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4-HYDROXY-2-QUINOLONES 137*. SYNTHESIS, STRUCTURE, AND SPECTROSCOPIC CHARACTERISTICS OF DIETHYL 2,2'-DIOXO-1,2,3,4,1',2',3',4'-OCTAHYDRO[4,4']BIQUINOLINYL-3,3'-DICARBOXYLATE

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Treatment of the ethyl esters of 1-R-4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylic acids with zinc dust in glacial acetic acid gives high yields of diethyl 2,2'-dioxo-1,2,3,4,1',2',3',4'-octahydro[4,4']biquinolinyl-3,3'-dicarboxylates. The structural features of the synthesized compounds together with their NMR and mass spectra are discussed.

Keywords: 4-chloro-2-oxo-1,2-dihydroquinolines, reductive dehalogenation, X-ray analysis.

Together with catalytic hydrogenation, various reductive systems of nonprecious metals and acids have been used for the direct exchange of halogen for hydrogen in organic compounds. In laboratory practice, zinc dust in conjunction with acetic acid is widely used [2]. However, our attempts to extend this rather simple and cheap method to ethyl 1-R-4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylates **1a-c** as a possible method of preparing the corresponding 4H-derivatives were unsuccessful.

It was found that the dehalogenation of the 4-chloro-substituted esters **1a-c** under the studied reaction conditions is accompanied by the unwanted (in this case) reduction of the $C_{(3)}$=$C_{(4)}$ bond together with a dimerization finally leading to good yields of the diethyl 2,2'-dioxo-1,2,3,4,1',2',3',4'-octahydro-[4,4']biquinolinyl-3,3'-dicarboxylates **2a-c**. It was interesting that partial formation of similar biquinolines (e.g. the NH derivative **2a**) was noted in the electrolysis of diethyl 2-nitrobenzylidenemalonates at a controlled potential [3].

An X-ray analysis of one of these compounds gave unambiguous evidence for their structure. It was found that the N-ethyl-substituted compound **2c** (Figure 1, Tables 1 and 2) is a dimer consisting of two monomer fragments (**A** and **B**) joined by a $C_{(7)}$–$C_{(7a)}$ bond which is orientated almost perpendicularly to the planes of the bicyclic fragments (torsional angle $C_{(1)}$–$C_{(6)}$–$C_{(7)}$–$C_{(7a)}$ 82.9(3)º).

* For Communication 136 see [1]

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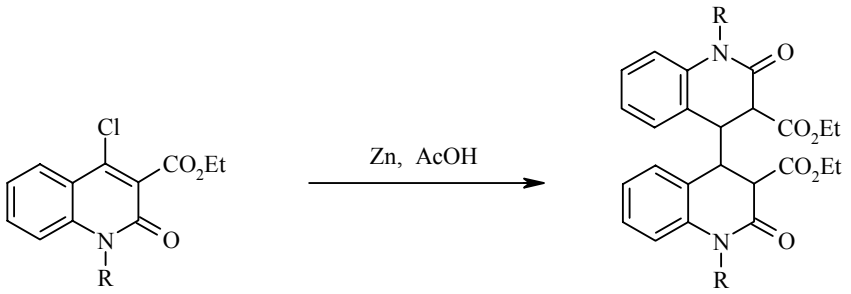


