ELECTROCHEMICAL REDUCTION OF 1-SULFONYLBENZ[c,d]INDOLIN-2-ONES, AND THE STRUCTURE OF THE FREE RADICALS THAT ARE FORMED

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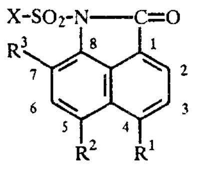
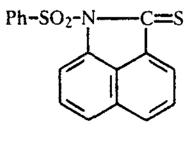
In the electrochemical reduction of N-sulfonylbenz[c,d]indolin-2-ones, anion radicals that are detectable by ESR may be formed, with structures that correspond to either the original molecule or isomers of that molecule. Substituents that localize the unpaired electron density on the naphthalene ring system increase the probability of forming ESR-detectable free radicals. In the primary anion radicals, the unpaired electron is localized mainly (> 70%) on the naphthalene nucleus. Replacement of the keto group in the molecules of naphthostyrils by a thiocarbonyl group increases the unpaired electron density on the naphthalene ring system of the primary anion radicals. For all of the compounds, parameters of electrochemical reduction in dimethylformamide have been established, under conditions of polarography and cyclic voltammetry.

N-Aryl and N-alkyl derivatives of 1-sulfonylbenz[c,d]indolin-2-ones (8-amino-1-naphtholactam, naphthostyril) are of interest because of their potential biological activity, and are of further interest as intermediates in organic synthesis. From this standpoint, information on the redox properties of these compounds is important, as well as information on the nature of the intermediates that are formed in the reaction, particularly the reactive free radicals. Dzhurka et al. [1] showed that unsubstituted naphthostyril and some of its monohalogen derivatives in an aprotic medium (dimethylformamide) are reduced electrochemically in two one-electron stages, apparently corresponding to stagewise reduction of the carbonyl group. It was suggested that anion radicals of the original compounds are formed in the first stage, with the second stage corresponding to reduction of the anion radical to a dianion. This sort of course of electroreduction can also be expected for N-sulfonylnaphthostyrils.

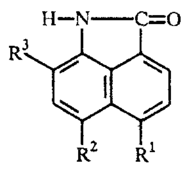
In the work reported here, we determined the electrochemical characteristics of compounds I-IV by polarography on a dropping-mercury electrode and cyclic voltammetry on a stationary vitreous carbon electrode; we also performed experiments on electrochemical generation of free radicals of the N-sulfonylnaphthostyrils (Ia-i) and the corresponding thio analog (II), and for comparison the naphthostyrils (IIIa-f) and their thio analog (IV).



Ia-i



II



IIIa-f

Ia-f $R^1 = R^2 = R^3 = H$; a X = Me, b X = Ph, c X = p-MeC_6H_4, d X = p-ClC_6H_4 e X = $NHCOMeC_6H_4$, f X = o-$NO_2C_6H_4$, I g-i X = Ph; g $R^1 = H$, $R^2 = R^3 = Cl$, h $R^1 = R^3 = H$, $R^2 = Br$, i $R^1 = R^3 = H$, $R^2 = NO_2$
III a-c,e,f $R^1 = H$; a $R^2 = R^3 = H$, b $R^2 = Br$, $R^3 = H$, c $R^2 = R^3 = Br$, e $R^2 = Cl$, $R^3 = H$, f $R^2 = R^3 = Cl$;
IIId $R^1 = R^2 = Br$, $R^3 = H$.

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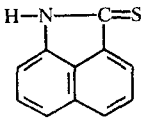

