and the mixture was stirred for 2 h. The precipitate was removed by filtration and recrystallized from formic acid to give 1.25 g (80%) of chloride IIg, which, with respect to its electronic spectrum, was identical to the chloride obtained by the first method.

2,2'-Dithiobis[6-(4-chlorophenylamino)benzo-1,2,3-dithiazoliun] Chloride (Ij). A) A 10-mmole sample of Ib was added to 12 mmole of dimethylamine (diethylamine) acetate in 10 ml of DMA, and the mixture was stirred for 24 h. The precipitate was removed by filtration and crystallized from formic acid to give 2.9 g of chloride Ij. Compound IIj was similarly obtained from salt IIb.

B) A 2.2-g (10 mmole) sample of salt Id was added to 1.6 g (5 mmole) of 2,2'-dithiobis(4-chloroaniline) in 10 ml of acetic acid, and the mixture was stirred for 48 h. The precipitate was removed by filtration and recrystallized from formic acid to give 2.5 g of chloride Ij. Compound IIj was similarly obtained from salt IId. The compounds obtained by methods A and B were identified from their electronic spectra.

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QUINONEIMINES AND QUINONEDIIMINES OF THE DIBENZO[ce][1,2]THIAZINE 5,5-DIOXIDE SERIES

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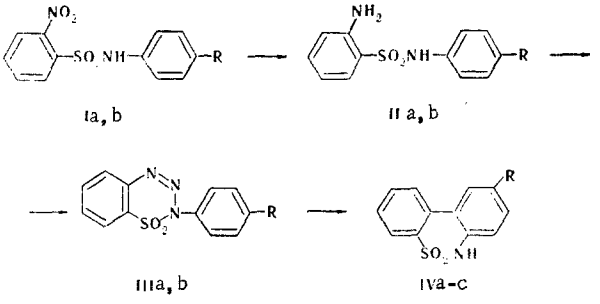
9(H)-Oxodibenzo[ce][1,2]thiazine 5,5-dioxide and its 9(H)-phenylsulfonylimino-substituted derivative were synthesized. It is shown that the direct bond between the quinoid ring and the substituent attached to nitrogen leads to a decrease in the redox potential of the system and a simultaneous increase in the electrophilic properties of the quinoneimine.

In order to determine the factors that affect the redox potentials of quinoneimines we synthesized heterocyclic quinoneimines of the dibenzo[ce][1,2]thiazine 5,5-dioxide (VIII) series, in which a direct bond between the substituent attached to the nitrogen atom and the quinoid ring is realized. The synthesized compounds are of interest in connection with the possibility of the use of the high reactivities of quinoneimines for the synthesis of biologically active compounds [1].

The starting 9-R-dibenzo[ce][1,2]thiazine 5,5-dioxides (IV) were synthesized by cyclization of 2-aminophenylsulfonyl(4-R-anilides) by the Ullmann–Gross method [2] via the following scheme:



I a, b — II a, b — III a, b — IV a-c

I–IV a R = OCH_3; b R = $NHSO_2C_6H_5$; IV c R = OH

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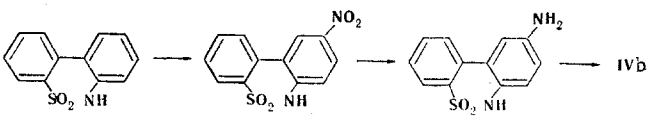
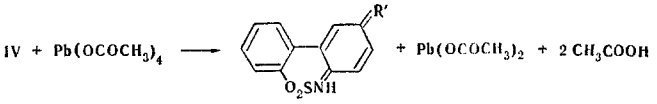
9-Hydroxydibenzo[ce][1,2]thiazine 5,5-dioxide (IVc) was obtained by demethylation of methoxy derivative IVa. 9-Phenylsulfamido-substituted IVb was also prepared from unsubstituted dibenzo[ce][1,2]thiazine 5,5-dioxide (V). The compound obtained through nitro product VI was found to be identical to the compound synthesized from phenylsulfonyl-4-aminoanilide via the scheme presented above. This method was used to prove that the nitration of V takes place in the 9 position, i.e., in the para position relative to the imino group.



