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ELECTROCHEMICAL CONVERSIONS OF 2-METHYL-3-NITRO-4-PHENYLQUINOLINE, ITS QUINOLINIUM SALTS, AND HYDROGENATED DERIVATIVES*

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Classical polarography, cyclic voltammetry, and EPR spectroscopy was used to study electrochemical reduction and oxidation of 3-nitro derivatives of 2-methyl-4-phenylquinoline, the corresponding quinolinium perchlorates, and 1,2- and 1,4-dihydroquinolines. The nitro derivatives of quinoline and 1,2-dihydroquinoline are reduced in the first step at the nitro group; the quinolinium cations are reduced at the heterocycle followed by reduction of the nitro group; and in 1,4-dihydroquinolines, the nitro group is not reduced. Electrochemical reduction processes associated with electron transfer in the heterocycle mainly display the same behavior as established for pyridine derivatives. But important differences were observed in electrochemical oxidation: the N-methyl derivative of 1,4-dihydroquinoline is oxidized significantly more easily than the corresponding N-unsubstituted derivative of 1,4-dihydroquinoline (in the 1,4-dihydropyridine series, the difference in potentials is fairly small), and even more easily than the corresponding N-methyl derivative of 1,2-dihydroquinoline.

Keywords: 3-nitro derivatives of 2-methyl-4-phenylquinoline, quinolinium perchlorates, 1,2- and 1,4-dihydroquinoline, EPR spectra, electrochemistry.

A characteristic feature of π-deficient heterocycles containing electron-acceptor substituents is that the electrochemical reduction process can involve two electron-acceptor parts of the molecule: the substituent and the heterocycle itself. Depending on the ratio of their electrophilicities, the structure of the heterocycle, conjugation with respect to the π-electron system, and the conformational features, electrochemical reduction may occur along different routes, with different intermediates and end products. Quinolines substituted at the 3 position by electron-acceptor groups are chemically reduced by sodium borohydride when boiled in ethanol to form 1,4-dihydroquinoline [1], while the corresponding quaternary quinolinium salts are reduced to form 1,2-dihydroquinolines [2]. 2-Substituted quinolines are reduced by sodium borohydride to 1,2-dihydroquinolines [3], while 2,3,4-substituted quinolines are reduced by sodium borohydride in acid medium to 1,2-dihydroquinolines with simultaneous partial substitution of the hydrogen atom on the nitrogen atom (to an ethyl group in acetic acid and to a methyl group in formic acid). It is only in reduction of 2-methyl-3-nitro-4-phenylquinoline that 1,4-dihydroquinoline is isolated in addition to N-ethyl- and N-unsubstituted

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* Dedicated to Professor L. I. Belen'kii on the occasion of his 70th birthday, as a sign of our deep respect and gratitude for his selfless efforts to support the scientific level of heterocyclic chemistry and our journal.

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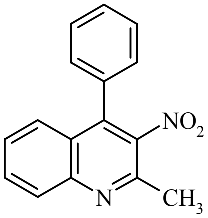
1,2-dihydroquinolines [4]. In reduction of the corresponding quinolinium salts, 1,2-dihydroquinoline is formed; and 1,4-dihydroquinoline is obtained only when a nitro group is present at the 3 position [5]. Consequently, depending on the reaction conditions for chemical reduction and the electron-acceptor properties of the substituent at the β-position, 2,3,4-substituted quinolines are reduced mainly with formation of 1,2-dihydro derivatives; and only 3-nitro derivatives can form the 1,4-dihydro structure.

The ability of the quinoline ring to undergo polarographic reduction was established long ago; the characteristics of electrochemical reduction of some quinoline derivatives in protogenic media have been studied [6-9]. New compounds have been synthesized which contain different substituents in different positions of the quinoline ring, but the electrochemical parameters of these compounds have not been determined. In this work, we have used polarography at a dropping mercury electrode, cyclic voltammetry at a stationary glass/graphite electrode, and EPR spectroscopy to study electrochemical reduction of 2-methyl-3-nitro-4-phenylquinoline (**1**), quinolinium perchlorates **2a,b**, 1,2- and 1,4-dihydroquinoline (types **3** and **4**) in an aprotic solvent, acetonitrile.



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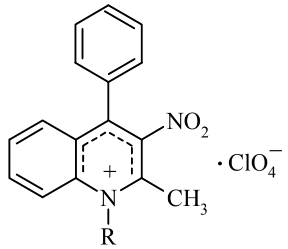
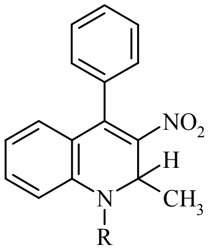
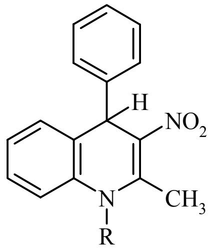


