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THE INVESTIGATION IN 2,3'-BIQUINOLINE SERIES 26.* REGIOSELECTIVE NITRATION OF 1'-ALKYL-1',4'-DIHYDRO-2,3'-BIQUINOLIN-4'-ONES AND 1'-ALKYL-1',2'-DIHYDRO-2,3'-BIQUINOLIN-2'-ONES

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The nitration of 1'-alkyl-1',4'-dihydro-2,3'-biquinolin-4'-ones and 1'-alkyl-1',2'-dihydro-2,3'-biquinolin-2'-ones has been investigated. It was shown that the regioselectivity of nitration of the first depends on the acidity of the medium and the order of adding reactants. In strongly acidic medium 1'-alkyl-5,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-ones or mixtures of them with 1'-alkyl-5-nitro-1',4'-dihydro-2,3'-biquinolin-4'-ones are formed. In less acidic media 1'-alkyl-6'-nitro-1',4'-dihydro-2,3'-biquinolin-4'-ones and then 1'-alkyl-6,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-ones are formed. Nitration of 1'-alkyl-1',2'-dihydro-2,3'-biquinolin-2'-ones leads to 1'-alkyl-6'-nitro-1',2'-dihydro-2,3'-biquinolin-2'-one and then 1'-alkyl-6,6',8'-trinitro-1',2'-dihydro-2,3'-biquinolin-2'-one.

Keywords: 1'-alkyl-1',2'-dihydro-2,3'-biquinolin-2'-ones, 1'-alkyl-1',4'-dihydro-2,3'-biquinolin-4'-ones, 2,3'-biquinoline, nitro-1'-alkyl-1',4'-dihydro-2,3'-biquinolin-4'-ones, nitro-1'-alkyl-1',2'-dihydro-2,3-biquinolin-2'-ones, nitration, regioselectivity.

The regioselectivity of electrophilic substitution in quinolines depends on the acidity of the medium [2, 3]. In strongly acidic media its conjugate acid participates in electrophilic substitution. Halogenation and nitration under these conditions proceeds at positions 5 and 8. It is considered that such orientation is the result of deactivation of the pyridine nucleus due to protonation. In less acidic media quinoline is substituted initially at position 3, and then in positions 6 and 8, which is explained by the formation of the corresponding dihydro derivatives. We showed previously [4] that nitration of 2,3'-biquinolines is effected at positions 5 and 8, which is explained by the direction of their monoprotonation to position 1'. The direction of halogenation depends on the acidity of the medium and is effected at positions 5 and 8 in strongly acidic media and at position 6' in weakly acidic media [5]. It might have been expected that the direction of nitration of 1'-alkyl-1',4'-dihydro-

