INVESTIGATION OF QUINONES

XXIX.* ANTHRA[2,3-c][1,2,5]-X-DIAZOLE-5,10-DIONES (X = O, S, Se) AND THEIR AMINATION

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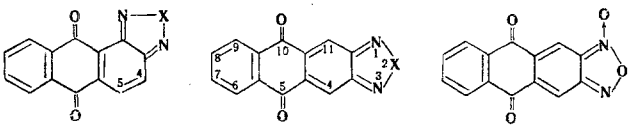
Anthraquinones that are linearly condensed with 1,2,5-thiazole, 1,2,5-selenadiazole, and furoxan were synthesized. When these quinones react with cyclohexylamine, the hydrogen atoms in the 4- and 11-positions are replaced to give 4-cyclohexylamino- and 4,11-dicyclohexylamino derivatives.

Angularly condensed heterocyclic anthraquinone derivative (I), containing a 1,2,5-oxa- [2], 1,2,5-thia- [3], 1,2,5-selenadiazole (I) [4] or 1,2,5-oxadiazole-N-oxide (furoxan) ring [5] have the unusual (for compounds of the anthraquinone series) ability to undergo nucleophilic addition in the 4-position.



I II, III IV

I X=O, S, Se; II X=S; III X=Se

It seemed of interest to study linearly condensed derivatives containing the same heterorings.

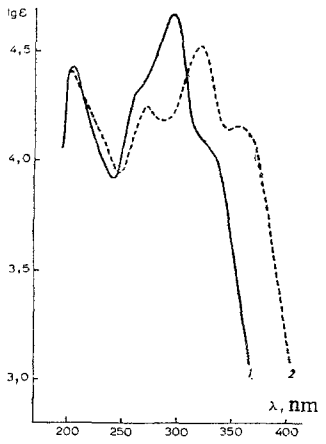


Fig. 1. Electronic spectra (in alcohol): 1) anthra[2,3-c]-[1,2,5]thiadiazole-5,10-dione (II); 2) anthra[2,3-c][1,2,5]-selenadiazole-5,10-dione (III).

2,3-Anthraquinonethia- (II) and 2,3-anthraquinoneselenadiazole (III) were obtained by the action of thionyl chloride and selenium dioxide, respectively, on 2,3-diaminoanthraquinone. 2,3-Anthraquinonefuroxan IV was synthesized by reaction of 3-chloro-2-nitroanthraquinone with sodium azide as a result of cyclization of the intermediate 3-azido-2-nitroanthraquinone.†

Quinones II-IV are light-yellow substances that are resistant to oxidizing agents. The electronic spectra of anthraquinone diazoles II and III (Fig. 1), which are similar to the spectra of the angular isomers [3], differ from them with respect to a hypsochromic shift of the less distinctly expressed longwave band, the greater intensity of the band at ~300 nm, and the bathochromic shift of the shortwave absorption. The band of stretching vibrations of the carbonyl group in the IR spectra lies at ~1680 cm^{-1}, which is the usual interval for anthraquinone derivatives.

Linear anthraquinone diazoles II and III are weaker oxidizing agents than the angular isomers. The half-wave potential of the first

* See [1] for the preceding communication.

† See [5] for a preliminary communication.

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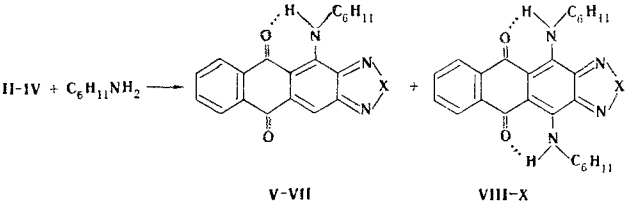
wave ($E^1_{1/2}$) is shifted to more negative values during polarographic reduction in DMFA: −0.75 V for II and III as compared with −0.43 V for quinones I, where X = S, Se [6] (relative to the standard calomel electrode). The $E^1_{1/2}$ value for 2,3-anthraquinonefuroxan IV is in a more positive region (−0.21 V) and is close to the half-wave potential of the angular isomer (−0.19 V), but the possibility that the heteroring is simultaneously involved with the quinone grouping in the electrode reaction cannot be excluded in this case.

Despite the lower electron affinities, the linear anthraquinonediazoles, like the angular isomers, are active with respect to certain nucleophilic agents. Thus, like 1,2-anthraquinoneselenadiazole [7], the heteroring of 2,3-anthraquinoneselenadiazole III opens under the influence of alkalis to give a diaminoanthraquinone.

2,3-Anthraquinonediazoles II-IV undergo hydrogen substitution with amines, for example, with cyclohexylamine, at room temperature or on gentle heating. It is noteworthy that the amination does not stop at the step involving the formation of monoamino derivatives V-VII but proceeds readily to give diamino derivatives VIII-X, which turn out to be the predominant products in the case of quinones III and IV. Diamines VIII-X are also formed by treatment of monoamines V-VII with cyclohexylamine. The overall yields of amino derivatives from quinones II and III are ~60%, as compared with ~45% from IV, and are not lowered in the absence of air oxygen. This indicates that a portion of the starting quinone, which undergoes profound decomposition, apparently acts as the necessary hydride-ion acceptor. As in the case of the angular isomer [5], the amination of 2,3-anthraquinonefuroxan IV is accompanied by elimination of oxygen with conversion of the furoxan ring to a furazan ring; this usually can be realized only by the action of phosphorus compounds [8, 9].