1a–c **2a–c**

1, 2 a R = H; **b** R = Me; **c** R = Et

The tetrahydroquinolone rings **A** and **B** in the studied compound are orientated on opposite sides of the $C_{(7)}$–$C_{(7a)}$ bond and differ from one another in some geometric parameters. Such a molecular structure leads to the formation of marked steric strain between the **A** and **B** fragments as indicated by the shortened intramolecular contacts: $H_{(7a)}\cdots C_{(9b)}$ 2.60 (sum of van der Waal radii 2.87 [4]), $H_{(7b)}\cdots C_{(9a)}$ 2.70 (2.87), $H_{(8a)}\cdots C_{(8b)}$ 2.66 (2.87), $H_{(8b)}\cdots C_{(8a)}$ 2.69 (2.87), and $H_{(8a)}\cdots H_{(8b)}$ 1.99 Å (2.34 Å). In both parts the pyridone ring occurs in a *twist boat* conformation with a different degree of folding (folding parameters [5]: S = 0.66, θ = 55.5, ψ =30.0 for **A** and S = 0.71, θ = 55.7º, ψ = 29.3º for **B**). The deviations of the atoms $C_{(8)}$ and $C_{(9)}$ from the mean square plane taken through the remaining ring atoms were -0.85 and -0.40 Å respectively in molecule **A** and 0.45 and 0.92 Å in molecule **B**. The ester substituents is axially orientated (torsional angle $C_{(10)}$–$C_{(8)}$–$C_{(9)}$–$N_{(1)}$ 87.1(3) in **A** and 88.7(3)º in **B)** and are twisted relative to the $C_{(9)}$–$C_{(8)}$ bond in opposite directions (torsional angle $C_{(9)}$–$C_{(8)}$–$C_{(10)}$–$O_{(2)}$ 18.2(4) in **A** and -135.3(4)º in **B**). The ethyl group of the ester substituent in fragment **A** is perpendicular to the $C_{(10)}$–$O_{(3)}$ bond (torsional angle $C_{(10)}$–$O_{(3)}$–$C_{(11)}$–$C_{(12)}$ -90.4(5)º). In the opposing fragment the ethyl group in the ester substituent occurs in a conformation intermediate between *–sc* and perpendicular (torsional angle $C_{(10)}$–$O_{(3)}$–$C_{(11)}$–$C_{(12)}$ just -78.6(5)º) which is likely stabilized by the attractive interaction $H_{(11d)}\cdots O_{(2b)}$ 2.39 Å (2.46 Å). Such a positioning of the ethyl groups in both ester substituents leads to formation of a shortened intramolecular contact $H_{(12a)}\cdots C_{(10)}$ of 2.75 in **A** and 2.83 Å in **B** (2.87 Å) (Figure 1).

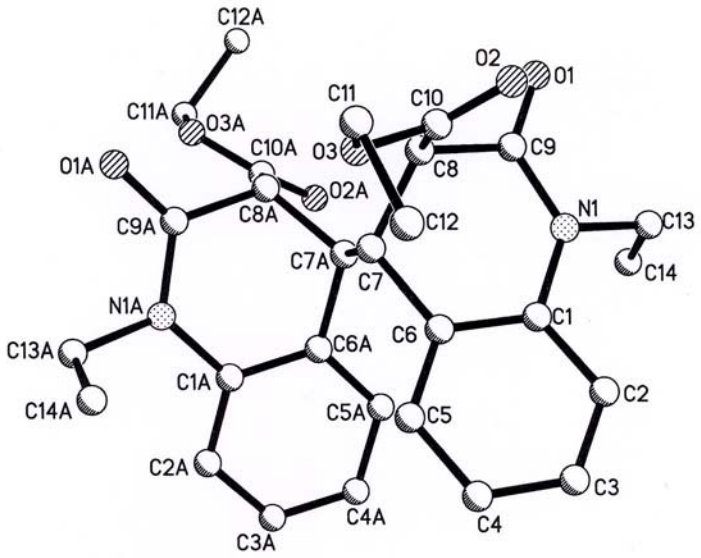


Fig. 1. Structure of the biquinoline molecule **2c** with atomic numbering.