2a R = CH$_3$, **2b** R = H



3a R = CH$_3$, **3c** R = C$_2$H$_5$



4a R = CH$_3$, **4b** R = H

2,4-Substituted 3-nitroquinoline 1 is reduced at a dropping mercury electrode with formation of three polarographic waves. The first wave at a potential of -1.25 V is a one-electron wave; and on the cyclic voltammetry curve, in addition to the cathodic reduction peak we see a reverse electrochemical oxidation peak. The second and third reduction waves at -1.75 and -2.32 V respectively are irreversible, and each wave corresponds to transfer of 2.2 electrons (Fig. 1). It has been shown [9] that unsubstituted quinoline in dimethylformamide is electrochemically reduced in two one-electron steps in the potential range from -2.0 to -2.6 V, while introducing an electron-acceptor substituent at the 4 position of the heterocycle facilitates reduction [10]. When a nitro group is present on the quinoline ring, it is specifically the nitro group which undergoes the primary reversible reduction. The primary radical anions **6** are formed in the first reduction step for **1**, and these radical anions are electrochemically stable. We recorded their EPR spectra under the electrochemical generation conditions of [11] at the potential of the first polarographic wave. Due to extensive conjugation of the π-electron system and interaction of the unpaired electron with all the paramagnetic nuclei, the spectrum contains a rich hyperfine structure (Fig. 2*a*). Even for a very high dilution (10-5 mol·l^{-1}), we can determine only two hyperfine coupling constants: specifically, for coupling with the nitrogen atom of the nitro group and for coupling with the two almost equivalent protons ($a_{N,NO2}$ = 8.45 G, $a_{Hi} \cong a_{Hj}$ = 2.0 G). If electrochemical reduction is performed up to the second step, then during reverse oxidation, in addition to the oxidation peak of the primary reduction product, on the cyclic voltammogram we see new products which

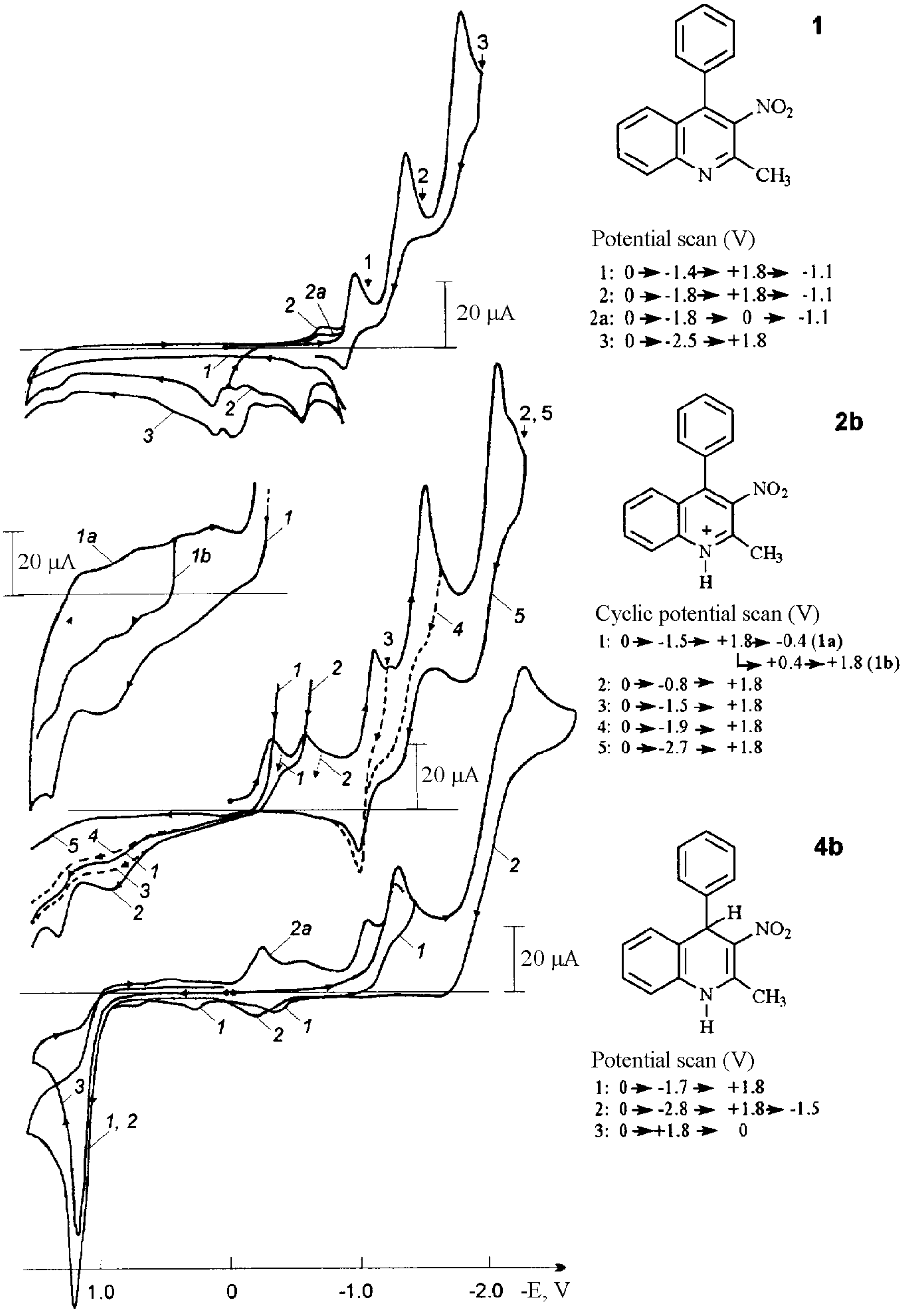


Fig. 1. Cyclic voltammograms for electrochemical reduction and oxidation of quinoline **1**, the N-unsubstituted quinolinium cation **2b**, 1,4-dihydroquinoline **4b**.

oxidize at potentials of -0.75, -0.30, -0.05 V, and at the positive potential of +0.15 V (Fig. 1). When the potential scan is repeated, a new reduction peak at -0.83 V is recorded. In analogy with previously studied nitrobenzene derivatives [12, 13], we may hypothesize that the redox system -0.83/-0.75 (V) corresponds to the nitroso product which arises as a result of oxidation of the hydroxylamine formed during primary reduction, but