IV

All of the compounds I-IV in dimethylformamide (DMF) are reduced in stages on the dropping-mercury electrode, forming two or more polarographic waves. As can be seen from Table 1, the N-arylsulfonylnaphthostyrils I and the thio analog II are reduced much more readily ($\Delta E = 0.3\text{-}0.4$ V) than the corresponding naphthostyrils III and IV. The replacement of the oxygen atom by a sulfur atom in the carbonyl grouping has identical effects on the naphthostyril IV and its N-phenylsulfonyl derivative II in terms of facilitating the primary reduction (by ~42 mV). Upon comparing the compounds of series I, which differ from each other only in the substituent X, we find that the potential of the first reduction wave varies in accordance with the electron donor properties of the substituent X as characterized by the Hammett σ-constant. This indicates electron conduction through the sulfonyl grouping in the molecule ($\rho\pi = 0.1$ V). If a substituent (halogen or nitro group) is introduced into the naphthalene ring system of N-phenylsulfonylnaphthostyril, the values of the first-wave reduction potential become more sensitive to changes in the electron donor properties of the substituent ($\rho\pi = 0.53$). The height of the first reduction wave, depending on the character of the substituents X, R^1, and R^2, changes from the one-electron to the two-electron level. Thus, while a distinct one-electron wave is observed for the N-methylsulfonyl derivative Ia, the change to N-phenylsulfonyl derivatives Ib-e leads to an increase of the height of the first reduction wave. And here we observe a trend: The stronger the electron acceptor properties of the substituent X, the more the first reduction wave tends toward the two-electron level. However, the introduction of a nitro group into the ortho position of the aryl ring (compound If) lowers the height of the first reduction wave.

It was established by means of cyclic voltammetry that the first stage of the reduction is reversible only for compounds Ia and Ii, with reversibility of the primary process also being observed for compound Ih at high rates of potential sweep (500 mV/sec). By analogy with naphthostyrils that had been studied previously [1], we can assume that for the type I compounds (other than Ii), the carbonyl group in the heterocycle is reduced in the first stage. Of this group, compound Ia is the only one to form a primary anion radical that is sufficiently stable for ESR detection.

The second wave of electrochemical reduction of Ia-h lies in the potential interval from −1.09 V (for If) to −1.70 V. On the polarograms, this wave is quite weak, in some cases failing to reach the 0.1 electron level. On the cyclic voltammetric curves, however, there is a more clearly defined redox system corresponding to this wave, with the system remaining unchanged in repetitive sweeps of the potential, when the reduction product corresponding to the first polarographic wave gradually disappears. The potentials of the second wave are close to the first reduction wave of the corresponding type III model compounds. For compounds Ia-e, this wave conforms to the first reduction wave of compound IIIa with respect to potential and reversibility; for compound Ig, the wave corresponds to IIIf, and for compound Ih, to IIIb, i.e., to the analogous naphthostyrils. This suggests that in the first stage of reduction, a certain part of the molecule, after the addition of the first electron, undergoes rupture of the $N\text{-}SO_2$ bond. For compound Ii, the second reduction wave is strictly one-electron and reversible, probably corresponding to the reduction of the nitro group in the naphthalene ring system. In contrast, for compound If, which contains a nitro group on the aryl ring, the second reduction wave does not reach the one-electron level; and, following this wave, a third reduction wave is formed at −1.35 V, exceeding the one-electron level. On the cyclic voltammetric curves, reversible redox systems correspond to both of the waves.

In the interval of more negative potentials (−2.0 to −2.5 V), one or two more polarographic waves are registered (Table 1). The voltammetric curves indicate that the processes taking place at these potentials are irreversible; however, the unidentified products can be oxidized electrochemically in the potential interval from −0.3 to −0.6 V. The same oxidation products have been detected in the reduction of the model compounds III and IV to the corresponding potential.

A necessary but not always sufficient condition for ESR detection of free radicals is reversibility of formation of the species (on the time scale of cyclic voltammetry) with a relatively high concentration of depolarizer [2]. As can be seen from Table 1, there is no such reversibility in the first stage of reduction for the N-sulfonylnaphthostyrils Ib,c,e,g,h or the thio analog II; therefore, in the course of electrochemical generation of free radicals of these compounds, we cannot expect the formation of primary anion radicals that are amenable to investigation of their structure by means of ESR. Formation of primary anion radicals can be expected only in the reduction of the original compounds Ia,i, but free radicals formed in the course of subsequent conversions can be expected in the reduction of compounds Ia-f,i. The reversibility of the process of

TABLE 1. Potentials of Polarographic Waves ($E_{1/2}$, V), Numbers of Electrons (n), and Reversibility (+/–) of Individual Stages of Electrochemical Reduction with Potential Sweep Rate 20 mV/sec, for Compounds I-IV in DMF in Background Electrolyte 0.1 M Tetrabutylammonium Perchlorate