TABLE 1. Bond Lengths (*l*) in the Biquinoline **2c** Structure

Bond	*l*, Å	Bond	*l*, Å
$N_{(1A)}$–$C_{(9A)}$	1.362(4)	$N_{(1A)}$–$C_{(1A)}$	1.429(4)
$N_{(1A)}$–$C_{(13A)}$	1.476(4)	$O_{(1A)}$–$C_{(9A)}$	1.234(4)
$O_{(2A)}$–$C_{(10A)}$	1.209(1)	$O_{(3A)}$–$C_{(10A)}$	1.299(4)
$O_{(3A)}$–$C_{(11A)}$	1.447(5)	$C_{(1A)}$–$C_{(6A)}$	1.377(4)
$C_{(1A)}$–$C_{(2A)}$	1.383(5)	$C_{(2A)}$–$C_{(3A)}$	1.380(6)
$C_{(3A)}$–$C_{(4A)}$	1.339(6)	$C_{(4A)}$–$C_{(5A)}$	1.380(5)
$C_{(5A)}$–$C_{(6A)}$	1.398(4)	$C_{(6A)}$–$C_{(7A)}$	1.498(4)
$C_{(7A)}$–$C_{(8A)}$	1.535(4)	$C_{(8A)}$–$C_{(10A)}$	1.486(4)
$C_{(8A)}$–$C_{(9A)}$	1.513(4)	$C_{(11A)}$–$C_{(12A)}$	1.510(4)
$C_{(13A)}$–$C_{(14A)}$	1.530(4)	$N_{(1B)}$–$C_{(9B)}$	1.357(4)
$N_{(1B)}$–$C_{(1B)}$	1.431(4)	$N_{(1B)}$–$C_{(13B)}$	1.460(4)
$O_{(1B)}$–$C_{(9B)}$	1.224(4)	$O_{(2B)}$–$C_{(10B)}$	1.208(1)
$O_{(3B)}$–$C_{(10B)}$	1.306(4)	$O_{(3B)}$–$C_{(11B)}$	1.469(4)
$C_{(1B)}$–$C_{(2B)}$	1.388(4)	$C_{(1B)}$–$C_{(6B)}$	1.390(4)
$C_{(2B)}$–$C_{(3B)}$	1.358(5)	$C_{(3B)}$–$C_{(4B)}$	1.355(5)
$C_{(4B)}$–$C_{(5B)}$	1.395(4)	$C_{(5B)}$–$C_{(6B)}$	1.372(4)
$C_{(6B)}$–$C_{(7B)}$	1.498(4)	$C_{(7B)}$–$C_{(8B)}$	1.529(4)
$C_{(7B)}$–$C_{(7A)}$	1.554(4)	$C_{(8B)}$–$C_{(10B)}$	1.493(4)
$C_{(8B)}$–$C_{(9B)}$	1.502(4)	$C_{(11B)}$–$C_{(12B)}$	1.515(4)
$C_{(13B)}$–$C_{(14B)}$	1.514(4)		