V VI VII

Quinoneimines VIII were obtained by oxidation of the corresponding dihydro compounds IVb, c with lead tetraacetate in glacial acetic acid.

The redox potentials of N-arylsulfonyl-1,4-benzoquinoneimine–4-arylsulfamidophenol systems in 0.5 M anhydrous sodium acetate solution in 99.8% acetic acid were determined in [3]. The potentials were determined by potentiometric titration with lead tetraacetate. A value of 0.753 V* was obtained for N-phenylsulfonyl-1,4-benzoquinoneimine; this value is 0.169 V higher than the potential of 1,4-benzoquinone determined under the same conditions. We attempted to carry out the potentiometric titration of the synthesized compounds under the conditions indicated in [3] with lead tetraacetate solution in accordance with the equation



VIIIa, b

VIII a R′ = O; b R′ = $NSO_2C_6H_5$

However, the accurate determination of the potentials was found to be impossible because of the instability of the potential during titration. For this reason the redox potentials of the IVc–VIIa and IVb–VIIIb systems were determined by measurement of the potentials of mixtures of equimolar amounts of the indicated compounds. Since the potential of the mixture decreased with time, evidently due to reaction of the oxidized forms with acetate ions, the potential was found by extrapolation of the potential–time curve to t = 0. This dependence had curvilinear character in its initial section, after which it became linear. A similar method was used by Fieser in the determination of the potentials of unstable systems [4]. The redox potential of the IVc–VIIIa system is 0.715 V (average error 0.005 V), which is 0.038 V less than the potential of N-phenylsulfonyl-1,4-benzoquinoneimine [3]. This constitutes evidence for a high degree of conjugation of the quinoid ring with the nonquinoid ring and for an increase in the delocalization of the π electrons. The potential of the IVb–VIIIb system is 0.853 V, which is 0.138 V higher than the potential of the IVc–VIIIa system, i.e., replacement of the oxygen atom by a phenylsulfonylimino group in quinoneimine increases the potential by 0.138 V.

In contrast to N-phenylsulfonyl-1,4-benzoquinoneimine [5], 9(H)-oxodibenzo[ce][1,2]thiazine 5,5-dioxide (VIIIa) does not display an indophenol reaction with phenol and 1-naphthol in alkaline and ammoniacal solutions; this indicates the absence of cleavage at the $SO_2N=$ bond (ring cleavage is less favorable). 9(H)-Phenylsulfonyliminodibenzo[ce][1,2]thiazine 5,5-dioxide (VIIIb) displays an indophenol reaction with phenol and 1-naphthol only in ammoniacal solution (a dirty-green coloration with phenol and a blue-green coloration with 1-naphthol) and does not give any sign of reaction in alkaline solutions. Despite the absence of hydroxyl and imino groups, VIII dissolve quite rapidly in cold 1 M sodium hydroxide solution to give yellow-brown solutions.

Thus in addition to an increase in the electrophilicity of the quinoid ring and a tendency to react with nucleophiles (OH^-, CH_3COO^-), a certain decrease in the redox potential as compared with quinoneimines without a direct bond between the quinoid ring and the substituent attached to the nitrogen atom is observed for the synthesized cyclic quinoneimines VIII.

The IR spectra of quinoneimines VIII do not contain absorption bands in the region of stretching vibrations of N–H and O–H bonds (3200-3600 cm^{-1}); the absorption at 3070 cm^{-1} in the spectrum of monoimine VIIIa and at 3080 cm^{-1} in the spectrum of diimine VIIIb should be ascribed to excitation of the stretching vibrations of the aromatic ring C–H bonds. Intense bands at 1655 (C = O) and 1630 and 1565 cm^{-1} (C = N) are observed in the spectrum of quinoneimine VIIIa; intense bands at 1585 (exocyclic C = N) and 1570 cm^{-1} (ring C = N) are observed in the spectrum of quinonediimine VIIIb. For comparison we point out that intense absorption bands