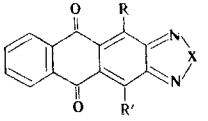
V, VIII X = S; VI, IX X = Se; VII, X X = O

The ring adjacent to the heteroring undergoes amination, inasmuch as the benzoid ring, which is removed from the heteroring, retains the inertness peculiar to anthraquinone itself under the reaction conditions. In fact, signals of H-4 and H-11 protons, which are present in the spectra of the starting quinones (singlets at 9.53 and 9.42 ppm, respectively), are absent in the PMR spectra of dicyclohexylamino derivatives VIII and IX, but two groups of multiplets at 8.54 (H-7 and H-8 protons) and 8.85 ppm (H-6 and H-9 protons) are retained.

The IR spectral data, which attest to a strong intramolecular hydrogen bond (IHB), indicate a peri orientation of the amino groups. In addition to the absorption of a free CO group at 1680 cm^{-1}, a band of a CO group tied up in an IHB at 1620-1630 cm^{-1} appears in the spectra of the monoamines, while the band at 1680 cm^{-1} vanishes completely in the spectra of the diamines, in which both of the CO groups participate in an IHB, and only the band of carbonyl groups tied up in IHB remains.

The electronic spectra of derivatives VIII-X have the characteristic (for 1,4-diamino-substituted anthraquinones) band with two maxima in the visible region. Despite the expected bathochromic shift on introduction of electron-acceptor substituents into the 2 and 3 positions [10], the longwave band in the spectra of 4,11-dicyclohexylaminoanthraquinonediazoles VIII-X is shifted as compared with the analogous band in the spectrum of 1,4-dicyclohexylaminoanthraquinone by 90-100 nm to the shortwave side. A hypsochromic shift is also observed in the spectra of 4-cyclohexylaminoanthraquinonediazoles V-VII with respect to the spectrum of 1-cyclohexylaminoanthraquinone. This is in sharp contrast to the effect of the same heterorings when they are angularly oriented. The introduction of condensed 1,2,5-thia- and 1,2,5-selenadiazole rings into the 3,4-positions of 1-cyclohexylaminoanthraquinone causes a bathchromic shift of 95 and 150 nm, respectively [2, 3], while the introduction of the same rings into the 2,3-positions causes a hypsochromic shift of 40 nm.

The amination of anthraquinonediazoles should be considered to be a nucleophilic addition reaction, which is possible because of disruption of the equalization of the bonds that is typical for anthraquinone [11]. The localization of C−C bonds of increased multiplicity under the influence of a condensed 1,2,5-X-diazole ring (X = O, S, Se) is shown by x-ray diffraction analysis of benzo- [12, 13] and 1,2-anthraquinone-

TABLE 1. Anthra[2,3-c](1,2,5]-X-diazole-5,10-diones 

Compound	X	R	R′	mp, °C	Empirical formula	Found, %				Calc., %				λ_{max}, nm (lg ε) in $CHCl_3$	ν_{CO}, cm^{-1}	Yield, %
						C	H	N	S	C	H	N	S			
II	S	H	H	248—248,5	$C_{14}H_6N_2O_2S$	63,1	2,1	10,6	11,9	63,1	2,3	10,5	12,0		1681	82
III	Se	H	H	280—281	$C_{14}H_6N_2O_2Se$	—	—	8,8	—	—	—	8,9	—		1679	93
IV	O, N-Oxide	H	H	249—250	$C_{14}H_6N_2O_4$	63,2	2,3	10,6	—	63,2	2,3	10,5	—		1678	75
V	S	NHC_6H_{11}	H	202—202,5	$C_{20}H_{17}N_3O_2S$	66,0	4,5	11,4	8,7	66,1	4,7	11,6	8,8	485 (4,02)	1672 1620	51
VIII	S	NHC_6H_{11}	NHC_6H_{11}	251,5—252	$C_{26}H_{28}N_4O_2S$	67,5	6,2	12,3	7,0	67,8	6,1	12,2	7,0	582 (4,24) 546 (4,20)	1620 sh	11
VI	Se	NHC_6H_{11}	H	263—264	$C_{20}H_{17}N_3O_2Se$	—	—	10,2	—	—	—	10,2	—	484 (3,94)	1674 1618	26
IX	Se	NHC_6H_{11}	NHC_6H_{11}	234—235	$C_{26}H_{28}N_4O_2Se$	—	—	11,1	—	—	—	11,0	—	568 (4,38) 530 (4,25)	1620 sh	35
VII	O	NHC_6H_{11}	H	216—216,5	$C_{20}H_{17}N_3O_3$	69,2	4,9	12,0	—	69,1	4,9	12,1	—	462 (4,07)	1673 1628	20
X	O	NHC_6H_{11}	NHC_6H_{11}	272—273	$C_{26}H_8N_4O_3$	70,3	6,2	12,7	—	70,2	6,3	12,6	—	559 (4,25) 525 (4,22)	1605	24