TABLE 2. Valence Angles (ω) in the Biquinoline **2c** Structure

Angle	ω, deg.	Angle	ω, deg.
$C_{(9A)}$–$N_{(1A)}$–$C_{(1A)}$	123.2(3)	$C_{(9A)}$–$N_{(1A)}$–$C_{(13A)}$	116.4(3)
$C_{(1A)}$–$N_{(1A)}$–$C_{(13A)}$	120.0(3)	$C_{(10A)}$–$O_{(3A)}$–$C_{(11A)}$	118.9(3)
$C_{(6A)}$–$C_{(1A)}$–$C_{(2A)}$	119.3(3)	$C_{(6A)}$–$C_{(1A)}$–$N_{(1A)}$	118.8(3)
$C_{(2A)}$–$C_{(1A)}$–$N_{(1A)}$	121.9(3)	$C_{(3A)}$–$C_{(2A)}$–$C_{(1A)}$	120.5(4)
$C_{(4A)}$–$C_{(3A)}$–$C_{(2A)}$	121.1(4)	$C_{(3A)}$–$C_{(4A)}$–$C_{(5A)}$	119.3(4)
$C_{(4A)}$–$C_{(5A)}$–$C_{(6A)}$	121.1(4)	$C_{(1A)}$–$C_{(6A)}$–$C_{(5A)}$	118.8(3)
$C_{(1A)}$–$C_{(6A)}$–$C_{(7A)}$	119.2(3)	$C_{(5A)}$–$C_{(6A)}$–$C_{(7A)}$	122.0(3)
$C_{(6A)}$–$C_{(7A)}$–$C_{(8A)}$	109.1(2)	$C_{(6A)}$–$C_{(7A)}$–$C_{(7B)}$	112.9(2)
$C_{(8A)}$–$C_{(7A)}$–$C_{(7B)}$	110.2(2)	$C_{(10A)}$–$C_{(8A)}$–$C_{(9A)}$	111.8(2)
$C_{(10A)}$–$C_{(8A)}$–$C_{(7A)}$	111.9(2)	$C_{(9A)}$–$C_{(8A)}$–$C_{(7A)}$	111.2(2)
$O_{(1A)}$–$C_{(9A)}$–$N_{(1A)}$	123.3(3)	$O_{(1A)}$–$C_{(9A)}$–$C_{(8A)}$	120.9(3)
$N_{(1A)}$–$C_{(9A)}$–$C_{(8A)}$	115.8(3)	$O_{(2A)}$–$C_{(10A)}$–$O_{(3A)}$	123.1(4)
$O_{(2A)}$–$C_{(10A)}$–$C_{(8A)}$	123.5(3)	$O_{(3A)}$–$C_{(10A)}$–$C_{(8A)}$	113.4(3)
$O_{(3A)}$–$C_{(11A)}$–$C_{(12A)}$	109.3(4)	$N_{(1A)}$–$C_{(13A)}$–$C_{(14A)}$	110.0(3)
$C_{(9B)}$–$N_{(1B)}$–$C_{(1B)}$	121.1(2)	$C_{(9B)}$–$N_{(1B)}$–$C_{(13B)}$	118.3(3)
$C_{(1B)}$–$N_{(1B)}$–$C_{(13B)}$	120.5(2)	$C_{(10B)}$–$O_{(3B)}$–$C_{(11B)}$	118.6(3)
$C_{(2B)}$–$C_{(1B)}$–$C_{(6B)}$	119.9(3)	$C_{(2B)}$–$C_{(1B)}$–$N_{(1B)}$	121.6(3)
$C_{(6B)}$–$C_{(1B)}$–$N_{(1B)}$	118.5(2)	$C_{(3B)}$–$C_{(2B)}$–$C_{(1B)}$	119.8(3)
$C_{(4B)}$–$C_{(3B)}$–$C_{(2B)}$	121.9(3)	$C_{(3B)}$–$C_{(4B)}$–$C_{(5B)}$	118.4(3)
$C_{(6B)}$–$C_{(5B)}$–$C_{(4B)}$	121.4(3)	$C_{(5B)}$–$C_{(6B)}$–$C_{(1B)}$	118.6(2)
$C_{(5B)}$–$C_{(6B)}$–$C_{(7B)}$	122.7(2)	$C_{(1B)}$–$C_{(6B)}$–$C_{(7B)}$	118.8(3)
$C_{(6B)}$–$C_{(7B)}$–$C_{(8B)}$	107.5(2)	$C_{(6B)}$–$C_{(7B)}$–$C_{(7A)}$	112.3(2)
$C_{(8B)}$–$C_{(7B)}$–$C_{(7A)}$	111.3(2)	$C_{(10B)}$–$C_{(8B)}$–$C_{(9B)}$	110.9(2)
$C_{(10B)}$–$C_{(8B)}$–$C_{(7B)}$	114.2(2)	$C_{(9B)}$–$C_{(8B)}$–$C_{(7B)}$	109.5(2)
$O_{(1B)}$–$C_{(9B)}$–$N_{(1B)}$	121.4(3)	$O_{(1B)}$–$C_{(9B)}$–$C_{(8B)}$	121.1(3)
$N_{(1B)}$–$C_{(9B)}$–$C_{(8B)}$	117.5(3)	$O_{(2B)}$–$C_{(10B)}$–$O_{(3B)}$	123.7(3)
$O_{(2B)}$–$C_{(10B)}$–$C_{(8B)}$	122.8(3)	$O_{(3B)}$–$C_{(10B)}$–$C_{(8B)}$	113.4(2)
$O_{(3B)}$–$C_{(11B)}$–$C_{(12B)}$	106.6(4)	$N_{(1B)}$–$C_{(13B)}$–$C_{(14B)}$	111.7(3)

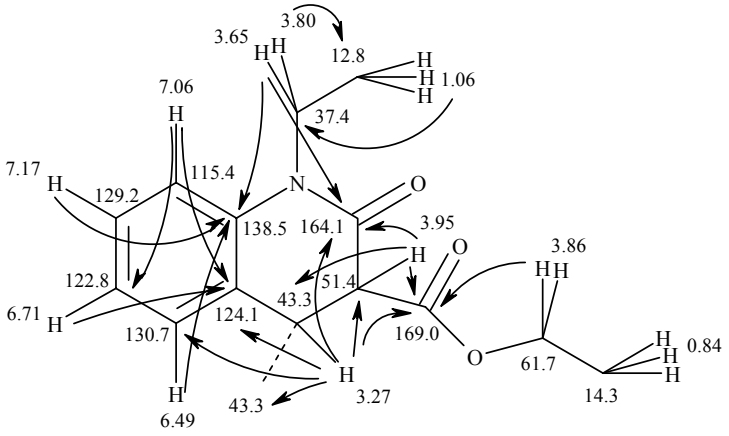
A marked repulsion between the ethyl substituent at atom $N_{(1)}$ and the neighboring carbonyl group and benzene ring atoms (shortened intramolecular contacts $H_{(2)}\cdots C_{(13)}$ 2.67 in **A** and 2.64 in **B** (2.87), $H_{(2)}\cdots H_{(13a)}$ 2.11 in **A** and 2.02 in **B** (2.34), $H_{(13a\})}\cdots C_{(2)}$ 2.67 in **A** and 2.59 in **B** (2.87), $H_{(13b)}\cdots O_{(1)}$ 2.30 in **A** and 2.32 Å in **B** (2.46 Å)) leads to the fact that the ethyl group is located virtually perpendicularly to the bicyclic plane (torsional angle $C_{(1)}–N_{(1)}–C_{(13)}–C_{(14)}$ 81.4(4) in **A** and 72.2(4)º in **B**).