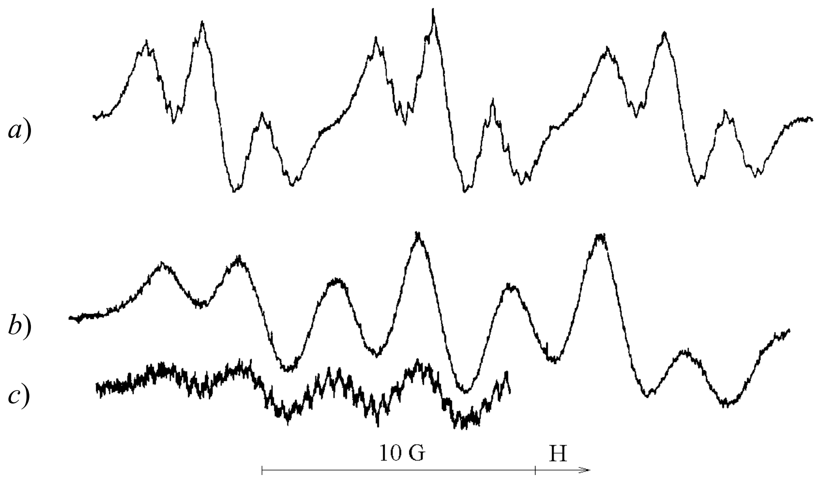


Fig. 2. EPR spectra of radical anions formed during electrochemical generation: *a*) at the potential of the first polarographic wave of compound **1** and at the potential of the third polarographic wave of compound **2b**; *b*) at the potential of the first polarographic wave of compound **3a** and at the potential of the second polarographic wave of compound **2a**; *c*) additional splitting of the signals of spectrum (*b*) with reduced modulation amplitude.

EPR spectra could not be detected for a 3-nitrosoquinoline structure. If electrochemical reduction is performed up to the third wave (-2.6 V), then on the anodic branch the oxidation peaks recorded during reduction up to the first wave are retained. It is only the height of the oxidation peak of the primary product that decreases. The intensity of the peak at the potential -0.05 V increases, while in the positive potential range a new product is formed which oxidizes at the potential of +1.50 V (Fig. 1).

3-Nitroquinolinium salts 2a,b are electrochemically reduced in a much more complicated way. 2,3,4-Substituted N-methylquinolinium perchlorate **2a** in the potential range from 0 to -2.8 V is reduced with formation of three polarographic waves, while the N-substituted analog **2b** forms five polarographic waves of different heights and degrees of reversibility.

The first reduction wave of compound **2a** at -0.62 V does not reach the one-electron level and is irreversible. The second wave at a potential of -1.22 V also does not reach the one-electron level, but electron transfer in this step is clearly reversible. The third wave, recorded at a potential of -1.70 V (the height of this wave corresponds to transfer of one electron) is irreversible. If the potential scan is performed in the range from 0 to -0.75 V, the first reduction step is irreversible; but if the scan is held at the potential of the first wave (-0.75 V), then a product is formed in the reaction which is oxidized at -0.53 V (Fig. 3). In addition, on the anodic branch of the cycle, in the positive potential range three new oxidation peaks are formed at +0.80, +1.20, and +1.55 V. If during electrochemical reduction the cyclic scan is continued up to the potential of the second polarographic wave or held at the potential of the first reduction step, then on the anodic branch we see two oxidation peaks corresponding to reversible oxidation of the second reduction step and a product oxidized at -0.53 V. In the positive potential range, we observe a change in the peak height ratio for the oxidation peaks at +0.80 and +1.20 V, i.e., the peak intensity at 1.20 V increases. If reduction is performed up to the third step, then the reversible oxidation peak of the second wave decreases, the oxidation peak of the product at -0.53 V increases, a new oxidation peak appears at +0.70 V, and the products oxidizing at potentials of +0.80 and +1.20 V disappear (Fig. 3). We recorded the EPR spectra of a fairly unstable free radical during electrochemical generation for **2a** at the potential of the first wave (total length of the spectrum, 35 G). The hyperfine structure constants could not be determined due to considerable signal overlap and the close values of the constants. At

