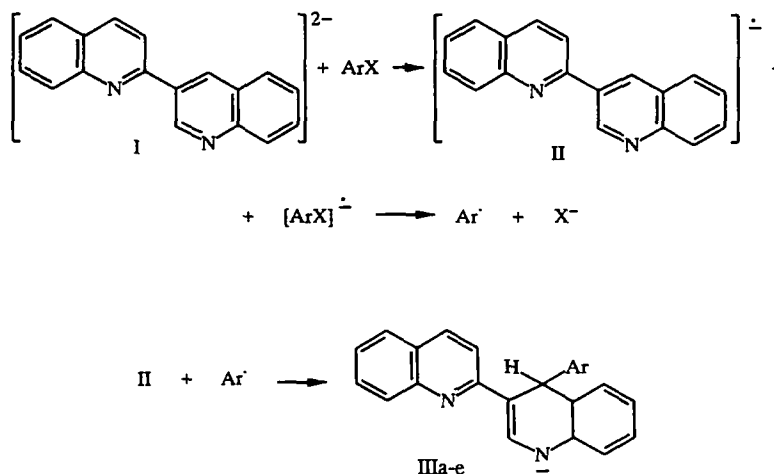
A. V. Aksenov, I. V. Aksenova, I. V. Borovlev,
and Yu. I. Smushkevich

The 2,3'-biquinolyl dianion, when reacting with aryl- and hetaryl halides, forms arylation products at the 4' position, and treatment of these products with alkyl halides or water yields 1'-alkyl-4'-aryl-1',4'-dihydro-2,3'-biquinolyls or 4'-aryl-1',4'-dihydro-2,3'-biquinolyls, respectively. Oxidation of the latter yields 4'-aryl-2,3'-biquinolyls. The cation dependence of the arylation reaction is demonstrated.

We recently [1] devised a method of producing 2,3'-biquinolyl (I) dianion, so that its properties can now be studied. The present article reports on its arylation and hetarylation.

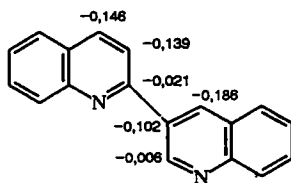
Known reactions of such molecules with aryl halides usually include electron transfer from the dianion (radical-anion) to the halogen derivative [2-4]. Thus, diphenyl dianion reacts with halobenzenes to form benzoic acid after treatment of the reaction mixture with carbon dioxide [2]. We postulated that dianion I would also be an electron donor with respect to aryl halides, but because of the high electron affinity of 2,3'-biquinolyl as compared to biphenyl, the process can be limited to the transfer of only one electron. This will result in the formation of a radical-anion (II), in which the maximum spin density, based on quantum-mechanical calculations, is localized in the 4' position (Fig. 1).

Scheme 1



ArX = PhBr, 1-Bromonaphthalene, 2-fluoropyridine, 1-methyl-2-chlorobenzimidazole, 1-isopropyl-2-chlorobenzimidazole; III a Ar = Ph; b Ar = 1-C₁₀H₇; c Ar = 2-C₅H₄N; d Ar = 1-methyl-2-benzimidazolyl; e Ar = 1-isopropyl-2-benzimidazolyl

Stavropol' State University, Stavropol' 355009. Russian Chemical Engineering University, Moscow 125190. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1094-1099, August, 1997. Original article submitted April 29, 1997.

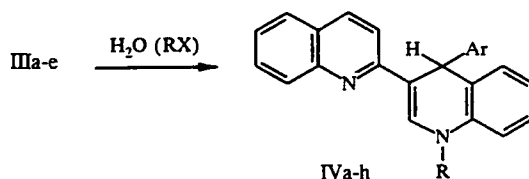


Distribution of spin density in the radical-anion II (MNDO method).

In such a case, the aryl radical formed after the splitting off of the halide ion will react with the radical-anion (II) to form the anion (III) (Scheme 1).