*All of the redox potentials presented were measured relative to a standard hydrogen electrode.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		N	S		N	S	
Ia	105—106	9,08 8,85	10,56 10,12	$C_{13}H_{12}N_2O_5S$	9,09	10,40	70
Ib	194—197	9,71 9,96	14,76 14,45	$C_{18}H_{15}N_3O_6S_2$	9,70	14,79	92
IIa	125—129	8,61 8,81	10,06 10,12	$C_{13}H_{14}N_2O_3S \cdot HCl$	8,90	10,18	80
IIb	226—228	10,43 10,28	15,99 16,02	$C_{18}H_{17}N_3O_4S_2$	10,42	15,89	67
IVa	203—205	5,54 5,43	12,11 12,07	$C_{13}H_{11}NO_3S$	5,36	12,27	80
IVb (from IIb)	231—233 (dec.)	7,20 7,22	16,48 16,32	$C_{18}H_{14}N_2O_4S_2$	7,25	16,59	83
IVc	238—239	5,49 5,47	12,98 12,90	$C_{12}H_9NO_3S$	5,66	12,97	75
VI	244—247	10,15 9,98	11,47 11,45	$C_{12}H_8N_2O_4S$	10,14	11,61	84
VII	180—182	11,45 11,21	12,94 13,16	$C_{12}H_{10}N_2O_2S$	11,37	13,02	70
VIIIa	181—183 (dec.)	5,50 5,75	13,24 13,02	$C_{12}H_7NO_3S$	5,71	13,07	40
VIIIb	204—205 (dec.)	7,00 7,19	16,76 16,45	$C_{18}H_{12}N_2O_4S_2$	7,29	16,68	90

at 3060 (C—H), 1670 (C=O), 1620 (C=N), and 1540 cm^{-1} are present in the spectrum of N-phenylsulfonyl-1,4-benzoquinoneimine. Intense bands at 3070 (C—H), 1580 (C=N), and 1570 cm^{-1} are observed in the spectrum of N,N-bis(phenylsulfonyl)-1,4-benzoquinonediimine. The spectra of starting IV contain intense absorption bands at 3200-3300 cm^{-1} (N—H and OH).

It is interesting to note that quinonediimine VIIIb crystallizes from benzene in the form of orange-brown needles of the crystal solvate (an additive complex) with one molecule of benzene. At 80 deg C the crystals lose benzene and are converted to a bright-yellow powder.

EXPERIMENTAL

The IR spectra of KBr pellets of the synthesized compounds were recorded with a UR-20 spectrometer. The potentials were measured with a P37-1 potentiometer. The indicator electrode was platinum, and the comparison electrode was silver chloride (saturated).

2-Nitrophenylsulfonyl(4-methoxyanilide) (Ia). A 10 ml-sample of pyridine and 0.1 mole of 2-nitrobenzenesulfonyl chloride were added to a solution of 0.1 mole of 4-aminoanisole in 100 ml of alcohol. After 12 h, the mixture was poured into 500 ml of 5% hydrochloric acid, and the precipitate was removed by filtration and purified by dissolving in alkali and precipitation by the addition of acid. The product was crystallized from alcohol. Product Ia was also obtained by reaction of the amine with 2-nitrobenzenesulfonyl chloride in a suspension of sodium carbonate. 2-Nitrophenylsulfonyl(4-phenylsulfamidoanilide) (Ib) was similarly obtained from 4-phenylsulfamidoaniline.

2-Aminophenylsulfonyl(4-methoxyanilide) (IIa). A 0.01-mole sample of Ia was added to a suspension of 3.0 g (0.05 mole) of powdered pig iron in a mixture of 100 ml of alcohol, 5 ml of water, and 0.5 ml of 36% hydrochloric acid, after which the mixture was refluxed for 4 h. Alcohol (75 ml) was removed by distillation, 200 ml of 2% sodium carbonate solution was added to the residue, and the mixture was heated to the boiling point and treated with 5 g of sodium hydroxide. The hot solution was filtered, and amine IIa in the filtrate was precipitated by the addition of acetic acid. The product was obtained in the form of a light-colored viscous mass, which was purified by conversion to the hydrochloride. 2-Aminophenylsulfonyl(4-phenylsulfamidoanilide) (IIb) was similarly obtained.