Compound	Substituent				1st wave			2nd wave			3rd wave			4th wave		
	X	R^1	R^2	R^3	$-E_{1/2}$	*n*	+/–	$-E_{1/2}$	*n*	+/–	$-E_{1/2}$	n	+/–	$-E_{1/2}$	*n*	+/–
Ia	CH_3	H	H	H	1,36	1,0	+	1,70	0,2	+	2,37	0,5	-	—	—	-
Ib	C_6H_5	H	H	H	1,33	1,4	-	1,70	0,2	+	2,27	1,0	-	—	—	-
Ic	*p*-$CH_3C_6H_4$	H	H	H	1,36	1,1	-	1,70	0,1	+	2,40	1,0	-	—	—	-
Id	*p*-ClC_6H_4	H	H	H	1,28	1,7	-	1,70	< 0,4	+	2,27	1,0	-	—	—	-
Ie	*p*-$CH_3CONHC_6H_4$	H	H	H	1,35	1,1	-	1,70	0,1	+	2,20	0,5	-	—	—	-
If	*o*-$NO_2C_6H_4$	H	H	H	0,82	1,2	-	1,09	0,3	+	1,35	1,2	+	—	—	-
Ig	C_6H_5	H	Cl	Cl	1,09	1,1	-	1,40	0,2	-	1,98	1,3	-	2,30	1,3	-
Ih	C_6H_5	H	Br	H	1,19	1,0	+/–*	1,46	0,1	-	2,00	1,1	-	2,40	0,7	-
Ii	C_6H_5	H	NO_2	H	0,72	1,0	+	1,24	1,0	+	2,46	3,5	-	—	—	-
II	C_6H_5	H	H	H	0,91	1,0	+/–*	1,33	0,6	+/–*	1,58	0,1	-	1,89	2,5	-
IIIa	—	H	H	H	1,69	1,0	+	2,49	1,0	+	—	—	-	—	—	-
IIIb	—	H	Br	H	1,48	1,0	-	1,69	0,5	+/–*	2,48	2,0	-	—	—	-
IIIc	—	H	Br	Br	1,25	1,0	-	1,43	1,0	-	1,67	0,4	+/–*	2,10	2,0	-
IIId	—	Br	Br	H	1,29	1,0	-	1,47	0,7	-	1,65	0,2	+/–*	2,15	2,5	-
IIIe	—	H	Cl	H	1,52	1,0	+	1,65	0,2	-	2,36	1,2	-	—	—	-
IIIf	—	H	Cl	Cl	1,41	1,0	+/–*	2,30	3,0	-	—	—	-	—	—	-
IV	—	H	H	H	1,25	1,0	+	2,10	1,0	-	—	—	-	—	—	-

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*On the cyclic voltammetric curves, an oxidation peak corresponding to the peak of electrochemical reduction of the product is manifested only when the potential sweep rate is at least 500 mV/sec.

forming such species in the primary reduction of these compounds depends on the properties of the substituents, both those on the sulfonyl grouping and those on the naphthalene nucleus. With the set of compounds available for our investigation, we were unable to establish any rigorous relationships, but certain correlations are still evident. For example, owing to the irreversibility of the first stage in the electroreduction of the N-sulfonylaryl derivatives of the naphthostyrils, with the exception of compounds Ih,i, it is impossible to expect that this process will form any free radicals that are sufficiently stable for investigation by means of ESR.

The reversibility of the first stage of the reduction of compound Ii can be explained by the formation of anion radicals that are not of the naphthostyril type, but rather of the nitronaphthostyril type. Of the compounds that we have examined, the most readily reduced in the primary process are the nitro-substituted compounds If,i. In these compounds, the nitro group, as the most electrophilic substituent, may be a reaction center of primary reduction of the compound to the anion–radical state, reversible (if it is sufficiently stable) to the original molecule.

This is characteristic for compound Ii, the nitro group of which is located on the naphthalene nucleus. For compound If, however, where the reaction center of primary reduction is also a nitro group, we fomd that the process of forming primary anion-radicals is not reversible. In this case (see also [3]), the anion-radical state has been used in the process of transformation of another, less electrophilic reaction center, resulting in loss of the radical state but preservation of the nitro group in a new, less electrophilic species. This is evidenced by the second and third stages of electroreduction of compound If, which are accomplished at more negative potentials, where free radicals of a nitro-substituted compound are also formed.