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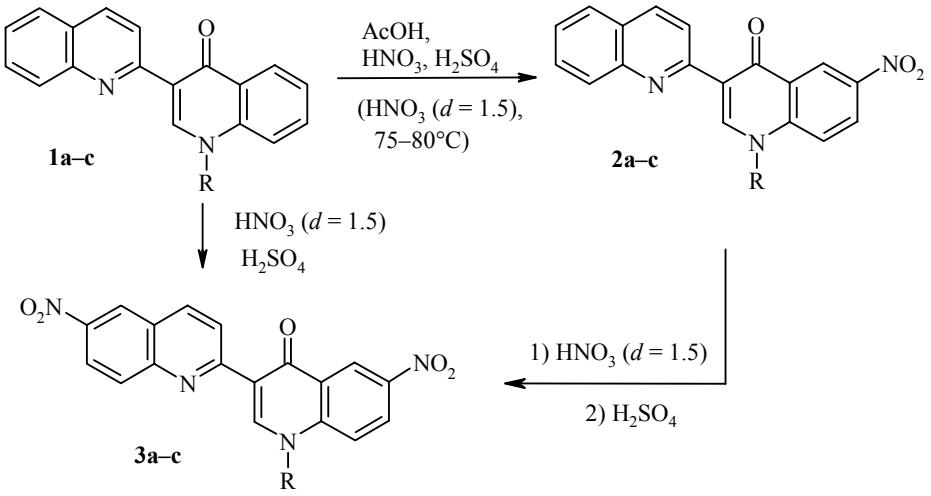
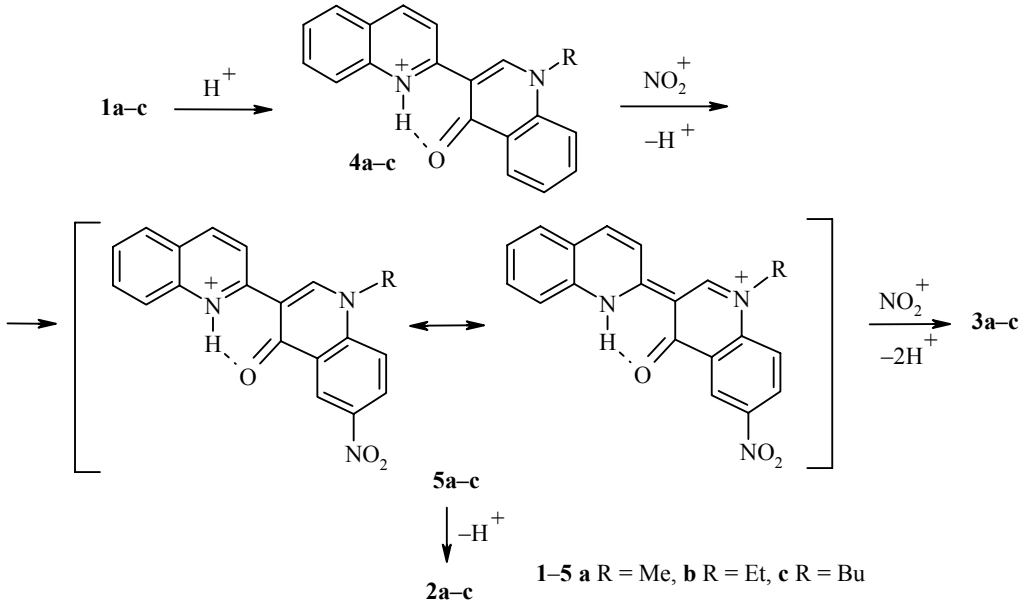
2,3'-biquinolin-4'-ones **1** and 1'-alkyl-1',2'-dihydro-2,3'-biquinolin-2'-ones **9** will also be changed depending on the acidity of the medium. Consequently the aim of the present work was the investigation of the regioselectivity of nitrating compounds **1** and **9**.

We showed that on boiling compounds **1** in glacial acetic acid for 5-6 h with a nitrating mixture based on nitric acid (d = 1.41 g/ml) (under these conditions the nitration of quinoline does not proceed) products of mononitration **2** at position 6' are formed in close to quantitative yield. In a similar manner nitration of compounds **1** with nitric acid (d = 1.5 g/ml) proceeds at 75-80°C.



1–3 a R = Me, **b** R = Et, **c** R = Bu

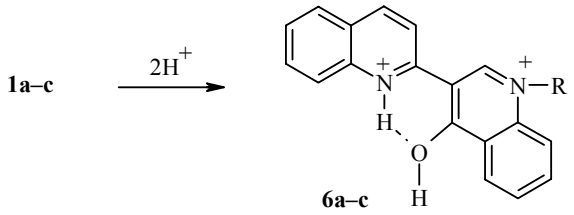
If nitration of compounds **1** is effected with a nitrating mixture based on nitric acid of density 1.5 g/ml at room temperature, or sulfuric acid is added to a solution of compound **1** in nitric acid (d = 1.5 g/ml), the sole reaction products are 6,6'-dinitrobiquinolines **3**. Compounds **3** are also formed on nitrating 6'-nitro derivatives **2** under the conditions for dinitrating biquinolones **1**.



1–5 a R = Me, **b** R = Et, **c** R = Bu

Such a result of nitration and dinitration is in accordance with the direction of monoprotonation of biquinolones **1** at the nitrogen atom in position 1, which has no effect on the orienting action of the nitrogen atom in position 1'. Protonated biquinolones **4** are nitrated at position 6' with the formation of protonated nitrobiquinolones **5**, the further nitration of which proceeds in position 6.

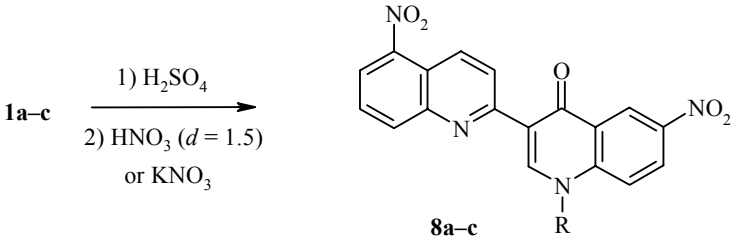
Evidently an increase in acidity of the medium will lead to the formation of diprotonated biquinolones. The regioselectivity of nitration must be changed by this. The most probable directions for diprotonation are the nitrogen atoms in position 1 and the oxygen atom.