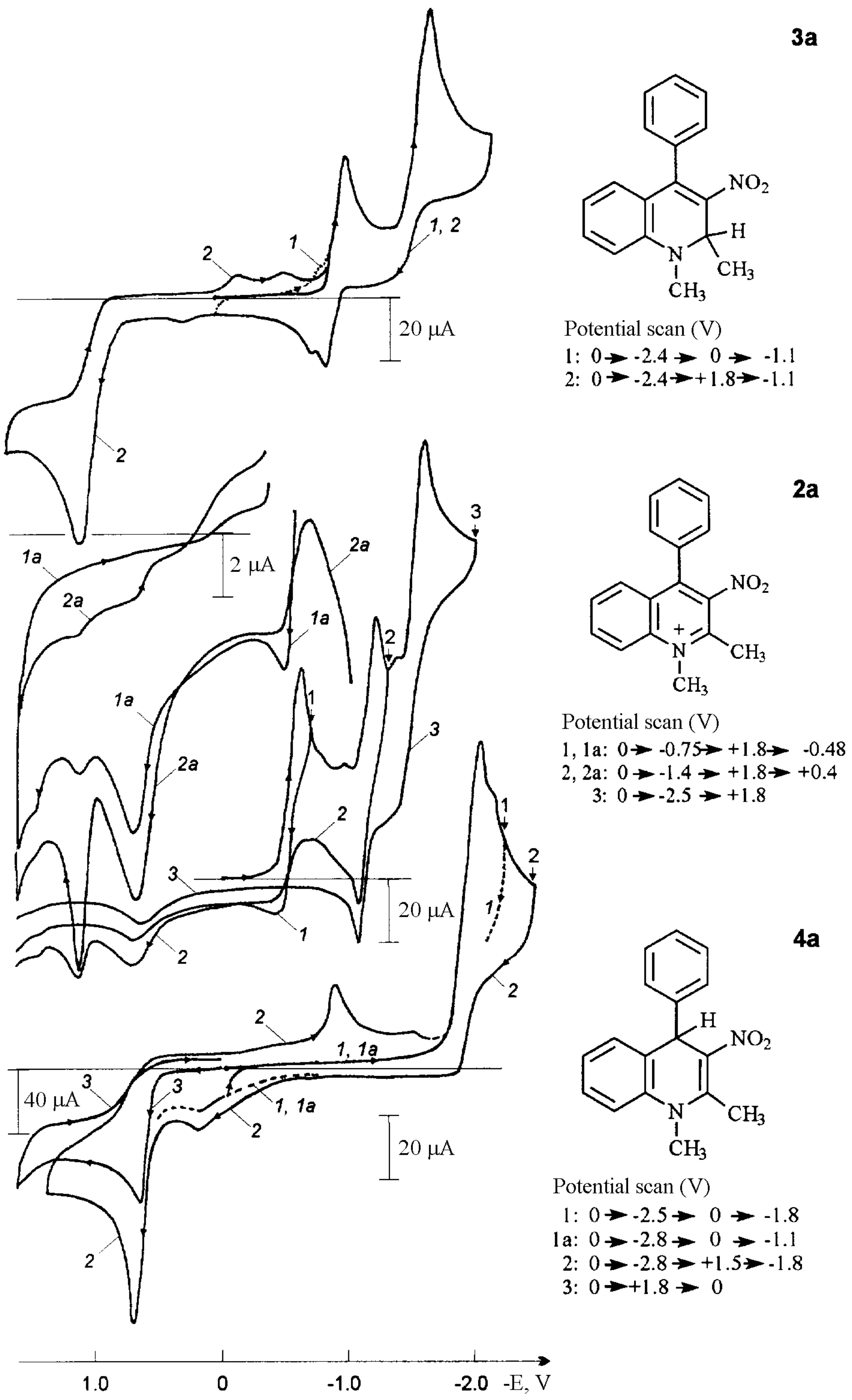


Fig. 3. Cyclic voltammograms for electrochemical reduction and oxidation in acetonitrile of: N-methyl-1,2-dihydroquinoline **3a**, the N-methylquinolinium cation **2a**, N-methyl-1,4-dihydroquinoline **4a**.

the potential of the second polarographic wave, we recorded EPR signals from a rather stable free radical (Fig. 2*b*,*c*). But even in this case, because of the considerable signal overlap we selected and determined only the two largest hyperfine structure constants, due to interaction of the unpaired electron with the nitrogen atom of the nitro group (6.6 G) and with the two equivalent protons (3.0 G). The spin density distribution in this radical is significantly different from that in the 3-nitroquinoline radical anion **5**.

The N-unsubstituted quinolinium cation **2b** forms polarographic waves at potentials of -0.37 (transfer of 0.5 electrons), -0.72 (0.5 electrons), -1.25 (0.9 electrons), -1.72 (1.5 electrons), and poorly separated waves at potentials of -2.20 and -2.44 V (total height corresponds to transfer of 2.5 electrons). On the cyclic voltammograms, reversible electron transfer is observed only for the third reduction wave, which, like the next waves, has practically the same electrochemical reduction potentials as compound **1**. On the cyclic voltammograms, the first two waves are irreversible; the third is reversible; the next waves are irreversible (Fig. 1). But even for reduction up to the first polarographic wave, two oxidation peaks are formed in the positive potential range: one at +1.60 V, and another broad peak at +1.0 V. For a potential scan up to the next reduction waves, the broad peak is gradually shifted toward more positive values. If the potential scan is performed only in the positive region in the second cycle, then instead of a single broad peak we observe two oxidation peaks at +0.85 and +1.33 V. During electrochemical generation at a potential of -1.3 V, we recorded an EPR spectrum for radical anions which matched the EPR spectrum of the 3-nitroquinoline radical anion **5** with respect to its general shape and the values of the two selected hyperfine structure constants (Fig. 2).

3-Nitro-substituted 1,2-dihydroquinolines 3a,c are reduced with formation of two polarographic waves. Substitution of the methyl group at the nitrogen atom by an ethyl group has practically no effect on the electrochemical reduction process (Table 1). The first reduction step for compounds **3a,c** is a one-electron process and reversible, and leads to formation of primary radical anions. The second step corresponds to irreversible transfer of 1.4 electrons. During the reverse potential scan, in the negative potential range we detect a new redox system $E_{\text{red}}/E_{\text{ox}}$ = -0.94/-0.88 (V), and in the positive potential range we see the oxidation peak for the starting compound at a potential of +1.15 V and an indistinct peak at +0.27 V (Fig. 3). The EPR spectra recorded during electrochemical generation of radicals at a potential of -1.2 V (Fig. 2) contain a number of hyperfine structure constants, of which we determined only two. One of them (a_N = 6.6 G) is due to interaction

TABLE 1. Half-wave Potentials ($E_{1/2}$, V, relative to the saturated calomel electrode) and Number of Electrons (*n*) for Polarographic Reduction at a Dropping Mercury Electrode and Peak Potentials for Electrochemical Oxidation (E_{ox}, V, relative to the saturated calomel electrode) at a Stationary Glass/Graphite Electrode for Compounds **1-4** in Acetonitrile (supporting electrolyte, 0.1 mol·l^{-1} $(C_4H_9)_4NPF_6$)