In the crystal the molecules of the biquinoline **2c** form a 3D lattice and are inter connected by weak intermolecular hydrogen bonds: $C_{(11a)}–H_{(11b)}\cdots O_{(2a')}$ (2-*x*, -*y*, -*z*), H···O 2.40 Å, C–H···O 151º; $C_{(14b)}–H_{(14c)}\cdots O_{(2a')}$ (1+*x*, *y*, *z*), H···O 2.41 Å, C–H···O 168º and $C_{(8)}–H_{(8b)}\cdots O_{(1b')}$ (2-*x*, -*y*, 1-*z*), H···O 2.39 Å, C–H···O 137º. The crystal also shows a shortened intermolecular contact $H_{(12d)}\cdots H_{(13d)}$ (1+*x*, *y*, *z*) 2.10 Å (2.34 Å).

The unusual spatial structure of the biquinolines **2** is undoubtedly of interest and was further investigated by conventional spectroscopic study, e.g. using NMR and mass spectrometry.

Thus in the ^{1}H NMR spectrum of the N,N'-diethyl derivative **2c** all of the signals fit the structural formula. However, besides these there are observed signals of a minor component, the nature of which fully replicates that of the main compound. It follows that a solution of the compound studied is a mixture of diastereomers or rotamers. This situation is not changed when the solvent is changed from DMSO to deuterochloroform. Signals for the minor component are also seen in the carbon spectrum. Starting from the structural formula of biquinoline **2c** found by X-ray analysis it can be proposed that this compound exists as a mixture of two diastereomers. This is possible since the molecule contains asymmetric carbon atoms. Alternatively, the compound may have stable conformations of the tetrahydropyridin-2-one ring. To clear this situation up we have measured the spectra of the biquinoline **2c** in DMSO solution when heated. Since it was observed that increasing the temperature to 90ºC had no effect at all on the nature of the spectrum it infers the absence of interconverting components. Hence it follows that we are dealing with a mixture of two diastereomers.

The ^{13}C NMR spectrum also does not oppose the structure of this compound but assignment of all of the signals could not be made without additional investigations. With this in mind we have measured the $^{13}C–^1H$ NMR heteronuclear correlation spectra through one (HMQC) and through 2 or 3 (sometimes 4) chemical bonds (HMBC) (Table 3).



2c

The HMQC spectra gave a full, unambiguous assignment of the signals for all of the protonated carbon atoms and the correlations in the HMBC spectra gave the possibility of assigning the quaternary carbon atoms. The arrows show the most important correlations in the HMBC spectrum which served as the basis for the assignments made above.

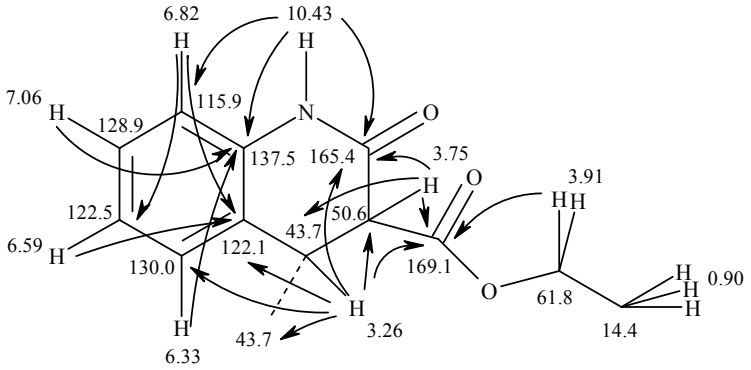
Hence the signal at 138.5 ppm is assigned to the $C_{(8a)}$ atom on the basis of the correlation with the signals for the $H_{(5)}$ and $H_{(7)}$ protons and also the protons of the methylene group at $N_{(1)}$. The signal at 124.1 ppm is