1, 6 a R = Me, **b** R = Et, **c** R = Bu

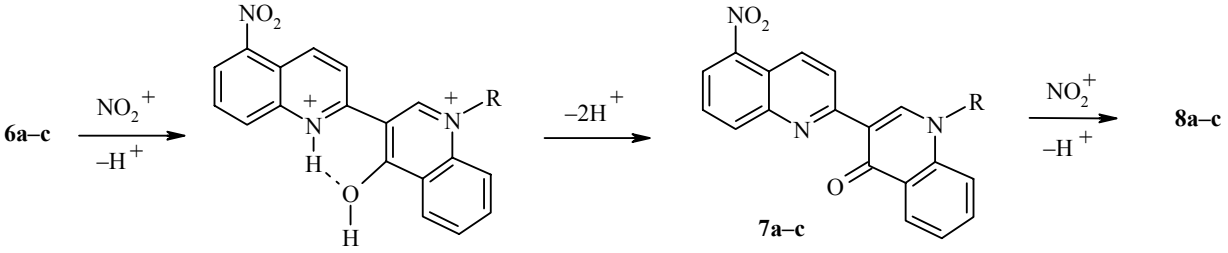
Such a direction of diprotonation must firstly make passive the 3'-quinoline fragment, consequently the formation of nitration products in positions 5 and 8 in the other quinoline nucleus was expected, and allowing for the steric factor the 5-nitro isomer must predominate.

We showed that a change in regioselectivity may be achieved by changing the order of adding reactants in the course of nitration. If nitric acid (d = 1.5 g/ml) or KNO_3 is added after dissolving compounds **1a-c** in sulfuric acid, then 5,6'-dinitroquinolones **8a-c** are formed in high yield.



1, **8 a** R = Me, **b** R = Et, **c** R = Bu

Probably diprotonation occurs on dissolving biquinolones **1** in conc. H_2SO_4, then mononitration at position 2 occurs. The introduction of a nitro group reduces the basicity and makes passive the 2-quinoline fragment, consequently the subsequent nitration is effected in the 3-quinoline fragment. Allowing for the effect of the N(1') atom and steric factors built up by the alkyl substituent, substitution proceeds at position 6'.

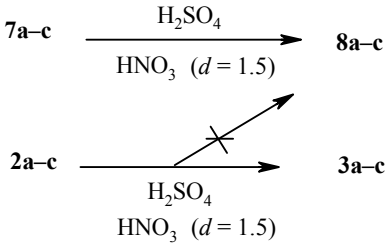


6–8 a R = Me, **b** R = Et, **c** R = Bu

The following experimental data confirm the proposed scheme for nitration:

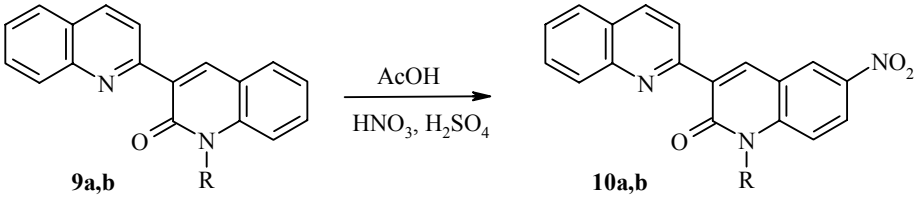
1. If the reaction does not go to completion, then a mixture is formed of 5-nitro derivatives **7a-c** and 5,6'-dinitro derivatives **8a-c**.

2. On using compounds **7a-c** as substrate the dinitro derivatives **8a-c** are formed in quantitative yield under the reaction conditions described above, while 6'-nitrobiquinolones **2a-c** under these conditions form exclusively 6,6'-dinitrobiquinolones **3a-c**.



Probably the absence of a product substituted at position 8 in the first nitration of the compound is linked, as in the case of quinoline N-oxides [6], with steric factors.

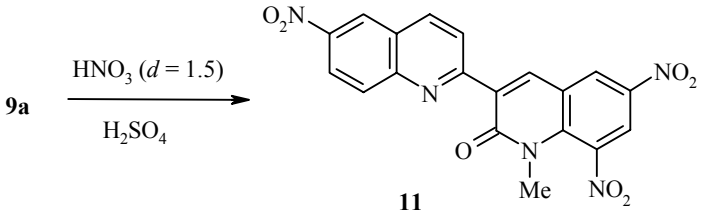
The nitration of biquinolones **9** with nitrating mixture based on nitric acid of density 1.41 g/ml on boiling in glacial acetic acid leads to the formation of 6'-nitro derivatives **10** in 82-86% yield.