Compound	Reduction										E_{ox}, V
	1st wave		2nd wave		3rd wave		4th wave		5th wave		
	$-E_{1/2}$, V	*n*	$-E_{1/2}$, V	*n*	$-E_{1/2}$, V	*n*	$-E_{1/2}$, V	*n*	$-E_{1/2}$, V	*n*	
1	1.25	1.0	1.75	2.2	2.32	2.2					
2a	0.62	0.7	1.22	0.7	1.70	2.0					
2b	0.37	0.5	0.72	0.5	1.25	1.0	1.72	1.7	2.20 2.44	0.6 1.9	
3a	1.12	1.0	1.83	1.4							1.15
3c	1.13	1.0	1.85	1.4							1.13
4a	2.17 2.37	0.7 0.3									0.80
4b	1.47	0.8	2.25 2.45	0.8 0.8							1.37

of the unpaired electron with the nitrogen atom of the nitro group, while the other one is due to interaction of the unpaired electron with two protons ($a_{\mathrm{Hi}} \cong a_{\mathrm{Hj}} = 3.0$ G). From the ratio of the signal intensities in the three major groups and the distribution of signals in the additional splitting, we see that these protons are not completely equivalent and the values of the constants are slightly different. But it is difficult to establish the exact values and to assign the constants *a*H to definite positions in the molecule. We can only hypothesize that these may be protons at two of the 5, 7, and 8 positions of the dihydroquinoline ring, or protons *ortho* (relative to the heterocycle) at the phenyl substituent, since in quinoline radical anions the highest unpaired electron density is concentrated specifically in the 4 position [14]. We assign the constant a_{N} to this atom in the nitro group based on data on the spin density distribution in radical anions of 3- and 3,5-nitro-substituted 1,2-dihydropyridines [15, 16].

Electrochemical reduction of **3-nitro-1,4-dihydroquinoline derivatives 4a,b** proceeds in an unusual fashion. The N-methyl-substituted 3-nitro-1,4-dihydroquinoline **4a** is polarographically reduced with formation of two close waves at very negative potentials (-2.17 and -2.37 V) with total height corresponding to transfer of one electron. On the cyclic voltammogram, we observe an indistinct peak for reversible oxidation of the product formed at a potential of -2.05 V, while in the positive potential range we detect a weak peak for oxidation of the product at +0.17 V and a clear peak for oxidation of the starting 1,4-dihydroquinoline **4a** at a potential of +0.80 V. During the repeat potential scan, we detect two new reduction peaks at -0.95 and -1.58 V. During electrochemical reduction of N-unsubstituted 3-nitro-1,4-dihydroquinoline **4b**, three polarographic waves are formed ($E_{1/2}$ = -1.47, -2.25, and -2.45 V). From its height, the first wave corresponds to transfer of 0.8 electrons per molecule; the second and third waves are partially merged, and their overall height corresponds to transfer of 1.6 electrons. During the reverse potential scan, on the cyclic voltammogram we do not detect reversibility of electron transfer in any electrochemical reduction step, but new oxidation peaks are formed at -0.42 and -0.20 V. Continuing the potential scan into the positive potential range up to +1.8 V, we obtain a peak for irreversible electrochemical oxidation of the starting compound **4b** at a potential of +1.32 V. When the potential scan is repeated, we detect new reduction peaks at -0.25, -0.60, and -1.20 V.

Despite the fact that during electrochemical reduction of **4a,b** we do not observe reversible redox systems for the formation of radical anions of the starting compound, we attempted electrochemical generation and recording of the EPR spectra of free-radical species in the potential range from -2.0 to -2.5 V; and at -2.2 V for both compounds we detected low-intensity EPR signals for a very short-lived radical. The spectrum consists of five narrow lines with a single hyperfine structure constant of 5.71 G for **4a** (Fig. 4) and 5.63 G for **4b**. The EPR signal intensity ratio, 1:2:3:2:1, indicates that these spectra are due to interaction of the unpaired electron with two equivalent nitrogen nuclei in the molecule. The signal intensity decreases if the spectrum is recorded again or if the generation potential is changed. We could not unambiguously assign the spectrum to a free radical of a definite structure.