TABLE 3. Heteronuclear ^{1}H–^{13}C Correlations found for Biquinoline **2c.**

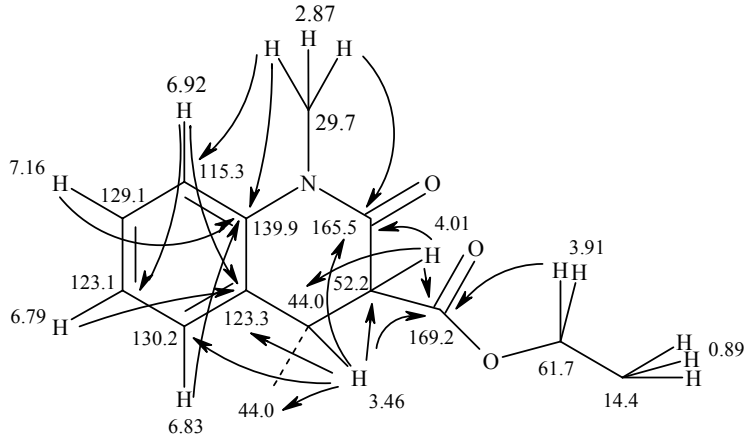
δ, ppm	HMQC	HMBC
7.17	129.2	138.5; 130.7; 124.1
7.06	115.4	138.5; 129.2; 124.1; 122.8
6.71	122.8	138.5; 130.7; 124.1; 115.4
6.49	130.7	138.5; 129.2; 124.1; 122.8; 115.4; 43.3
3.95	51.4	124.1; 169.0; 164.1; 43.2;
3.86	61.7	169.0; 14.3
3.80	37.4	138.5; 164.1; 12.8
3.65	37.4	138.5; 164.1; 12.8
3.27	43.3	138.5; 130.7; 124.1; 169.0; 164.1; 51.4; 43.3 ($C_{(4')}$)
1.06	12.8	37.4
0.84	14.3	61.7

due to atom $C_{(4a)}$ since it correlates with the $H_{(6)}$, $H_{(8)}$, and $H_{(4)}$ signals. Atom $C_{(2)}$ has a chemical shift of 164.1 ppm confirmed by correlation with the signals for the $H_{(3)}$ and $H_{(4)}$ atoms as well as with the methylene protons at $N_{(1)}$. It was interesting that the dimer structure for the investigated compound follows directly from the HMBC spectrum. This judgement is based on the presence of the correlation between the $H_{(4)}$ proton signal at 3.27 ppm and the $C_{(4')}$ signal which coincides with the signal for the $C_{(4)}$ atom and has a chemical shift of 43.3 ppm.

The ^{13}C–^{1}H heteronuclear correlations spectra for the homologs of N,N'-diethyl-substituted derivative **2c** which contained methyl groups (biquinoline **2b**) or hydrogen atoms (biquinoline **2a**) on the heterocyclic nitrogen atoms were similar as expected. The assignments of the signals in their proton and carbon spectra are given in the scheme below together with the most important HMBC correlations.



2a



2b

The heteronuclear correlations discovered do not leave doubt regarding the structure of the synthesized compounds. It should be noted that, as in the example of the analog **2c** described above, the ^{1}H NMR spectrum of the biquinoline **2b** shows the presence of a minor component (15%). At the same time the signal for the N-methyl substituent is not split into two equally intense components, in contrast to the signal of the N-methylene group in biquinoline **2c**. This helps to confirm that the separation of this signal in compound **2c** is associated with hindrance to rotation of the N-ethyl substituent and thus with the appearance of diastereotopism for the methylene group signal. The minor component signal is absent in the proton spectrum of the NH derivative **2a**.