9, **10 a** R = Me; **b** R = Et

Treatment of compound **9** with nitrating mixture based on nitric acid (d = 1.41 g/ml) at room temperature without solvent also leads to the same result, but in this case the reaction proceeded for 30 min, unlike the first case when the reaction proceeded for 5-6 h.

Under more rigid conditions the trinitration product **11** is formed from compound **9a**.



Products of nitration at position 5 were not successfully obtained, which is explained by the lower basicity of biquinolones **9** in comparison with compounds **1**.

The regioselectivity of nitration of biquinolones **1**, unlike biquinolones **9**, therefore depends on the acidity of the medium. On monoprotonation nitration proceeds at position 6' and then at position 6. Under diprotonation conditions the 5-nitro derivative is formed first.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker WP-200 instrument (200 MHz), internal standard was TMS. A check on the progress of reactions and the homogeneity of the synthesized compounds was effected on Silufol UV-254 plates, solvent was ethyl acetate.

1'-Alkyl-6'-nitro-1',4'-dihydro-2,3'-biquinolin-4'-ones 2a-c (General Method). Nitrating mixture (1 ml), prepared at 0°C from conc. H_2SO_4 (2 ml) and HNO_3 (d = 1.41 g/ml) (2 ml) was added to a solution of the appropriate 1'-alkyl-1',4'-dihydro-2,3'-biquinolin-4'-one **1** (1 mmol) in glacial acetic acid. The mixture was boiled for 1 h 30 min, further HNO_3 (0.5 ml) was added, and then boiled for 3 h. The reaction mixture was then poured into water (20 ml), and neutralized with ammonia solution, the precipitated solid was filtered off, and recrystallized from alcohol.

1'-Methyl-6'-nitro-1',4'-dihydro-2,3'-biquinolin-4'-one (2a) was obtained from 1'-methyl-1'-4'-dihydro-2,3'-biquinolin-4'-one (**1a**), yield was 0.28 g (84%). Yellow crystals, mp 312-313°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 4.09 (3H, s, CH_3); 7.58 (1H, ddd, $J_{5,6}$ = 8.2, $J_{6,7}$ = 7.0, $J_{6,8}$ = 1.2, H-6); 7.76 (1H, ddd, $J_{6,7}$ = 7.0, $J_{7,8}$ = 8.2, $J_{5,7}$ = 1.2, H-7); 7.97 (1H, dd, $J_{5,6}$ = 8.2, $J_{5,7}$ = 1.2, H-5); 8.00 (1H, d, $J_{7',8'}$ = 9.5, H-8'); 8.04 (1H, dd, $J_{7,8}$ = 8.2, $J_{6,8}$ = 1.2, H-8); 8.38 (1H, d, $J_{3,4}$ = 8.5, H-3); 8.53 (1H, dd, $J_{7',8'}$ = 9.5, $J_{5',7'}$ = 2.4, H-7'); 8.64 (1H, d, $J_{3,4}$ = 8.5, H-4); 9.07 (1H, d, $J_{5',7'}$ = 2.4, H-5'); 9.09 (1H, s, H-2'). Found, %: C 68.99; H 3.88; N 12.64. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

1'-Ethyl-6'-nitro-1',4'-dihydro-2,3'-biquinolin-4'-one (2b) was obtained from 1'-ethyl-1',4'-dihydro-2,3'-biquinolin-4'-one (**1b**), yield was 0.3 g (88%). Yellow crystals, mp 273-274°C (DMF). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (J, Hz): 1.43 (3H, t, J = 6.8, 1'-$CH_2C\underline{H}_3$); 4.57 (2H, q, J = 6.8, 1'-$C\underline{H}_2CH_3$); 7.58 (1H, ddd, $J_{5,6}$ = 8.2, $J_{6,7}$ = 7.0, $J_{6,8}$ = 1.2, H-6); 7.76 (1H, ddd, $J_{6,7}$ = 7.0, $J_{7,8}$ = 8.2, $J_{5,7}$ = 1.2, H-7); 7.97 (1H, dd, $J_{5,6}$ = 8.2, $J_{5,7}$ = 1.2, H-5); 8.00 (1H, d, $J_{7',8'}$ = 9.5, H-8'); 8.04 (1H, dd, $J_{7,8}$ = 8.2, $J_{6,8}$ = 1.2, H-8); 8.38 (1H, d, $J_{3,4}$ = 8.5, H-3); 8.53 (1H, dd, $J_{7',8'}$ = 9.5, $J_{5',7'}$ = 2.4, H-7'); 8.64 (1H, d, $J_{3,4}$ = 8.5, H-4); 9.07 (1H, d, $J_{5',7'}$ = 2.4, H-5'); 9.09 (1H, s, H-2'). Found, %: C 69.63; H 4.32; N 12.14. $C_{20}H_{15}N_3O_3$. Calculated, %: C 69.56; H 4.38; N 12.17.