Indeed, on gradual addition of aryl- or hetaryl halides to the dianion I, obtained by reaction of 2,3'-biquinolyl with metallic lithium in THF [1] and subsequent treatment of the reaction with water, there are formed 4'-aryl(hetaryl)-1',4'-dihydro, 2,3'-biquinolyls (IVa-e) in a 64-78% yield. Use of alkyl halides instead of water in the final stage of the reaction leads to formation of products of N-alkylation, i.e., 1'-alkyl-4'-aryl(hetaryl)-1',4'-dihydro-2,3'-biquinolyls (IVf-h) in a 72-75% yield (Scheme 2).

Scheme 2



IV a Ar = Ph, R = H; b Ar = 1-C₁₀H₇, R = H; c Ar = 2-C₅H₄N, R = H; d Ar = 1-methyl-2-benzimidazolyl, R = H; e Ar = 1-isopropyl-2-benzimidazolyl, R = H; f Ar = Ph, R = Me; g Ar = 1-C₁₀H₇, R = Me; h Ar = 1-C₁₀H₇, R = CH₂Ph; RX = MeI, PhCH₂Cl

Similar results were obtained for the dianion I, generated by means of metallic potassium or naphthalenylpotassium. Use of the latter two was found to be less convenient than that of lithium, but a study of the role of the metal cation in the reaction of naphthalenylpotassium with 2,3'-biquinolyl made it possible to show that it can play an important role in the electron transfer process. Thus, 2,3'-biquinolyl does not react with a solution of naphthalenylpotassium in absolute THF in the presence of a 1.2-fold molar excess of 18-crown-6 ester based on potassium even with prolonged agitation. The reaction starts when dry potassium iodide is added to the reaction mixture.

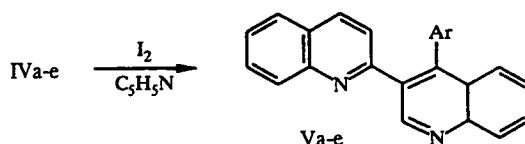
We obtained similar results in a study of the arylation reaction. For example, the dianion I, obtained from 1.25 mmole of 2,3'-biquinolyl and 2.7 mmole of metallic potassium, in the presence of 3 mmole of 18-crown-6, does not react with bromobenzene even with boiling for two hours. When 1.5 mmole of KI is added to the reaction mixture in question, the reaction begins to take place in the usual manner and ends in the formation of IVa.

Compounds IVa-e are readily oxidized by iodine in pyridine to 4'-aryl-2,3'-biquinolyls (Va-e). The yield is nearly quantitative (Scheme 3).

The structure of the compounds obtained was confirmed by ESR spectroscopy. A characteristic feature of the spectra of compounds Va-e was a displacement of the signal of the proton in the 3 position to a strong field (Va 6.97, Vb 6.83, Vc 7.08, Vd 7.32, Ve 7.43 as compared to 8.04 ppm for 2,3'-biquinolyl). This in our view is explained by the location of the aryl substituent in a perpendicular plane and the screening of the proton in the 3 position by the aromatic ring.

Of interest is the nonequivalency of the protons of the two methyl groups in compounds IVe and Ve (IVe: 1.73 (1H, e), 1.85 (1H, e), Ve: 0.75 ppm (1H, e), 1.24 ppm (1H, e)). This is due to their diastereotopicity. Whereas the diastereotopicity of the methyl groups of IVe is due to the presence of an asymmetric carbon atom in the 4' position, in compound Ve there is no such carbon atom. However, molecule Ve contains an asymmetric center as a result of the hindered rotation about the C_(4')-C_(2') bond (of the benzimidazole ring), due to the presence of bulky substituents in both the quinoline and benzimidazole fragments.

Scheme 3



V a Ar = Ph; b Ar = 1-C₁₀H₇; c Ar = 2-C₅H₄N; d Ar = 1-methyl-2-benzimidazolyl; e Ar = 1-isopropyl-2-benzimidazolyl

The arylation direction was confirmed by experiments with 4'-D-2-3'-biquinolyl. The ESR spectra of compounds IVa-e, show a decrease in the signal intensity of the proton in the 4' position that corresponds to the degree of deuterio exchange in the initial biquinolyl. In compounds Va-e, the "marker" disappears.