In the electrochemical generation of radicals of compounds Ib-e,g,h and II, ESR does not detect the formation of free radicals that are the intermediates in electroreduction of these compounds, even though the cyclic voltammetric curves indicate reversible formation of intermediate species in the course of reduction of these compounds. Apparently, these species are not free radicals, or possibly the concentration of the radical species that are formed is too low to be registered by ESR. Out of the entire group of N-sulfonylnaphthostyrils Ia-i, the formation of free radicals in electrochemical reduction could be registered by ESR for only three of them, Ia,f,i (Table 2); here, free radicals of the naphthalene type were registered only in the reduction of compounds Ia,i.

With electrochemical generation potentials close to the voltammetric potentials of the primary reversible electroreduction of compounds Ia and Ii, their anion radicals are obtained. The ESR spectra of these radicals have a complex hyperfine structure that is difficult to decipher, owing to delocalization of the unpaired electron throughout the entire naphthalene ring system (the unpaired electron interacts with seven nuclei of naphthalene ring atoms with nonequivalent environment).

The hyperfine structure constants of the ESR spectra of the anion radicals of these compounds, and also of other free radicals with the naphthalene structure that were registered, have been assigned to certain atoms (Table 2) by analogy with other naphthalene-type free radicals that had been obtained previously [4]. With electrochemical generation potentials close to the potentials of the secondary electroreduction of compounds Ia and Ii, for which the cyclic voltammetric curves indicate partial reversibility of the process (see Table 1), secondary free radicals are registered, also of the naphthalene type.

In studying compound If at the same generation potential, three types of radicals are registered, two of which have the structure of nitrobenzene-type radicals. The hyperfine structure of the ESR spectra of two of these radicals (see Table 2) indicates delocalization of the unpaired electron through the nitrobenzene system of π-electrons. The character of the hyperfine structure of one of the free radicals ($3_N \cdot 3_H \cdot 2_H \cdot 3_H$), along with the values of its constants, which are close to those found previously for nitrobenzene [5], indicate the formation of the anion radical of unsubstituted nitrobenzene. It has also been established that the other radical is the anion radical of ortho-substituted nitrobenzene (the density of the unpaired electron on the nitrobenzene fragment of this radical is lower than for the anion radical of nitrobenzene, and it indicates an electrophilic property of the ortho-substituent). The absence of any hyperfine structure due to the presence of nuclei of the substituent atoms indicates that in the substituent, at least at the α-atom, there are no atoms with a magnetic nucleus (N, H), and that the α-atom of the substituent, localizing on itself part of the density of the unpaired electron, prevents further delocalization of this electron through the substituent. In our case, such an α-fragment of the substituent may be the $-SO_2$ grouping, which, as found previously [6], when it participates in delocalization of an unpaired electron, prevents its further delocalization. The electrochemical generation potential of these radicals, and also the irreversibility of the primary electroreduction of compound If, together with the observed hyperfine structure of the ESR spectra, indicate that none of these radicals is the primary anion radical of the original compound, but that it has the structure of intermediate products of further electrochemical conversions,

TABLE 2. Electrochemical Generation Potentials (E, V, relative to Ag electrode) of Free Radicals of Compounds Ia,f,i, IIIa,e,f, and IV in DMF, and Hyperfine Structure Constants (G) of ESR Spectra of the Resulting Free Radicals

Compound	Substituent				-E, V	Hyperfine interaction constants, a, G							
	X	R^1	R^2	R^3		$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	$H_{(6)}$	$H_{(7)}$	N	H(N)
Ia	CH_3	H	H	H	1,4	5,44	0,12	7,70	3,01	0,99	1,75	0,99	—
					1,8	2,77	—	3,86	1,85	0,88	0,88	0,25	—
If*	o-$NO_2C_6H_4$	H	H	H	1,1	9,50 (N); 3,82 (2H); 3,19 (H); 1,01 (2H)							
					1,1	9,11 (N); 3,70 (H); 2,98 (H); 1,01 (2H)							
Ii	C_6H_5	H	NO_2	H	0,9	1,25	0, 76	1,84	4,10 (N)	0,76	1,00	1,05	—
					1,6	...	2,10	0,70	8,99 (N)	4,96	1,42	0,70	—
IIIa	—	H	H	H	1,8	6,00	0,22	7,09	2,00	0,21	1,80	1,20	1,20
					2,1	5,65	0,12	5,95	1,85	0,50	0,70	1,25	
IIIe	—	H	Cl	H	1,8	4,12	0,17	4,87	—	0,17	1,34	0,61	1,34
					2,0	1,30 (H); 0,67 (2H); 0,45 (N)							
IIIf	—	H	Cl	Cl	1,8	4,12	0,17	4,87	—	0,17	1,34	0,61	1,34
					2,0	1,30 (H); 0,67 (2H); 0,45 (N)							
IV	—	H	H	H	1,3	5,80	0,25	6,64	2,94	0,25	2,94	0,80	1,18
					2,5	1,38 (H); 0,79 (2H); 0,53(N)							