Chromato-mass spectrometric investigation of the biquinolines **2** (at least with the use of gas chromatography) proved impossible. As they possess quite high molecular weights these substances cannot be converted to the gaseous phase and pass through a chromatographic column without degradation. Direct introduction was successful in producing the molecular ions but the peak intensities were low and did not exceed 18%. Electron impact initially broke up the $C_{(4)}$–$C_{(4')}$ bond which conjugates quinolone rings and the mass spectra of the biquinolines **2a-c** showed maximum intensity peaks for fragment ions with *m/z* 218, 232, and 246 respectively. After that the main direction of formation of fragment ions was due to fission of C–C or C–OEt bonds on both sides of the ester fragment carbonyl group. In the case of the N-alkyl-substituted biquinolines **2b-c** the elimination of the whole ethoxycarbonyl group was preferred as indicated by the more intense (up to 80%) peaks with *m/z* 160 and 174. Less likely, but achieved all the same, is a second route involving initial loss of a molecule of ethanol with corresponding peak intensities for *m/z* 186 and 200 not greater than 22%. For the NH derivative **2a** the probability of decomposition by one of the indicated routes is approximately the same.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra for the biquinolines **2a-c** and HMQC and HMBC heteronuclear correlation spectra were recorded on a Varian Mercury-400 spectrometer (400 and 100 MHz respectively). All of the 2D experiments were carried out with gradient selection of useful signals. The mixing times in the pulse sequences were $^1J_{CH}$ = 140 and $^{2\text{-}3}J_{CH}$ = 8 Hz. The number of increments was 128 in the HMQC spectra and 400 in the HMBC spectra. In all cases, DMSO-d_6 was used as solvent and TMS as internal standard. Mass spectra were recorded on a Varian 1200L spectrometer in full scanning mode in the range 35-700 *m/z* and electron impact ionization 70 eV using direct introduction.

Diethyl 2,2'-Dioxo-1,2,3,4,1',2',3',4'-octahydro[4,4']biquinolinyl-3,3'-dicarboxylate (2a). Zinc powder (5 g) was added in small portions with stirring to a refluxing solution of the 4-chloro-substituted ester **1a** (2.51 g, 0.01 mol) in glacial acetic acid (30 ml). After all of the zinc addition it was refluxed with stirring for 6 h. The reaction mixture was cooled and filtered. The residue on the filter was washed several times with 2-propanol. The mixture of solvents was removed from the filtrate *in vacuo*. The residue was thoroughly triturated with hexane (15 ml) and placed in a freeze drier for several hours. The residue of biquinoline **1a** was filtered off, washed with cold hexane, and dried. Yield 1.50 g (69%); mp 211-213ºC (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.43 (2H, s, 2NH); 7.06 (2H, t, *J* = 7.8, H-7,7'); 6.82 (2H, d, *J* = 7.8, H-8,8'); 6.59 (2H, t, *J* = 7.7, H-6,6'); 6.33 (2H, d, *J* = 7.5, H-5,5'); 3.91 (4H, q, *J* = 7.0, 2OCH_2); 3.75 (2H, s, H-3,3'); 3.26 (2H, s, H-4,4'); 0.90 (6H, t, *J* = 7.1, 2$OCH_2C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 169.1 (COO), 165.4 ($C_{(2)}$), 137.5 ($C_{(8a)}$), 130.0 ($C_{(5)}$), 128.9 ($C_{(7)}$), 122.5 ($C_{(6)}$), 122.1 ($C_{(4a)}$), 115.9 ($C_{(8)}$), 61.8 ($COO\underline{C}H_2$), 50.6 ($C_{(3)}$), 43.7 ($C_{(4)}$), 14.4 ($OCH_2\underline{C}H_3$). Mass spectrum, *m/z* (I_{rel}, %): 436 $[M]^+$ (7), 218 $[M/2]^+$ (100), 172 $[M/2\text{-EtOH}]^+$ (21), 146 $[M/2\text{-}COOC_2H_4]^+$ (26). Found, %: C 66.13; H 5.66; N 6.34. $C_{24}H_{24}N_2O_6$. Calculated, %: C 66.05; H 5.54; N 6.42.

Compounds 2b,c were prepared by a similar method.

Diethyl 1,1'-Dimethyl-2,2'-dioxo-1,2,3,4,1',2',3',4'-octahydro[4,4']biquinolinyl-3,3'-dicarboxylate (2b). Yield 75%; mp 146-148ºC (aqueous 2-propanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.16 (2H, t, *J* = 7.4, H-7,7'); 6.92 (2H, d, *J* = 7.4, H-8,8'); 6.83 (2H, d, *J* = 7.0, H-5,5'); 6.79 (2H, t, *J* = 7.0, H-6,6'); 4.01 (2H, s, H-3,3'); 3.91 (4H, m, $2OCH_2$); 3.46 (2H, s, H-4,4'); 2.87 (6H, s, $2NCH_3$); 0.89 (6H, t, *J* = 7.0, $2OCH_2C\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 169.2 (COO), 165.5 ($C_{(2)}$), 139.9 ($C_{(8a)}$), 130.2 ($C_{(5)}$), 129.1 ($C_{(7)}$), 123.3 ($C_{(4a)}$), 123.1 ($C_{(6)}$), 115.3 ($C_{(8)}$), 61.7 ($COO\underline{C}H_2$), 52.2 ($C_{(3)}$), 44.0 ($C_{(4)}$), 29.7 (NCH_3), 14.4 ($OCH_2\underline{C}H_3$). Mass spectrum, *m/z* (I_{rel}, %): 464 $[M]^+$ (14), 232 $[M/2]^+$ (100), 186 $(M/2\text{-EtOH})^+$ (20), 160 $[M/2\text{-}COOC_2H_4]^+$ (88). Found, %: C 67.33; H 6.17; N 6.12. $C_{26}H_{28}N_2O_6$. Calculated, %: C 67.23; H 6.08; N 6.03.