EXPERIMENTAL

The mass spectra were recorded on a Varian MAT-331A instrument, and the ESR spectra on a Bruker WP-200 instrument. The course of the reactions and purity of the synthesized compounds were monitored on Silufol UV-254 wafers, the solvent system used being 2:1 ethyl acetate-hexane. Tetrahydrofuran was purified by distillation over LiAlH₄, then over ketyl radical, and 2,3'-biquinolyl was purified by recrystallization from benzene, followed by distillation.

4'-Phenyl-1',4'-dihydro-2,3'-biquinolyl (IVa). A mixture of 0.64 g (2.5 mmole) of 2,3'-biquinolyl and 0.05 g (7 mmole) of ground-up metallic lithium in 10 ml of THF is stirred in an argon atmosphere for 3 h at room temperature. A solution of 0.71 g (4.5 mmole) of bromobenzene in 4 ml of THF is then added dropwise. The reaction mixture is stirred for 1 h at room temperature, boiled for another 1 h, then 40 ml of water is added, and the mixture is extracted with benzene (3 × 30 ml). The organic layer is evaporated off. A yellow oil is obtained which crystallizes on addition of benzene. Yield, 65 g (78%), mp 212-213°C (from benzene). ESR spectrum (CDCl₃): 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''); 7.23 (1H, d, J_{5'6'} = 7.64 Hz, 5'-H); 7.34 (1H, d.d, J₅₆ = 8.02, J₆₇ = 7.51 Hz, 6-H); 7.38 (1H, d, J₃₄ = 8.91 Hz, 3-H); 7.46 (2H, d, J = 7.1 Hz, 2''-H, 6''-H); 7.61 (1H, d.d, J₆₇ = 7.51, J₇₈ = 8.61 Hz, 7-H); 7.62 (1H, d, J₅₆ = 8.02 Hz, 5-H); 7.77 (1H, d, J_{NH-2'H} = 5.5 Hz, 2'-H); 7.86 (1H, d, J₃₄ = 8.91 Hz, 4-H); 7.98 ppm (1H, d, J₇₈ = 8.61 Hz, 8-H). Found, %: C 86.28; H 5.29; N 8.43. C₂₄H₁₈N₂. Calculated, %: C 86.19; H 5.43; N 8.38.

4'-(1-Naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IVb) is obtained similarly to 4'-phenyl-1',4'-dihydro-2,3'-biquinolyl from 0.64 g (2.5 mmole) of 2,3'-biquinolyl, 0.05 g (7 mmole) of lithium and 0.72 g (3.5 mmole) of 1-bromonaphthalene. Yield, 0.7 g (73%), mp 196-197°C (from benzene). ESR spectrum (CDCl₃): 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, J₃₄ = 8.83 Hz, 3-H); 7.51-7.8 (7H, m, arom.); 7.81 (1H, d, J₃₄ = 8.83 Hz, 4-H); 7.86 (1H, d, J_{NH-2'H} = 5.7 Hz, 2'-H); 9.01 ppm (1H, d, J = 8.54 Hz, 8''-H or 8-H). Found, %: C 87.71; H 5.12; N 7.17. C₂₈H₂₀N₂. Calculated, %: C 87.46; H 5.25; N 7.29.

4'-(2-Pyridyl)-1',4'-dihydro-2,3'-biquinolyl (IVc) is obtained similarly to 4'-phenyl-1',4'-dihydro-2,3'-biquinolyl from 0.64 g (2.5 mmole) of 2,3'-biquinolyl, 0.05 g (7 mmole) of lithium and 0.34 g (3.5 mmole) of 2-fluoropyridine. Yield, 0.56 g (67%), mp 219-220°C (from benzene). ESR spectrum (CDCl₃): 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, J₅₆ = 7.98, J₆₇ = 7.62 Hz, 6-H); 7.46 (1H, d, J₃₄ = 8.96 Hz, 3-H); 7.5 (2H, m, 3''-H, 4''-H); 7.57 (1H, d.d, J₆₇ = 7.62, J₇₈ = 8.46 Hz, 7-H); 7.62 (1H, d, J₅₆ = 7.98 Hz, 5-H); 7.88 (1H, d, J₃₄ = 8.96 Hz, 4-H); 7.90 (1H, d, J₇₈ = 8.46, J₆₈ = 1.1 Hz, 8-H); 7.92 (1H, d, J_{NH-2'H} = 5.3 Hz, 2'-H); 8.51 ppm (1H, d.d, J_{5'6''} = 4.7, J_{4'6''} = 1.7 Hz, 6''-H). Found, %: C 82.64; H 4.98; N 12.38. C₂₃H₁₇N₃. Calculated, %: C 82.36; H 5.11; N 12.53.