diazoles [14-16]. 1,6-Addition along the chain consisting of the CO group and the conjugated (with it) "diene" system, which includes shortened $C_{5a}-C_{11a}$ and C_4-C_5 bonds, the latter of which from their lengths (1.32-1.34 Å) are double bonds, is realized in angular 1,2-anthraquinonediazoles I. However, disruption of the equalization of the bonds in 2,3-anthraquinonediazoles II-IV leads to fixation of two α,β-unsaturated $-C=C-C=O$ groupings, each of which is capable of involvement in nucleophilic 1,4-addition, and entry of an amine into one of the groupings does not substantially hinder nucleophilic attack of the other.

EXPERIMENTAL*

The PMR spectra of D_2SO_4 solutions of the compounds were measured with a Tesla BS-487B spectrometer (80 MHz) with hexamethyldisiloxane as the external standard. The IR spectra of KBr pellets were recorded with a UR-10 spectrometer. The electronic spectra were recorded with a Perkin-Elmer-402 spectrophotometer. The polarograms of DMFA solutions of the compounds were recorded with an LP-60 electronic polarograph with 0.1 N tetraethylammonium perchlorate as the base electrolyte; the characteristics of the mercury capillary were as follows: m 2.253 mg/sec and t 3.3 sec.

Anthra[2,3-c][1,2,5]thiadiazole-5,10-dione (II). A mixture of 2 ml of pyridine and 4 ml of dioxane was added in the course of 30 min at 70° to a mixture of 0.48 g (2 mmole) of 2,3-diaminoanthraquinone [17], 15 ml of dioxane, and 1.15 g (12 mmole) of thionyl chloride, and the mixture was heated for 1.5 h, after which it was cooled and poured into water. The resulting thiadiazole (II) was purified by chromatography in chloroform with a column filled with Al_2O_3. The product was obtained as pale-yellow needles (from benzene or acetic acid) (Table 1). IR spectrum,† cm^{-1}: 1680 s, 1590 s, 1516 m, 1450 m, 1370 w, 1337 s, 1297 s, 1253 s, 1160 w, 1140 m, 983 m, 930 w, 915 w, 878 m, 830 m, 795 w, 760 w, and 720 s.

Anthra[2,3-c][1,2,5]selenadiazole-5,10-dione (III). A solution of 0.9 g (8 mmole) of selenium dioxide in 3 ml of water was added to a boiling solution of 0.48 g (2 mmole) of 2,3-diaminoanthraquinone in 75 ml of acetic acid. The brown-red color of the mixture changed to yellow. The greater portion of the solvent was removed by distillation, and the pale-yellow needles of selenadiazole III were removed by filtration. IR spectrum, cm^{-1}: 1679 s, 1585 s, 1500 s, 1450 s, 1345 s, 1300 s, 1269 s, 1170 w, 1144 m, 1130 w, 972 m, 932 w, 914 w, 823 w, 795 w, 768 m, and 720 s.

Anthra[2,3-c][1,2,5]oxadiazole-5,10-dione 1-Oxide (IV). A solution of 0.65 g (10 mmole) of sodium azide in 3 ml of water was added to a mixture of 0.86 g (3 mmole) of 2-chloro-3-nitroanthraquinone [18] and 30 ml of dioxane, and the mixture was then refluxed for 30 min and poured into water. The resulting precipitate was separated and chromatographed in benzene on Al_2O_3 to give light-yellow plates (from benzene). Electronic spectrum in alcohol, λ_{max}, nm (log ε): 204 (4.27), 226 (4.34), 259 (4.39), and 390 (3.56); λ_{min}, nm (log ε): 211 (4.26), 241 (4.23), and 365 (3.41).

Reaction of Quinones II-IV with Cyclohexylamine. A 2-mmole sample of the quinone was stirred in 8 ml of cyclohexylamine at 50° (quinones II and III) or at room temperature (quinone IV) for 2 h, and the solution was then poured into dilute HCl. The resulting precipitate was removed by filtration, washed with water, dried, and chromatographed on Al_2O_3; a violet band of the diamino derivatives (VIII-X) was eluted initially and was followed by an orange-red band of the monoamino derivative (V-VII). In the case of quinone II, the first product was eluted with benzene, while the second was eluted with chloroform; in the case of quinone III, both products were eluted with chloroform; in the case of IV, both products were eluted with benzene. The products were crystallized from dioxane, benzene, or acetic acid.

Reaction of Anthra[2,3-c][1,2,5]selenadiazole-5,10-dione (III) with Sodium Hydroxide. A 0.5-ml sample of 40% NaOH solution was added to a suspension of 0.31 g (10 mmole) of quinone III in 10 ml of 50% aqueous dioxane, and the mixture was refluxed for 30 min. It was then cooled, diluted with water, and filtered to give 0.21 g (88%) of 2,3-diaminoanthraquinone.

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*With the participation of A. A. Sakharova.

† The following abbreviations are used here and subsequently: s is strong, m is medium, and w is weak.

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