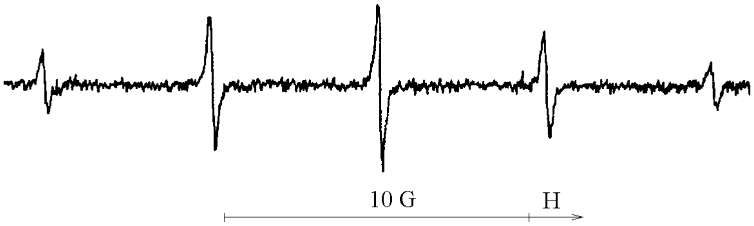
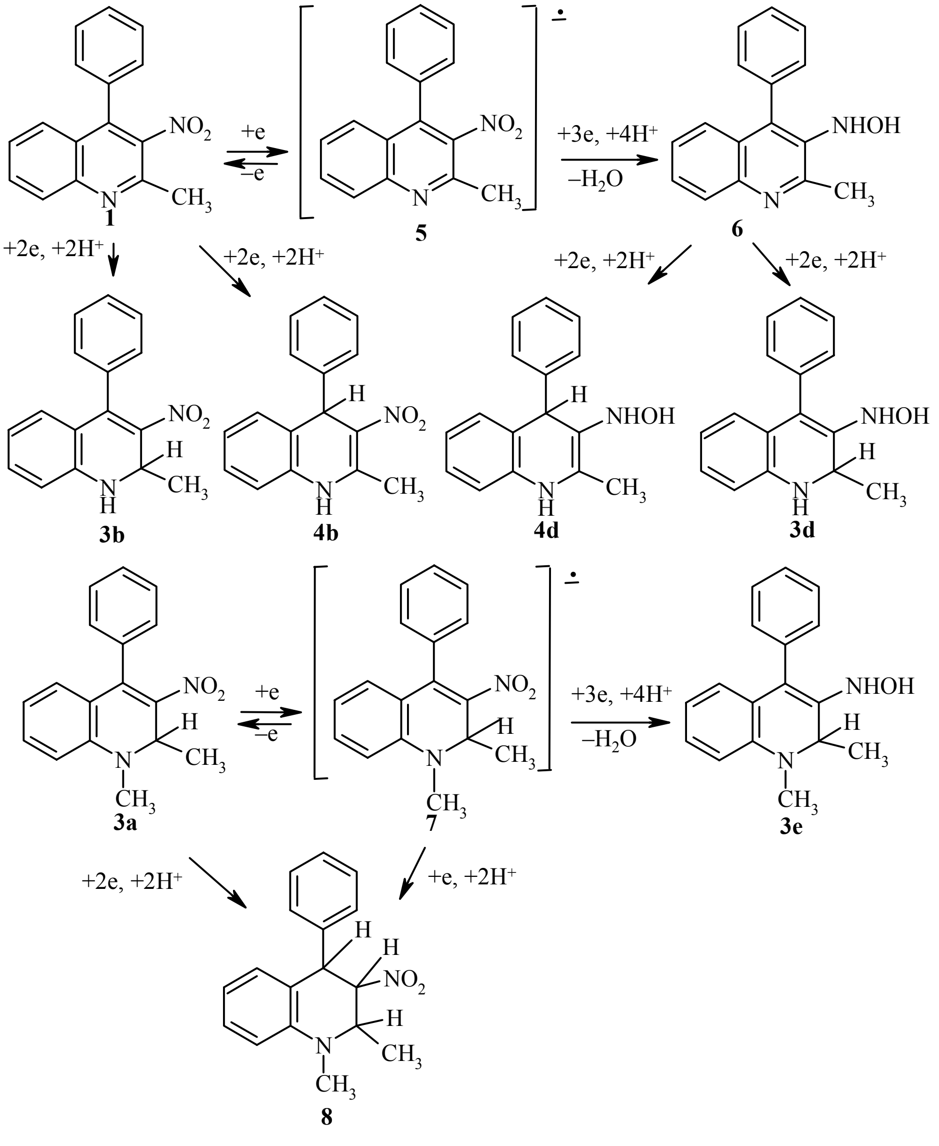
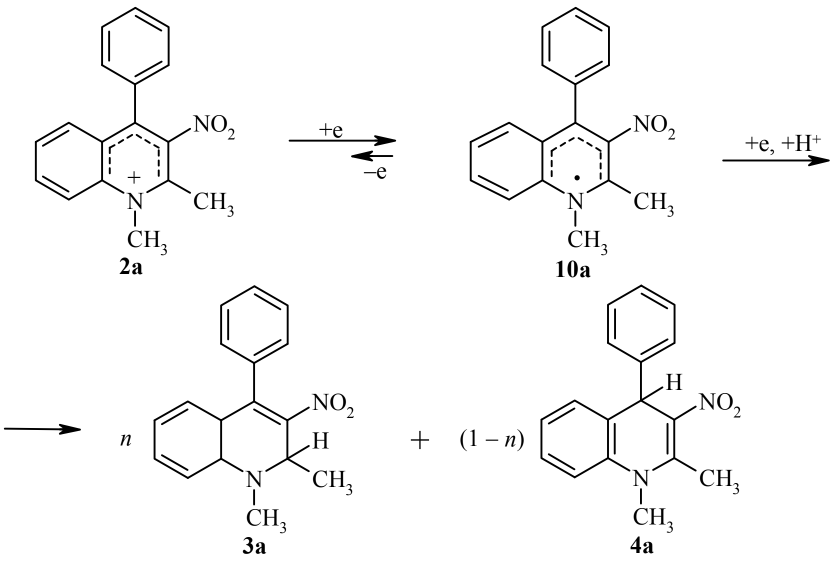


Fig. 4. EPR spectrum of free radicals formed during electrochemical generation of compound **4a** at a potential of -2.2 V.

From the experimental data it follows that only 3-nitroquinoline **1** and 3-nitro-1,2-dihydroquinolines **3a,c** in the first one-electron reversible step of electrochemical reduction form sufficiently stable primary products: radical anions of the starting compounds **5** and **6** respectively. In addition, attack by the electron occurs at the nitro group. Further reduction of these compounds also is mainly due to step-by-step electrochemical reduction of the nitro group to the hydroxylamine (compounds **6** and **3e**), since on the cyclic voltammograms we do not observe sufficient amounts of products suggesting reduction of the quinoline or 1,2-dihydroquinoline ring. But, considering that the total height of the second and third reduction waves for compound **1** is greater than the 3e level (further reduction of the nitro group to the hydroxyl amine), we may hypothesize that some of the molecules are reduced in parallel at the heterocycle. In the case of 3-nitroquinoline **1**, possibly compounds form with a 1,2- (compounds **3b,d**) and 1,4-dihydroquinoline structure (compounds **4b,d**), while in the case of reduction of 1,2-dihydroquinolines **3a,b**, the tetrahydroquinolines **8** may form in parallel. Electrochemical reduction of the quinoline ring occurs at very negative potentials [9], so possibly the majority of the molecules are reduced at the nitro group to the hydroxylamine compound and only then is the heterocycle reduced, while some of the molecules, approaching the electrode as a result of diffusion, may be reduced at the heterocycle without preliminary reduction of the nitro group.