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*Three varieties of free radicals are generated simultaneously; the hyperfine structure has not been established.

in the course of which the SO_2–C or N–SO_2 bond is cleaved. Cleavage of the N–SO_2 bond was also observed previously in the electrochemical reduction of N-sulfonylarylbenzoquinonimines [6]. The stability of the third type of free radical proved to be inadequate for deciphering the hyperfine structure of the ESR spectrum, or for establishing the structure of the radicals.

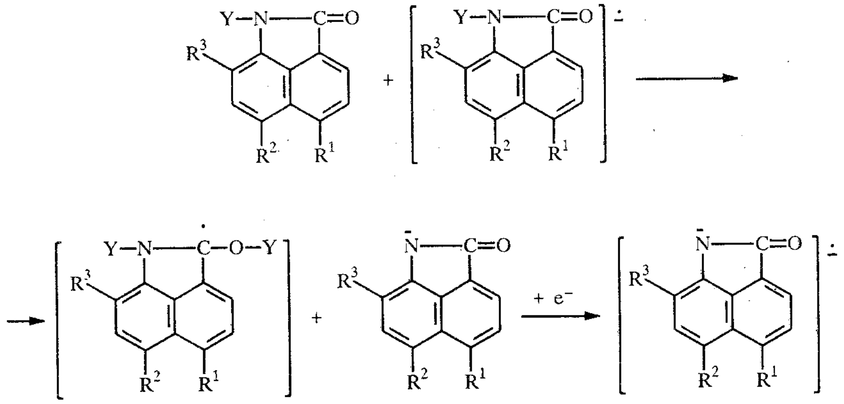
In the series of naphthostyrils III, anion radicals are obtained only for the unsubstituted naphthostyril IIIa and its 5-chloro derivative IIIe (see Table 2). For the 5,7-dichloro-substituted naphthostyril IIIf, the primary process of electroreduction includes splitting out the chlorine atom in position 7 and the subsequent formation of the same free radicals as in the case of the 5-chloro derivative IIIe — specifically, the anion radical of monochloro-substituted naphthostyril and a radical giving an ESR spectrum with the characteristic hyperfine structure $2_{H}\cdot 3_{N}\cdot 3_{H}$, similar to the secondary free radical of compound IIIe (see Table 2). In the course of electrochemical generation of free radicals of the bromine-substituted naphthostyrils IIIb-d, ESR was unable to register any radical formation.

Analysis of the hyperfine structure of the ESR spectra of the primary anion radicals of compounds Ia, IIIa, and IV, which do not contain any substituents on the naphthalene rings ($R^1 = R^2 = R^3 = H$), indicates that the unpaired electron is mainly delocalized on the naphthalene ring system (~70%), although the addition of the first electron to the molecule apparently takes place at the carbonyl group of the indoline ring. When the keto group in naphthostyrils is replaced by a thio group (the change from IIIa to IV), there is an increase in the unpaired electron density of the primary anion radicals on the naphthalene ring system; this is explained by a change in electronic properties of the heterocycle in the electron-donor direction when the change is made from the oxygen atom to the sulfur atom.

By electrochemical generation, anion radicals of the thio analog of naphthostyril IV have been obtained. In the secondary processes of electrochemical reduction of this compound, free radicals are formed, with a structure that is similar to that of the secondary free radical of compound IIIe, for which the structure has not been established.