1'-Butyl-6'-nitro-1',4'-dihydro-2,3'-biquinolin-4'-one (2c) was obtained from 1'-butyl-1',4'-dihydro-2,3'-biquinolin-4'-one (**1c**), yield was 0.33 g (89%). Yellow crystals, mp 203-204°C (DMF). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1.04 (3H, t, J = 7.3, 1'-$CH_2CH_2CH_2C\underline{H}_3$); 1.52 (2H, m, 1'-$CH_2CH_2C\underline{H}_2CH_3$); 1.96 (2H, m, 1'-$CH_2C\underline{H}_2CH_2CH_3$); 4.36 (2H, t, J = 7.3, 1'-$C\underline{H}_2CH_2CH_2CH_3$); 7.53 (1H, ddd, $J_{5,6}$ = 8.0, $J_{6,7}$ = 7.1, $J_{6,8}$ = 1.2, H-6); 7.59 (1H, d, $J_{7',8'}$ = 9.1, H-8'); 7.72 (1H, ddd, $J_{6,7}$ = 7.1, $J_{7,8}$ = 8.4, $J_{5,7}$ = 1.2, H-7); 7.84 (1H, dd, $J_{5,6}$ = 8.0, $J_{5,7}$ = 1.2, H-5); 8.08 (1H, dd, $J_{7,8}$ = 8.4, $J_{6.8}$ = 1.2, H-8); 8.25 (1H, d, $J_{3,4}$ = 8.4, H-4); 8.46 (1H, dd, $J_{7',8'}$ = 9.1, $J_{5',7'}$ = 2.6, H-7'); 8.79 (1H, d, $J_{3,4}$ = 8.4, H-3); 9.02 (1H, s, H-2'); 9.44 (1H, d, $J_{5',7'}$ = 2.6, H-5'). Found, %: C 70.89; H 5.07; N 11.19. $C_{22}H_{19}N_3O_3$. Calculated, %: C 70.76; H 5.13; N 11.25.

1'-Alkyl-6,6'-dinitro-1',4'-dihydro-2,3'-quinolin-4'-ones 3a-c (General Method). Conc. H_2SO_4 (2 ml) was added to a solution of the appropriate compound **1** (1 mmol) in conc. HNO_3 (d = 1.5 g/ml), the mixture was maintained at ~20°C for 30 min, poured into water (20 ml), and neutralized with ammonia solution. The precipitated solid was filtered off, and recrystallized from DMF.

1'-Methyl-6,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-one (3a) was obtained from compound **1a**, yield was 0.35 g (92%). Yellow crystals, mp >350°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 4.13 (3H, s, CH_3); 8.04 (1H, d, $J_{7',8'}$ = 9.35, H-8); 8.23 (1H, d, $J_{7,8}$ = 9.35, H-8); 8.47 (1H, dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 8.5, H-7); 8.56 (1H, dd, $J_{7',8'}$ = 9.35, $J_{5',7'}$ = 2.2, H-7'); 8.71 (1H, d, $J_{3,4}$ = 8.8, H-4); 8.90 (1H, d, $J_{3,4}$ = 8.8, H-3); 9.01 (1H, d, $J_{5,7}$ = 2.2, H-5); 9.12 (1H, d, $J_{5',7'}$ = 2.2, H-5'); 9.22 (1H, s, H-2'). Found, %: C 60.85; H 3.17; N 14.77. $C_{19}H_{12}N_4O_5$. Calculated, %: C 60.64; H 3.21; N 14.89.