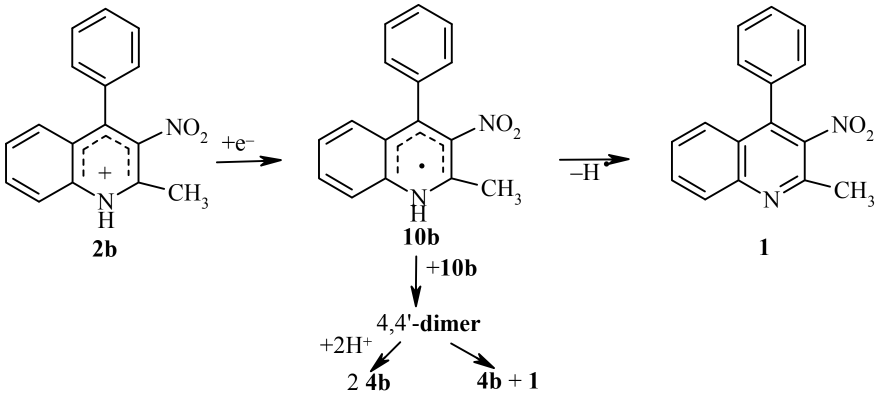


3-nitroquinolinium cations **2a,b** are reduced significantly more easily. The potential of the first reduction wave for the N-unsubstituted derivative **2b** is shifted toward the positive range by 900 mV compared with the corresponding quinoline **1**, while the N-substituted cation **2a** is reduced more easily by 800 mV compared with 1,2-dihydroquinoline **3a**. In quinolinium cations, first the quinoline portion of the molecule is reduced. Addition of the first electron leads to formation of a fairly unstable neutral radical **10**, which in analogy to pyridyl radicals [17, 18] either may be reduced further or a hydrogen atom may be abstracted to form a molecule of the corresponding quinoline, or it may be dimerized [19, 20]. We suggest that the free radical of compound **2a** is reduced further, undergoes chemical conversions, and as a result 1,2-dihydroquinoline **3a** is formed, which is immediately reduced at the nitro group, since the potential of the first wave for reduction of 1,2-dihydroquinoline **3a** at 100 mV is more positive than the potential of the second step of reduction of **2a**:



Such a conclusion is supported by the potentials for further reduction and the EPR spectra of electrochemically generated radical anions of the corresponding 1,2-dihydroquinoline **7**, and also the clear oxidation peaks in the positive range of the cyclic voltammogram, with values coinciding with the oxidation potentials of 1,2-dihydro- and 1,4-dihydroquinolines **3a** and **4a** respectively. We note that the rate of formation of the product which is hydrogenated at the 4 position is faster than the rate of formation of 1,2-dihydroquinoline, as is also observed during chemical reduction of **2a** by sodium borohydride [4].

As a result of reduction of the quinolyl free radical **10b** of compound **2b**, the quinoline **1** is formed, whose structure is supported by the EPR spectra of radical anion **5** and the reduction potentials.



Analysis of the peaks formed in the positive part of the anodic branch of the voltammogram indicates that some of the neutral quinolyl radicals **10b** may be dimerized, and then the dihydroquinoline structure forms. Indirect evidence for such a conclusion is the appearance of a blue-green color on the surface of the cathode and also around the metallic sodium during chemical reduction of quinoline **1**. We isolated 3-nitro-1,4-dihydroquinoline **4b** as the end product in chemical reduction of **1**. This indicates preferential dimerization in the 4 position of the quinoline ring and is consistent with results for pyridine derivatives [20, 21].

We already mentioned the unusual behavior of electrochemical reduction of 3-nitro-substituted derivatives of 1,4-dihydroquinoline **4a** and **4b**. In contrast to the compounds considered above, they are not reduced at the nitro group. For **4a**, the two poorly separated, irreversible polarographic waves at negative potentials beyond -2.0 V may be due to 2e-reduction of the double bond in the pyridine portion of the molecule and formation of tetrahydroquinoline (but the sum of the heights of the two waves does not correspond to transfer of two electrons), or parallel 1e-reduction of the quinoline ring and the nitro group to the radical anion, which then may undergo various chemical conversions. The N-unsubstituted derivative of 3-nitro-1,4-dihydroquinoline **4b** during electrochemical reduction gives one more wave at a more positive potential (-1.4 V) in the region of possible reduction of the nitro group, but the lack of reversibility of the wave and the similarity of the EPR spectra recorded at the potential of the second reduction wave with those for the N-substituted representative **4a** indicate that even in this case, electrochemical reduction does not involve the nitro group. For analogous N-unsubstituted 3-nitro derivatives of 1,4-dihydropyridine (R^2 = H, CH_3; R^5 = COOAlk; R^6 = CH_3), during electrochemical reduction the first irreversible reduction wave was observed in the range from -1.2 to -1.4 V; but the corresponding N-substituted 3-nitro derivatives of 1,4-dihydropyridine were also reduced in the same potential range [22]. We may hypothesize that the first wave for reduction of the N-unsubstituted compound **4b** is due to reduction of the proton on the nitrogen atom and formation of the 1,4-dihydroquinoline anion, which then is reduced at the heterocycle.