4'-(1-Methyl-2-benzimidazolyl)-1',4'-dihydro-2',3'-biquinolyl (IVd) is obtained similarly to 4'-phenyl-1',4'-dihydro-2,3'-biquinolyl from 0.64 g (2.5 mmole) of 2,3'-biquinolyl, 0.05 g (7 mmole) of lithium and 0.58 g (3.5 mmole) of 1-methyl-2

chlorobenzimidazole. Yield, 0.66 g (68%), mp 266-267°C (from benzene). ESR spectrum (CDCl₃): 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, J_{5'6'} = 7.68 Hz, J_{6'7'} = 7.34 Hz, 6'-H); 6.92 (1H, d, J_{6'7'} = 7.34 Hz, J_{7'8'} = 8.05 Hz, 7'-H); 7.09 (1H, d, J_{5'6'} = 7.68 Hz, 5'-H); 7.13 (1H, d, J_{4'5'} = 8.55 Hz, J_{5'6'} = 7.38 Hz, J_{5'7'} = 1.63 Hz, 5''-H); 7.21 (1H, d, J_{5'6'} = 7.38 Hz, J_{6'7'} = 7.67 Hz, J_{4'5'} = 2.35 Hz, 6''-H); 7.29 (1H, d, J₅₆ = 8.04 Hz, J₆₇ = 7.31 Hz, 6-H); 7.38 (1H, d, J_{6'7'} = 7.67 Hz, 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, J₃₄ = 9.14 Hz, 3-H); 7.53 (1H, d, J₆₇ = 7.31 Hz, J₇₈ = 8.04 Hz, 7-H); 7.59 (1H, d, J_{4'5'} = 8.55 Hz, J_{4'6'} = 2.35 Hz, 4''-H); 7.6 (1H, d, J₅₆ = 8.04 Hz, 5-H); 7.78 (1H, d, J₇₈ = 8.04 Hz, 8-H); 7.80 (1H, d, J₃₄ = 9.14 Hz, 4-H); 10.39 ppm (1H, d, J_{NH-2'H} = 5.49 Hz, NH). Found, %: C 80.63; H 5.11; N 14.26. C₂₆H₂₀N₄. Calculated, %: C 80.39; H 5.19; N 14.42.

4'-(1-Isopropyl-2-benzimidazolyl)-1'-4'-dihydro-2,3'-biquinolyl (IVe) is obtained similarly to 4'-phenyl-1'-4'-dihydro-2,3'-biquinolyl from 0.64 g (2.5 mmole) of 2,3'-biquinolyl, 0.05 g (7 mmole) of lithium and 0.68 g (3.5 mmole) of 1-isopropyl-2-chlorobenzimidazole. Yield, 0.67 g (64%), 206-208°C (from benzene). ESR spectrum (CDCl₃): 1.73 (3H, d, J = 6.95 Hz, Me); 1.85 (3H, d, J = 6.95 Hz, 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, J_{5'6'} = 7.58 Hz, J_{6'7'} = 7.42 Hz, 6'-H); 7.0 (1H, d, J_{6'7'} = 7.42 Hz, 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, J₅₆ = 8.08 Hz, J₆₇ = 7.41 Hz, 6-H); 7.48 (1H, d, J₃₄ = 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, J₃₄ = 9.05 Hz, 4-H); 7.88 (1H, d, J₇₈ = 8.34 Hz, 8-H); 10.33 ppm (1H, d, J_{NH-2'H} = 5.49 Hz, NH). Found, %: C 80.95, H 5.68; N 13.37. C₂₈H₂₄N₄. Calculated, %: C 80.74, H 5.81; N 13.45.