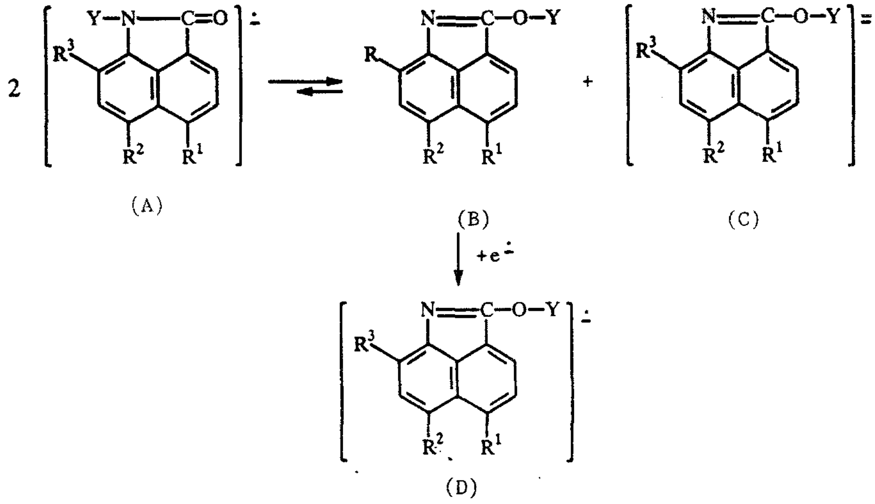
From the ESR data we can define more precisely the probable character of the species formed in electroreduction on the second wave of the original molecules, in contrast to earlier views that had been expressed on the basis of polarographic data alone [1]. The hyperfine structure of the ESR spectra of the secondary free radicals of the naphthalene type that were registered for compounds Ia, Ii, and IIIa provides an unambiguous characterization of the chemical structure of the radicals.

One of the conceivable versions of the formation of these secondary radicals might be represented, as was observed in the case of dihydropyridines [7], by the following scheme:



If this scheme were realized, the secondary radicals would be anion radicals of the original compounds in which the substituent Y had been split out. In connection with the increase of electron-donor properties of the nitrogen atom in these radicals, we should have expected an increase of unpaired electron density on the naphthalene ring system [4] in comparison with the primary radicals; however, the ESR spectra indicate the exact opposite. The decrease of unpaired electron density on the naphthalene ring system of the secondary radicals of this type in comparison with the primary radicals (from >10% for IIIa to >50%) is explained by a redislocation of the unpaired electron onto the heterocycle. However, the hypothetical structure of the secondary radicals is also unacceptable because in this case, the structure of the secondary radicals would not depend on the substituent Y, in contradiction to the hyperfine structure of the ESR spectra of the radicals that are registered for compounds Ia and IIIa.

The naphthalene-type secondary radicals evidently have the structure shown below as D: They are isomers of the primary anion radicals. One of the paths of their formation can be represented by the following scheme:



The free radicals D, apart from their formation by electrochemical one-electron reduction of the isomer B, may also be formed as a result of a number of other chemical processes:

$$2A \rightleftarrows 2D$$

$$A + B \rightleftarrows D + (A - e^{\overset{\cdot}{-}})$$

$$A + C \rightleftarrows D + (A + e^{\overset{\cdot}{-}})$$

$$B + C \rightleftarrows 2D$$

Apparently, the electronic properties of this compound and its primary anion radical A, and also the ability of the anion radical to isomerize, are responsible for the formation of the secondary free radical D in the second stage of electrochemical reduction of the molecules, where the isomeric form of this molecule is reduced, or where the radical D appears as a result of chemical conversions of the anion radicals A. A similar structure can probably be assigned to the secondary free radicals of the N-sulfonylnaphthostyrils Ia,i. In this case, a prerequisite for the postulated recombination is the possibility of rupture of the N-SO_2 bond. The possibility of such rupture is evidenced by the data from the electrochemical studies and also by the structure of the secondary radicals that are formed in the electrochemical reduction of compound If. In the case of the thio analogs II and IV, no reliable information was obtained on such isomerization of the compounds. Also, we did not observe any isomerization of these compounds in the original molecular state.

An expansion of the possibilities of π-electron delocalization by enlarging the condensed system of π-electron rings apparently favors the formation of secondary free radicals of the naphthalene type by recombination of primary anion radicals. This is evidenced by the decrease of unpaired electron density on the naphthalene ring system of the secondary free radical of the naphthalene type in comparison with the primary anion radical. The possibilities of forming one type or another of free radicals of N-sulfonylnaphthostyrils are governed by the unpaired electron density on the naphthalene ring system of the primary anion radical of the compound (either actually detected or hypothetical), which depends in turn on the electronic properties of the substituents on the naphthalene nucleus and the nitrogen atom. Substituents that localize unpaired electron density on the naphthalene ring system increase the probability of forming ESR-detectable anion radicals of naphthostyrils and their isomers.