The hydrogenated quinolines **3** and **4**, in addition to participating in electrochemical reduction, also participate in the process of electrochemical oxidation. Both 1,2- and 1,4-dihydroquinolines are oxidized in one step in the potential range from 0 to 1.8 V at a stationary glass/graphite electrode (Table 1). During the reverse potential scan, we do not observe peaks suggesting reversibility of the process. Electrochemical oxidation of 2-methyl-3-nitro-2-methyl-4-phenyl-1,4-dihydroquinoline **4b** is hindered compared with some familiar 3-nitro-substituted derivatives of 1,4-dihydropyridine [23], and specifically the electrochemical oxidation potential is shifted toward the positive range by 500 mV compared with 5-carbethoxy-2,6-dimethyl-3-nitro-4-phenyl-1,4-dihydropyridine, and by 750 mV compared with the analogous 1,4-dihydropyridine containing a COCH3 group at the 5 position. Comparing the electrochemical oxidation potentials, we see that for N-substituted derivatives of 1,2- and 1,4-dihydroquinoline, an inverted sequence of oxidation potentials is typical compared with dihydropyridine derivatives ($R^2 = R^6 = CH_3$; $R^3 = R^5 = COOC_2H_5$) [24], i.e., 1,2-dihydroquinolines **3** are more difficult to oxidize than 1,4-dihydroquinoline **4a** (the difference between the potentials is 350 mV). The correspondence to dihydropyridines is apparent if we compare the oxidation potentials for the unsubstituted and the methyl-substituted (at the nitrogen atom) 1,4-dihydro derivatives **4a** and **4b**: the N-substituted compound is oxidized more easily than the corresponding N-unsubstituted analog. But while the difference between the potentials for the dihydro derivatives of pyridine is about 100 mV [24], the oxidation potential for N-unsubstituted 1,4-dihydroquinoline **4b** is shifted toward the positive range by as much as 570 mV compared with the N-substituted 1,4-dihydroquinoline **4a**, and consequently **4a** is oxidized more easily than 1,2-dihydroquinolines **3a,c**; this is one more characteristic feature of the electrochemical behavior of 3-nitro derivatives of 1,4-dihydroquinoline. Experimental data on the structural features (such as X-ray diffraction characteristics) are not yet available which might help clarify the reasons for such unusual behavior of 3-nitro derivatives of 1,4-dihydroquinoline.

During electrochemical oxidation of compounds **3** and **4**, reduction peaks of the products formed are recorded in the negative potential range on the cyclic voltammograms for the reverse scan. For 1,2-dihydroquinolines **3**, we detect peaks at potentials of -0.2 and -0.6 V. The latter peak corresponds to the electrochemical reduction potential of the quinolinium cation **2a**, which is consistent with results obtained in electrochemical oxidation of 1,2-dihydropyridines [24]. For 1,4-dihydroquinoline **4b**, reduction peaks are also recorded in the negative potential range which correspond to the reduction peaks for the protonated quinoline **2b**. However, during oxidation of the N-substituted 3-nitro-1,4-dihydroquinoline **4a**, a product is formed for which the reduction potential is shifted 520 mV toward more negative values compared with the reduction potential for the quinolinium cation **2a**, and coincides with the reduction potential for the product detected after electrochemical reduction of 1,2-dihydroquinoline **3a** up to the potential of the second polarographic wave. The indistinct reduction peak at this potential is also observed during reduction of the quinolinium cation **2a** (Fig. 3). The nature of this compound has not been established. We can only hypothesize that it may be a product with a dimer structure, as has been observed for compounds with a pyridine ring [20, 25].

The experimental data presented suggest that the behavior of 2,4-substituted 3-nitroquinoline and its cation in the electrochemical process, both during reduction and during oxidation of the reduction products, is described by the general rules established for the behavior of the corresponding compounds with a pyridine ring. 3-Nitroquinoline **1** and 3-nitro-1,2-dihydroquinolines **3a,c** are reduced first at the nitro group and only after that is the heterocycle involved. 3-Nitro-1,2-dihydroquinolines and 3-nitro-1,2-dihydropyridines match with respect to the number of polarographic waves, the reversibility of electron transfer, the number of electrons in the individual steps, and the formation of rather stable radical anions of nitroaromatic structure. In the quinolinium cations **2a,b**, primary reduction occurs at the heterocycle. The nitro group, as a substituent with pronounced electron-acceptor properties, participates in the process of electrochemical reduction in parallel with the heterocycle. Either the nitro group or the heterocycle is reduced, depending on which part of the molecule or intermediate has the higher electron affinity.

EXPERIMENTAL

2-Methyl-3-nitro-4-phenylquinoline **1**, its quinolinium salts **2a,b** and hydrogenated derivatives **3a,c** and **4a,b** were synthesized by procedures given in [4, 5]. The electrochemical study of compounds **1-4** ($c = 5\cdot10^{-4}$ mol·l^{-1}) was carried out in acetonitrile [26] on a PAR-170 polarograph using a three-electrode cell. The supporting electrolyte was 0.1 mol·l^{-1} tetrabutylammonium hexafluorophosphate. The reference electrode was a double-junction aqueous saturated calomel electrode for working in nonaqueous solvents. The polarograms were recorded at a dropping mercury electrode with forced drop removal (t = 0.5 s, m = 0.90 mg·s^{-1}). To obtain the cyclic voltammograms, we used a stationary glass/graphite electrode and potential scan rate of 50 mV·s^{-1}.

Free radicals were generated under steady-state conditions using a three-electrode scheme on the surface of a platinum electrode in a cell placed in the cylindrical TM_{110} cavity of an SE/X 2547 EPR spectrometer, using a procedure we proposed in [11]. For electrochemical generation of free radicals, we used $5\cdot10^{-4}$-10^{-3} mol·l^{-1} solutions of compounds **1-4** in acetonitrile; the electrolyte was 0.1 mol·l^{-1} tetrabutylammonium hexafluorophosphate.

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