1'-Methyl-4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (IVf). A mixture of 0.64 g (2.5 mmole) of 2,3'-biquinolyl and 0.05 g (7 mmole) of ground-up metallic lithium in 10 ml of THF is stirred in an argon atmosphere for 3 h at room temperature. A solution of 0.71 g (4.5 mmole) of bromobenzene in 4 ml of THF is then added dropwise. The reaction mixture is stirred for 1 h at room temperature, then boiled for another 1 h, and cooled to room temperature; 0.71 g (5 mmole) of methyl iodide in 2 ml of THF is added, and the mixture is stirred for 1 h. It is then decanted into 50 ml of water and extracted with benzene (3 × 30 ml). The organic layer is evaporated off. A yellow oil is obtained that crystallizes on addition of hexane. Yield, 0.65 g (75%), mp 173-174°C (from alcohol). ESR spectrum (CDCl₃): 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, J_{5'6'} = 7.61 Hz, J_{6'7'} = 7.76 Hz, 6'-H); 7.12 (1H, d, J_{6'7'} = 7.76 Hz, 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, J₅₆ = 7.99 Hz, J₆₇ = 7.56 Hz, 6-H); 7.42 (1H, d, J₃₄ = 9.01 Hz, 3-H); 7.48 (2H, d, J = 7.13 Hz, 2''-H, 6''-H); 7.64 (1H, d, J₆₇ = 7.56 Hz, J₇₈ = 8.53 Hz, 7-H); 7.67 (1H, d, J₅₆ = 7.99 Hz, 5-H); 7.81 (1H, s, 2'-H); 7.91 (1H, d, J₃₄ = 9.01 Hz, 4-H); 7.99 ppm (1H, d, J₇₈ = 8.53 Hz, 8-H). Found, %: C 86.44; H 5.67; N 7.89. C₂₅H₂₀N₂. Calculated, %: C 86.18, H 5.79; N 8.03.

1'-Methyl-4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IVg) is obtained similarly to 1'-methyl-4'-phenyl-1',4'-dihydro-2,3'-biquinolyl from 0.64 g (2.5 mmole) of 2,3'-biquinolyl, 0.05 g (7 mmole) of lithium, 0.72 g (3.5 mmole) of 1-bromonaphthalene, and 0.71 g (5 mmole) of methyl iodide. Yield, 0.73 g (73%), mp 151-153°C (from benzene with hexane). ESR spectrum (CDCl₃): 3.51 (3H, s, Me); 6.59 (1H, c, 4'-H); 6.77 (1H, d, J_{5'6'} = 7.78 Hz, J_{6'7'} = 7.62 Hz, 6'-H); 6.88 (1H, d, J_{7'8'} = 8.04 Hz, 8'-H); 7.1 (1H, d, J_{6'7'} = 7.62 Hz, J_{7'8'} = 8.04 Hz, 7'-H); 7.23-7.28 (4H, m, 5'-H, 6'-H, 3''-H, 6''-H); 7.49 (1H, d, J₃₄ = 8.79 Hz, 3-H); 7.51-7.8 (7H, m, arom.); 7.81 (1H, d, J₃₄ = 8.88 Hz, 4-H); 7.83 (1H, s, 2'-H); 8.99 ppm (1H, d, J = 8.54 Hz, 8''-H or 8-H). Found, %: C 87.64; H 5.47; N 6.89. C₂₉H₂₂N₂. Calculated, %: C 87.41; H 5.56; N 7.03.

1'-Benzyl-4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IVh) from 0.64 g (2.5 mmole) of 2,3'-biquinolyl, 0.05 g (7 mmole) of lithium, 0.72 g (3.5 mmole) of 1-bromonaphthalene, and 0.44 g (3.5 mmole) of benzyl chloride. Yield 0.85 g (72%), mp 143-144°C (from alcohol). ESR spectrum (CDCl₃): 5.1 (2H, d, J = 4.38 Hz, CH₂); 6.69 (1H, s, 4'-H); 6.77 (1H, d, J_{5'6'} = 7.58 Hz, J_{6'7'} = 7.36 Hz, 6'-H); 6.78 (1H, d, J_{7'8'} = 7.82 Hz, 8'-H); 6.95 (1H, d, J_{6'7'} = 7.36 Hz, 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, J₃₄ = 8.91 Hz, 3-H); 7.42-7.8 (7H, m, arom.); 7.81 (1H, d, J₃₄ = 8.91 Hz, 4-H); 7.93 (1H, s, 2'-H); 9.03 ppm (1H, d, J = 8.56 Hz, 8''- or 8-H). Found, %: C 88.75; H 5.44; N 5.81. C₃₅H₂₆N₂. Calculated, %: C 88.58, H 5.52; N 5.90.