2-(4-Methoxyphenyl)benzo-1,2,3,4-thiatriazine 1,1-Dioxide (IIIa). A 0.2-mole sample of amine IIa was dissolved in 490 ml of water containing 8.8 g (0.22 mole) of sodium hydroxide and 15.2 g (0.22 mole) of sodium nitrate, and the solution was cooled to 5 deg C and added gradually to an ice-cooled mixture of 40 ml of 36% hydrochloric acid in 400 ml of water. The solution was filtered through fluted filter paper, and the product was precipitated from the filtrate by the addition of a solution of 60 g (0.76 mole) of anhydrous sodium acetate in 400 ml of water. After 1 h, the yellowish precipitate of triazine IIIa was removed by filtration, washed with water, and converted, without purification, to IVa. A portion of the precipitate was recrystallized from petroleum ether to give pale-yellow needles. Diazo coupling occurred immediately with 1-naphthol on the filter paper, and intense coloration developed. In this respect, benzo-1,2,3,4-thiatriazine differs from diazoamino

compounds, which display diazo coupling only when they are treated with hydrochloric acid vapors [6]. 2-(4-Phenylsulfamido)benzo-1,2,3,4-thiatriazine 1,1-dioxide(IIIb) was similarly obtained.

9-Methoxydibenzo[ce][1,2]thiazine 5,5-Dioxide (IVa). The entire yield of thiatriazine IIIa (crude; drying reduces the yield) was suspended in 200 ml of 10% sodium hydroxide, 40 g (0.62 mole) of powdered copper was added, and the mixture was stirred until nitrogen evolution ceased. The mixture was then filtered, and IVa was isolated by acidification with hydrochloric acid. 9-Phenylsulfamidobenzo[ce][1,2]thiazine 5,5-dioxide (IVb) was similarly obtained.

9-Hydroxydibenzo[ce][1,2]thiazine 5,5-Dioxide (IVc). A solution of 5.2 g (0.02 mole) of IVa in a mixture of 100 ml of acetic acid and 100 ml of 48% hydrobromic acid was refluxed for 10 h, after which the hot solution was filtered and diluted with 500 ml of hot water. The hot solution was allowed to cool, and the resulting yellow needles of IVc were removed by filtration.

9-Nitrodibenzo[ce][1,2]thiazine 5,5-Dioxide (VI). A solution of 6.74 g (0.08 mole) of 72% nitric acid in 30 ml of acetic acid was added dropwise at 20 deg C to a solution of 11.6 g (0.05 mole) of V in 130 ml of acetic acid. After 1 h, the precipitate was removed by filtration and dissolved in 150 ml of 10% alkali. The solution was acidified, and the precipitated VI was removed by filtration.

9-Aminodibenzo[ce][1,2]thiazine 5,5-Dioxide (VII). A 15.0-g (0.07 mole on a 100% basis) sample of hydrosulfite was added to a heated solution of 2.52 g (0.01 mole) of nitro compound VI in 50 ml of 6% sodium hydroxide solution. After the mixture became colorless, 10 g (0.25 mole) of ammonium chloride was added, and the reaction product was removed by filtration.

9(H)-Oxodibenzo[ce][1,2]thiazine 5,5-Dioxide (VIIIa). A 1.0-g (4 mmole) sample of IVc in 20 ml of acetic acid was stirred for 2 h with 2.0 g (4.5 mmole) of lead tetraacetate, after which 0.5 ml of ethylene glycol was added. After 15 min, the mixture was diluted with 50 ml of water, and the precipitate was removed by filtration and crystallized rapidly from benzene. 9(H)-Phenylsulfonyliminodibenzo[ce][1,2]thiazine 5,5-dioxide (VIIIb) was similarly obtained.

The alternative synthesis of IVb from amine VII was accomplished by a method similar to the method for the preparation of anilides I.

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