1'-Ethyl-6,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-one (3b) was obtained from compound **1b**, yield was 0.34 g (88%). Yellow crystals, mp 314-316°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 1.49 (3H, t, J = 7.15, 1'-$CH_2C\underline{H}_3$); 4.59 (2H, q, J = 7.15, 1'-$C\underline{H}_2CH_3$); 8.10 (1H, d, $J_{7',8'}$ = 9.35, H-8'); 8.20 (1H, d, $J_{7,8}$ = 9.35, H-8); 8.45 (1H, dd, $J_{6,7}$ = 9.35, $J_{5,7}$ = 2.75, H-7); 8.52 (1H, dd, $J_{7',8'}$ = 9.35, $J_{5',7'}$ = 2.75, H-7');

8.69 (1H, d, $J_{3,4}$ = 8.8, H-4); 8.88 (1H, d, $J_{3,4}$ = 8.8, H-3); 8.98 (1H, d, $J_{5,7}$ = 2.75, H-5); 9.10 (1H, d, $J_{5',7'}$ = 2.75, H-5'); 9.22 (1H, s, H-2'). Found, %: C 61.74; H 3.57; N 14.23. $C_{20}H_{14}N_4O_5$. Calculated, %: C 61.54; H 3.62; N 14.35.

1'-Butyl-6,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-one (3c) was obtained from compound **1c**, yield was 0.37 g (89%). Yellow crystals, mp 270-272°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.97 (3H, t, *J* = 7.7, 1'-$CH_2CH_2CH_2C\underline{H}_3$); 1.46 (2H, m, 1'-$CH_2CH_2C\underline{H}_2CH_3$); 1.87 (2H, m, 1'-$CH_2C\underline{H}_2CH_2CH_3$); 4.55 (2H, t, *J* = 7.7, 1'-$C\underline{H}_2CH_2CH_2CH_3$); 8.11 (1H, d, $J_{7',8'}$ = 9.35, H-8'); 8.21 (1H, d, $J_{7,8}$ = 9.35, H-8); 8.46 (1H, dd, $J_{7,8}$ = 9.35, $J_{5,7}$ = 2.2, H-7); 8.52 (1H, dd, $J_{7',8'}$ = 9.35, $J_{5',7'}$ = 2.75, H-7'); 8.70 (1H, d, $J_{3,4}$ = 8.8, H-4); 8.88 (1H, d, $J_{3,4}$ = 8.8, H-3); 9.00 (1H, d, $J_{5,7}$ = 2.2, H-5); 9.11 (1H, d, $J_{5',7'}$ = 2.75, H-5'); 9.21 (1H, s, H-2'). Found, %: C 62.93; H 4.28; N 13.27. $C_{22}H_{18}N_4O_5$. Calculated, %: C 63.15; H 4.34; N 13.39.

1'-Alkyl-5,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-ones 8a-c (General Method). Nitric acid (*d* = 1.5 g/ml) (0.38 g, 6 mmol) was added carefully to a solution of the appropriate compound **1** (5 mmol) in conc. H_2SO_4 (5 ml). The solution was maintained at ~20°C for 30 min, then carefully poured into water (20 ml), neutralized with ammonia solution, the precipitated solid was filtered off, and recrystallized from DMF.

1'-Methyl-5,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-one (8a) was obtained from compound **1a**, yield was 1.27 g (67%). Yellow crystals, mp 325-326°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.63 (3H, s, 1'-CH_3); 7.95 (1H, dd, $J_{6,7}$ = 8.25, $J_{5,6}$ = 8.25, H-6); 8.11 (1H, d, $J_{7',8'}$ = 9.35, H-8'); 8.42 (1H, dd, $J_{5,6}$ = 8.25, $J_{5,7}$ = 1.1, H-5); 8.47 (1H, dd, $J_{6,7}$ = 8.25, $J_{5,7}$ = 1.1, H-7); 8.51 (1H, dd, $J_{7',8'}$ = 9.35, $J_{5',7'}$ = 2.75, H-7'); 8.59 (1H, d, $J_{3,4}$ = 8.8, H-4); 8.86 (1H, d, $J_{3,4}$ = 8.8, H-3); 9.09 (1H, d, $J_{5',7'}$ = 2.75, H-5'); 9.19 (1H, s, H-2'). Found, %: C 60.73; H 3.15; N 14.82. $C_{29}H_{12}N_4O_5$. Calculated, %: C 60.64; H 3.21; N 14.89.