4'-Phenyl-2,3'-biquinolyl (Va). A mixture of 0.42 g (1.25 mmole) of 4'-phenyl-1',4'-dihydro-2,3'-biquinolyl and 0.33 g (1.3 mmole) of iodine in 5 ml of pyridine is boiled for 10 min under a reflux condenser. The reaction mixture is then poured into 100 ml of water containing 1 g of sodium thiosulfate and 0.5 g of sodium hydroxide, and the white precipitate formed is filtered off and washed with water (3 × 30 ml). Yield, 0.4 g (95%), mp 133-134°C (from benzene). ESR spectrum (CDCl₃): 6.97 (1H, d, J₃₄ = 8.54 Hz, 3-H); 7.35 (5H, m, Ph); 7.52 (1H, d, J_{5'6'} = 8.11 Hz, J_{6'7'} = 6.95 Hz, 6'-H); 7.56 (1H, d, J₅₆ = 8.04 Hz, J₆₇ = 7.01 Hz, 6-H); 7.72 (1H, d, J_{6'7'} = 6.95 Hz, J_{7'8'} = 8.38 Hz, 7'-H); 7.74 (1H, d, J₆₇ = 7.01 Hz, J₇₈ = 8.31 Hz, 7-H); 7.76 (1H, d, J₅₆ = 8.04 Hz, 5-H); 7.79 (1H, d, J_{5'6'} = 8.11 Hz, 5'-H); 7.84 (1H, d, J₃₄ = 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 ppm (1H, s, 2'-H). M^+ 332. Found, %: 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 (Vb) is obtained similarly to 4'-phenyl-2,3'-biquinolyl from 0.48 g (1.25 mmole) of 4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl and 0.33 g (1.3 mmole) of iodine. Yield, 0.44 g (92%), mp 158-159°C (from benzene with hexane). ESR 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 (1-H, 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 ppm (1H, s, 2'-H). M^+ 382. Found, %: 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 (Vc) is obtained similarly to 4'-phenyl-2,3'-biquinolyl from 0.42 g (1.25 mmole) of 4'-(2-pyridyl)-1',4'-dihydro-2,3'-biquinolyl and 0.33 g (1.3 mmole) of iodine. Yield, 0.4 g (94%), mp 93-94°C (from benzene). ESR 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 ppm (1H, s, 2'-H). M^+ 333. Found, %: 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-1-benzimidazolyl)-2,3'-biquinolyl (Vd) is obtained similarly to 4'-phenyl-2,3'-biquinolyl from 0.48 g (1.25 mmole) of 4'-(1-methyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl and 0.33 g (1.3 mmole) of iodine. Yield, 0.46 g (95%), mp 338-340°C (from alcohol). ESR 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, $J_{4'5''} = 8.52$, $J_{5'6''} = 1.61$ 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, $J_{6'7''} = 7.65$, $J_{5'7''} = 7.41$, $J_{5'7''} = 1.61$ 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 ppm (1H, s, 2'-H). M^+ 386. Found, %: C 80.94; H 4.59; N 14.47. $C_{26}H_{18}N_4$. Calculated, %: 80.81; H 4.69; N 14.5.

4'-(1-Isopropyl-2-benzimidazolyl)-2,3'-biquinolyl (Ve) is obtained similarly to 4'-phenyl-2,3'-biquinolyl from 0.52 g (1.25 mmole) of 4'-(1-isopropyl-2-benzimidazolyl)-1',4'-dihydro-2,3'-biquinolyl and 0.33 g (1.3 mmole) of iodine. Yield, 0.47 g (91%), mp 221-222°C (from benzene). ESR spectrum ($CDCl_3$): 0.72 (3-H, d, $J = 6.83$ Hz, Me); 1.24 (3H, d, $J = 6.83$ Hz, 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 ppm (1H, s, 2'-H). M^+ 414. Found, %: 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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