The hypothetical process of isomerization of anion radicals must be a slow reaction, since we do not observe any wave on the polarograms that would indicate the formation of species D. On the cyclic voltammetric curves, which register slower conversions, the corresponding redox systems are manifested. Thus, on the voltamperogram of compound Ia, in addition to the primary redox system, we observe reduction peaks at potentials of −1.76, −2.18, and −2.20 V, but no peak corresponding to the polarographic wave at −2.37 V. For compound Ib, additional peaks of product reduction are observed at potentials of −1.75, −2.10, and −2.40 V. Peaks of the same sort are registered for the other type I compounds. On the voltamperogram of the model compound IIIa, a peak corresponding to species D is manifested only as an indistinct shoulder on the main peak characterizing the process on the polarographic wave at −2.49 V. For the thio analog II, an additional peak that can be assigned to species D is observed at a potential of −1.28 V; and for the model compound IV, there are no additional peaks indicating any intermediate reactions. For compound IV, no species D can be detected by ESR; but in the process of extended electrochemical generation at a potential of −2.5 V, we have established the presence of other free radical species. The concentration of these radicals was found to increase with a decrease of the generation potential to 0 V. The values of the constants (see Table 2) and the character of the hyperfine structure, along with the method of generation, indicate that these radicals (which are possibly not ion radicals) are formed as a result of more extensive conversions of the reduction product. Analogous conversions evidently take place in the reduction of compounds IIIe and IIIf, for which the ESR spectra that were registered are similar in character and also have similar constants of hyperfine structure.

EXPERIMENTAL

The electrochemical reduction of compounds I-IV was carried out in anhydrous DMF [8] on a background of tetrabutylammonium perchlorate ($c = 10^{-1}$ M).

The polarograms and cyclic voltammetric curves were obtained by means of a PAR-170 electrochemical system (Princeton), using a three-electrode cell. The cathode was a dropping-mercury electrode with forced detachment of the drop ($t = 0.5$ sec, $m = 0.90$ mg/sec) or a stationary vitreous carbon electrode; the anode was a platinum wire; the comparison electrode was a saturated aqueous calomel electrode equipped with a connecting bridge for operation in nonaqueous solvents. The depolarizer concentration was $5 \cdot 10^{-4}$ M.

The free radicals were generated in the steady-state mode on the surface of a flat platinum electrode placed in a rectangular resonator (H_{102} type) of an ER-9 ESR spectrometer (Carl Zeiss), following a procedure described in [2]. The electrochemical generation potentials were measured in a three-electrode scheme relative to a silver electrode.

The ESR spectra were recorded with a magnetic field sweep rate of 0.04 G with a depth of high-frequency (100 kHz) modulation of the magnetic field 0.05-0.9 G and a registration time constant 0.45 sec. The sweep of the magnetic field was calibrated on the basis of the ESR spectrum of the nitrobenzene anion radical [9]. For the electrochemical generation of free radicals, we used solutions of compounds I-IV in DMF with concentrations from 10^{-4} to $5 \cdot 10^{-3}$ M.

Compounds Id, If, and II (Table 3*) were synthesized by an original procedure; the other compounds were synthesized by procedures described in [10-15].

1-(p-Chlorophenylsulfonyl)benz[c,d]indolin-2-one (Id); 1-(o-nitrophenylsulfonyl)benz[c,d]indolin-2-one (If). To a solution of 1.91 g (10 mmoles) of the sodium salt of naphthostyril in 7 ml of DMF, a solution of 11 mmoles of the appropriate sulfochloride in 5-6 ml of DMF was added in portions while stirring vigorously. The reaction mixture was stirred for 30 min at 20°C and then poured into 150 ml of water. The resulting precipitate was filtered off and treated to remove naphthostyril present as an impurity by boiling three times with 200-250 ml of water, followed by filtration of the hot solution. The precipitate was then dried and crystallized. Yield of Id 2.05 g (60.3%); mp from benzene 194-195°C; IR spectrum 1380 and 1240 cm^{-1} (SO_2), 1750 cm^{-1} (C=O). Yield of If 1.4 g (39.0%); mp from 2/1 mixture of nitrobenzene and acetic acid 252-253°C; IR spectrum 1385 and 1240 cm^{-1} (SO_2), 1745 cm^{-1} (C=O).