1'-Ethyl-5,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-one (8b) was obtained from compound **1b**, yield was 1.23 g (63%). Yellow crystals, mp 295-296°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.50 (3H, t, *J* = 7.15, 1'-$CH_2C\underline{H}_3$); 4.60 (2H, q, *J* = 7.15, 1'-$C\underline{H}_2CH_3$); 7.94 (1H, dd, $J_{6,7}$ = 8.25, $J_{5,6}$ = 8.25, H-6); 8.12 (1H, d, $J_{7',8'}$ = 9.35, H-8'); 8.39 (1H, dd, $J_{5,6}$ = 8.25, $J_{5,7}$ = 1.1, H-5), 8.45 (1H, dd, $J_{6,7}$ = 8.25, $J_{5,7}$ = 1.1, H-7); 8.53 (1H, dd, $J_{7',8'}$ = 9.35, $J_{5',7'}$ = 2.75, H-7'); 8.59 (1H, d, $J_{3,4}$ = 8.8, H-4); 8.86 (1H, d, $J_{3,4}$ = 8.8, H-3); 9.12 (1H, d, $J_{5',7'}$ = 2.75, H-5'); 9.21 (1H, s, H-2'). Found, %: C 61.73; H 3.55; N 14.24. $C_{20}H_{14}N_4O_5$. Calculated, %: C 61.54; H 3.62; N 14.35.

1'-Butyl-5,6'-dinitro-1',4'-dihydro-2,3'-biquinolin-4'-one (8c) was obtained from compound **1c**, yield was 1.32 g (63%). Yellow crystals, mp 270-272°C (DMF). ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 1.00 (3H, t, *J* = 7.3, 1'-$CH_2CH_2CH_2C\underline{H}_3$); 1.48 (2H, m, 1'-$CH_2CH_2C\underline{H}_2CH_3$); 1.89 (2H, m, 1'-$CH_2C\underline{H}_2CH_2CH_3$); 4.36 (2H, t, *J* = 7.3, 1'-$C\underline{H}_2CH_2CH_2CH_3$); 7.59 (1H, dd, $J_{5,6}$ = 7.7, $J_{6,7}$ = 8.0, H-6); 7.83 (1H, d, $J_{7',8'}$ = 9.5, H-8'); 8.07 (1H, dd, $J_{5,6}$ = 7.7, $J_{5,7}$ = 1.1, H-5); 8.11 (1H, dd, $J_{6,7}$ = 8.0, $J_{5,7}$ = 1.1, H-7); 8.39 (1H, d, $J_{3,4}$ = 8.9, H-4); 8.42 (1H, dd, $J_{7',8'}$ = 9.5, $J_{5',7'}$ = 2.8, H-7'); 8.93 (1H, d, $J_{3,4}$ = 8.9, H-3); 8.95 (1H, s, H-2'); 9.12 (1H, d, $J_{5',7'}$ = 2.8, H-5'). Found, %: C 62.92; H 4.29; N 13.25. $C_{22}H_{18}N_4O_5$. Calculated, %: C 63.15; H 4.34; N 13.39.

1'-Methyl-5-nitro-1',4'-dihydro-2,3'-biquinolin-4'-one (7a) was obtained from compound **1a**, on reducing the amount of nitric acid to 0.12 g. The mixture was separated by extracting compound **7a** with ethyl acetate and then by chromatography. Yield was 0.07 g (21%). Bright-yellow crystals, mp 245-247°C (ethyl acetate). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.02 (3H, s, CH_3); 7.54 (1H, ddd, $J_{5',6'}$ = 8.4, $J_{5',7'}$ = 7.9, $J_{6',8'}$ = 1.4, H-6'); 7.68 (1H, dd, $J_{6,7}$ = 7.6, $J_{7,8}$ = 7.6, H-7); 7.81 (2H, m, H-7',8'); 8.26 (2H, d, $J_{6,7}$ = 7.6, $J_{7,8}$ = 7.6, H-6,8); 8.40 (1H, d, $J_{5',6'}$ = 8.4, H-5'); 8.54 (1H, d, $J_{3,4}$ = 8.85, H-3); 8.86 (1H, s, H-4'); 8.96 (1H, d, $J_{3,4}$ = 8.85, H-4). Found, %: C 68.97; H 3.89; N 12.65. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

1'-Alkyl-6'-nitro-1',2'-dihydro-2,3'-biquinolin-2'-ones 10a,b (General Method). A. A mixture of the appropriate 1'-alkyl-1',2'-dihydro-2,3'-biquinolin-2'-one **9** (2 mmol), HNO_3 (*d* = 1.41 g/ml) (0.19 ml), conc. H_2SO_4 (0.63 ml), and glacial acetic acid (5 ml) was maintained at 80°C for 5-6 h, poured into water (100 ml), and neutralized with NaOH solution. The solid was then filtered off, and dried.

B. A mixture of the appropriate 1'-alkyl-1',2'-dihydro-2,3'-biquinolin-2'-one (2 mmol) and nitric acid (*d* = 1.5 g/ml) (10 ml) was maintained at 60°C for 30 min, poured into water (50 ml), neutralized with ammonia solution, the solid was filtered off, and dried.