Diethyl 1,1'-Diethyl-2,2'-dioxo-1,2,3,4,1',2',3',4'-octahydro[4,4']biquinolinyl-3,3'-dicarboxylate (2c). Yield 72%; mp 131-133ºC (hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.17 (2H, t, *J* = 7.5, H-7,7'); 7.06 (2H, d, *J* = 7.5, H-8,8'); 6.71 (2H, t, *J* = 7.7, H-6,6'); 6.49 (2H, d, *J* = 7.7, H-5,5'); 3.95 (2H, s, H-3,3'); 3.86 (4H, m, $2OCH_2$); 3.80 (2H, m, 2NCH); 3.65 (2H, m, 2NCH); 3.27 (2H, s, H-4,4'); 1.06 (6H, t, *J* = 7.2, $2NCH_2C\underline{H}_3$); 0.84 (6H, t, *J* = 7.4, $2OCH_2OC\underline{H}_3$). ^{13}C NMR spectrum, δ, ppm: 169.0 (COO), 164.1 ($C_{(2)}$), 138.5 ($C_{(8a)}$), 130.7 ($C_{(5)}$), 129.2 ($C_{(7)}$), 124.1 ($C_{(4a)}$), 122.8 ($C_{(6)}$), 115.4 ($C_{(8)}$), 61.7 ($COO\underline{C}H_2$), 51.4 ($C_{(3)}$), 43.3 ($C_{(4)}$), 37.4 ($N\underline{C}H_2$), 14.3 ($OCH_2\underline{C}H_3$), 12.8 ($NCH_2\underline{C}H_3$). Mass spectrum, *m/z* (I_{rel}, %): 492 $[M]^+$ (18), 246 $(M/2)^+$ (100), 200 $[M/2\text{-EtOH}]^+$ (22), 174 $[M/2\text{-}COOC_2H_4]^+$ (79). Found, %: C 68.21; H 6.59; N 5.63. $C_{28}H_{22}N_2O_6$. Calculated, %: C 68.28; H 6.55; N 5.69.

X-ray Structural Investigation. Crystals of the N,N'-diethyl-substituted biquinoline **2c** are triclinic (hexane), at 20ºC: a = 9.437(3), b = 10.499(6), c = 13.870(9) Å, α = 79.32(5)º, β = 76.86(4)º, γ = 86.10(4)º, V = 1315(1) Å^3, M_r = 492.56, Z = 2, space group $P\bar{1}$, d_{calc} = 1.244 g/cm^3, μ(MoKα) = 0.088 mm^{-1}, F(000) = 524. The unit cell parameters and intensities of 7116 reflections (4290 independent with R_{int} = 0.025) were measured on an Xcalibur-3 diffractometer (MoKα radiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 50º).

The structure was solved by a direct method using the SHELXTL program package [6]. In the refinement of the structure limits were placed on the bond lengths for $C_{(11)}$–$C_{(12)}$ and $C_{(13)}$–$C_{(14)}$ of 1.54 Å and for $C_{(sp^2)}$=O 1.21 Å. The positions of the hydrogen atoms were revealed from electron density difference synthesis and refined by the "riding" method with $U_{iso} = nU_{eq}$ for a non-hydrogen atom bonded to the given H atom (n = 1.5 for a methyl group and n = 1.2 for the remaining hydrogen atoms). The structure was refined in F^2 full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms to wR_2 = 0.145 for 4235 reflections (R_1 = 0.053 for 1780 reflections with $F > 4\sigma(F)$, S = 0.785). The full crystallographic information has been placed in the Cambridge structural database (reference No. CCDC 631477). The interatomic distances and valence angles are given in Tables 1 and 2.

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