1-Phenylsulfonylbenz[c,d]indolin-2-thione (II).

A. To a solution of 1.03 g (3.3 mmoles) of 1-phenylsulfonylbenz[c,d]indolin-2-one in 20 ml of m-xylene, prepared by heating the mixture, 1.1 g (5 mmoles) of phosphorus pentasulfide was added. The mixture was refluxed for 1 h and hot-filtered. From the filtrate, upon cooling, the reaction product precipitated in the form of crystals. Yield 0.77 g (71.4%); mp from acetic acid 205°C; IR spectrum 1372 and 1235 cm^{-1} (SO_2), 1120 cm^{-1} (C=S).

B. To a solution of 0.15 g (6 mmoles) of sodium in 10 ml of absolute alcohol, 0.9 g (5 mmoles) of thionaphthostyril [16] was added in portions, and the mixture was heated until the thionaphthostyril had completely dissolved. Then the solution was boiled down to 30% of its original volume, and 20-25 ml of n-hexane was added. The precipitate, the sodium salt of thionaphthostyril, was filtered off and dried. Yield 0.8 g (77.7%).

To a solution of 0.8 g (4 mmoles) of the sodium salt of thionaphthostyril in 8 ml of DMF, a solution of 0.9 g (5 mmoles) of phenyl sulfochloride in 3 ml of DMF was added over the course of 5 min while stirring vigorously. The reaction mixture was stirred for 20 min at 20°C and then poured into 250 ml of water. After 24 h, the resulting precipitate was filtered off, washed with water, and dried. Yield 0.38 g (30.5%); mp from acetic acid 205°C. The mixed melting point of this product with the product obtained by method A did not show any depression.

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*As in Russian original; no Table 3 is given in this article - Publisher.

The empirical formulas of the newly synthesized compounds, as determined by analysis, matched the calculated percentages of nitrogen and sulfur.

REFERENCES

1. G. F. Dzhurka, N. P. Shimanskaya, L. A. Kotov, and V. D. Bezuglyi, Zh. Obshch. Khim., **42**, No. 5, 1091 (1972).
2. Ya. P. Stradyn', R. A. Gavar, and L. Kh. Baumane, Izv. Akad. Nauk Latv. SSR, No. 2 (463), 73 (1986).
3. R. A. Gavar, Ya. P. Stradyn', L. Kh. Baumane, and K. Enish, Khim. Geterotsikl. Soedin., No. 12, 1631 (1991).
4. Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik., Neue Serie, Gesamtherausgeber K.-H. Hellwege, Springer Verlag, Berlin (1980), Group II, Vol. 9, No d1, p. 731.
5. Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik., Neue Serie, Gesamtherausgeber K.-H. Hellwege, Springer Verlag, Berlin (1980), Group II, Vol. 9, No d1, p. 437.
6. J. Stradins, R. Gavars, and L. Baumane, J. Mol. Struct., **259**, 57 (1991).
7. L. Kh. Baumane, Ya. P. Stradyn', R. A. Gavar, A. P. Gaukhman, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 11, 1494 (1988).
8. Yu. M. Kargin, V. V. Kondranina, and N. I. Semakhina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 278 (1971).
9. L. H. Piette, P. Ludwig, and R. N. Adams, Anal. Chem., **8**, 916 (1962).
10. A. P. Karishin and Yu. V. Samusenko, Zh. Org. Khim., **7**, No. 1, 150 (1971).
11. Yu. N. Rozhinskii and M. A. Mostoslavskii, Zh. Org. Khim., **10**, 2177 (1972).
12. Yu. V. Samusenko and V. I. Popov, Ukr. Khim. Zh., **54**, No. 6, 618 (1988).
13. A. P. Karishin, Zh. Obshch. Khim., **33**, 2250 (1963).
14. A. P. Karishin and D. M. Kustol, Zh. Obshch. Khim., **31**, 1655 (1961).
15. P. I. Mikhailenko, A. P. Karishin, G. F. Dzhurka, and A. A. Pechka, Vestn. Khar'kov. Politekh. Inst., Khim. Khim. Tekhnol., No. 7, 56 (1975).
16. N. S. Dokunikhin and L. A. Gaeva, Zh. Org. Khim., **28**, No. 10, 2670 (1958).