1'-Methyl-6'-nitro-1',2'-dihydro-2,3'-biquinolin-2'-one (10a) was obtained from 1'-methyl-1',2'-di-hydro-2,3'-biquinolin-2'-one (**9a**). Yield by method A was 0.56 g (84%), and by method B 0.59 g (88.5%). Light-yellow crystals, mp 295-296°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.51 (3H, s, CH_3); 7.65 (1H, ddd, $J_{5,6}$ = 7.95, $J_{6,7}$ = 7.0, $J_{6,8}$ = 1.2, H-6); 7.79 (1H, d, $J_{7',8'}$ = 9.2, H-8'); 7.82 (1H, ddd, $J_{6,7}$ = 7.0, $J_{7,8}$ = 8.85, $J_{5,7}$ = 1.2, H-7); 8.03 (1H, dd, $J_{5,6}$ = 7.95, $J_{5,7}$ = 1.2, H-5); 8.11 (1H, dd, $J_{7,8}$ = 8.85, $J_{6,8}$ = 1.2, H-8); 8.29 (1H, d, $J_{3,4}$ = 8.85, H-4); 8.43 (1H, d, $J_{3,4}$ = 8.85, H-3); 8.46 (1H, dd, $J_{7',8'}$ = 9.2, $J_{5',7'}$ = 2.4, H-7'); 8.90 (1H, s, H-4'); 8.96 (1H, d, $J_{5',7'}$ = 2.4, H-5'). Found, %: C 69.01; H 3.89; N 12.62. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

1'-Ethyl-6'-nitro-1',2'-dihydro-2,3'-biquinolin-2'-one (10b) was obtained from compound **9b**. Yield by method A was 0.6 g (87%), by method B 0.64 g (93%). Light-yellow crystals, mp 205-206°C (DMF). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 1.43 (3H, t, *J* = 6.8, 1'-$CH_2C\underline{H}_3$); 4.57 (2H, q, *J* = 6.8, 1'-$C\underline{H}_2CH_3$); 7.64 (1H, ddd, $J_{5,6}$ = 8.5, $J_{6,7}$ = 8.1, $J_{6,8}$ = 1.3, H-6); 7.81 (1H, ddd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 8.5, $J_{5,7}$ = 1.3, H-7); 7.88 (1H, d, $J_{7',8'}$ = 9.4, H-8'); 8.01 (1H, dd, $J_{5,6}$ = 8.5, $J_{5,7}$ = 1.3, H-5); 8.14 (1H, dd, $J_{7,8}$ = 8.5, $J_{6,8}$ = 1.3, H-8); 8.39 (1H, d, $J_{3,4}$ = 8.5, H-4); 8.49 (1H, dd, $J_{7',8'}$ = 9.4, $J_{5',7'}$ = 3.0, H-7'); 8.52 (1H, d, $J_{3,4}$ = 8.5, H-3); 8.90 (1H, d, $J_{5',7'}$ = 3.0, H-5'); 9.00 (1H, s, H-4'). Found, %: C 69.64; H 4.32; N 12.13. $C_{20}H_{15}N_3O_3$. Calculated, %: C 69.56; H 4.38; N 12.17.

1'-Methyl-6,6',8'-trinitro-1',2'-dihydro-2,3'-biquinolin-2'-one (11). Conc. H_2SO_4 (3 ml) was added to a solution of compound **9a** (0.286 g, 1 mmol) in HNO_3 (*d* = 1.5 g/ml) (5 ml), the mixture was maintained for 30 min at ~20°C, poured into water (30 ml), neutralized with ammonia solution, and the precipitated solid was filtered off. Yield was 0.35 g (83%). Yellow crystals, mp 345-346°C (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.49 (3H, s, CH_3); 8.30 (1H, d, $J_{7,8}$ = 9.2, H-8); 8.48 (1H, d, $J_{3,4}$ = 8.85, H-4); 8.52 (1H, dd, $J_{7,8}$ = 9.2, $J_{5,7}$ = 2.75, H-7); 8.82 (1H, d, $J_{3,4}$ = 8.85, H-3); 8.95 (1H, d, $J_{5',7'}$ = 2.45, H-5'); 9.11 (1H, d, $J_{5,7}$ = 2.75, H-5); 9.14 (1H, s, H-4'); 9.28 (1H, d, $J_{5'7'}$ = 2.45, H-7'). Found, %: C 54.29; H 2.58; N 16.57. $C_{19}H_{13}N_3O_3$. Calculated, %: C 54.16; H 2.63; N 16.62.

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