SYNTHESIS OF ANTHRA[9,1-cd]ISOTHIAZOLIUM DERIVATIVES AND THEIR REACTIONS WITH NUCLEOPHILES

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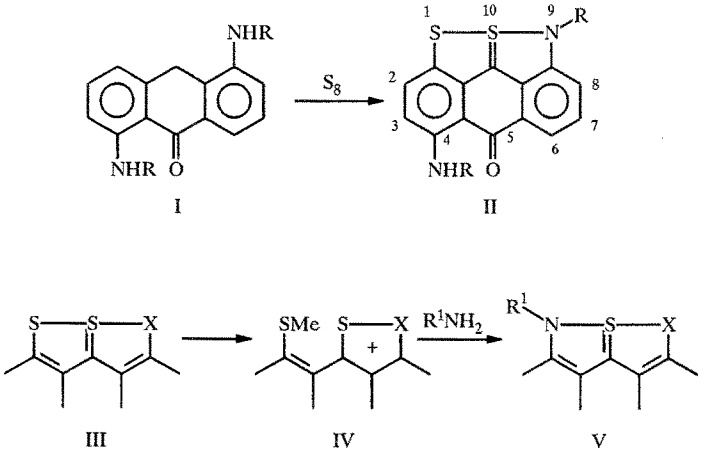
The methylation of 9-methyl-4-methylamino-5H-anthra[1,9,8-bcde]-1,10λ⁴-dithia-9-azapentalen-5-one takes place at the $S_{(1)}$ atom and leads to a 2-methyl-7-methylamino-10-methylthio-6-oxo-6H-anthra[9,1-cd]isothiazolium salt, while protonation is directed to the $N_{(9)}$ atom to give a 5,10-bis(methylamino)-6-oxo-6H-anthra[1,9-cd]dithiolium salt. Depending on their nature, substitution of the hydrogen atom in the 5 or 3 position, reversible addition of a hydroxide ion in the 10b position, demethylation, or opening of the heteroring occurs in the reaction of the anthraisothiazolium cation with nucleophilic reagents.

The reaction of N,N′-disubstituted 1,5-diaminoanthrones I with elementary sulfur in the presence of a base was previously used to synthesize II — the first representatives of the new 5H-anthra[1,9,8-bcde]-1,10λ⁴-dithia-9-azapentalen-5-one (dithiaazapentaleneanthrone) condensed heterocyclic system [1]. It is known that dithiaazapentalenes IIIa, which do not contain an annelated anthrone ring, are methylated at the $S_{(1)}$ atom to give 5-(methylthioethenyl)isothiazolium salts IVa, which are converted to thiadiazapentalenes Va by the action of methylamine [2]. Correspondingly, trithiapentalenes IIIb are converted to dithiaazapentalenes Vb as a result of methylation [3] (or ethylation [4]). It seemed of interest to accomplish the methylation of dithiaazapentaleneanthrones II in order to obtain derivatives of the unknown 6-oxo-6H-anthra[9,1-cd]isothiazolium heterocyclic system and study their reaction with amines and other nucleophilic reagents.



III - V a X=NR, b X=S

2-Methyl-7-methylamino-10-methylthio-6-oxo-6H-anthra[9,1-cd]isothiazolium methylsulfate (VII), which was converted to the perchlorate, iodide, and tetrafluoroborate for characterization, is isolated in almost quantitative yield when 4-methylamino-9-methyl-5H-anthra[1,9,8-bcde]-1,10λ⁴-dithia-9-azapentalen-5-one (VI) is treated with dimethyl sulfate in refluxing chlorobenzene. The fact that methylation takes place at the sulfur atom in the 1 position of VI was proved by synthesis of salt

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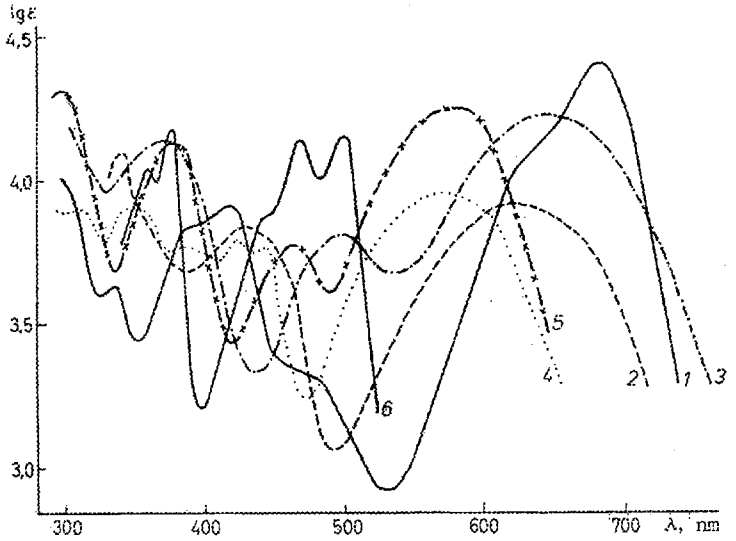
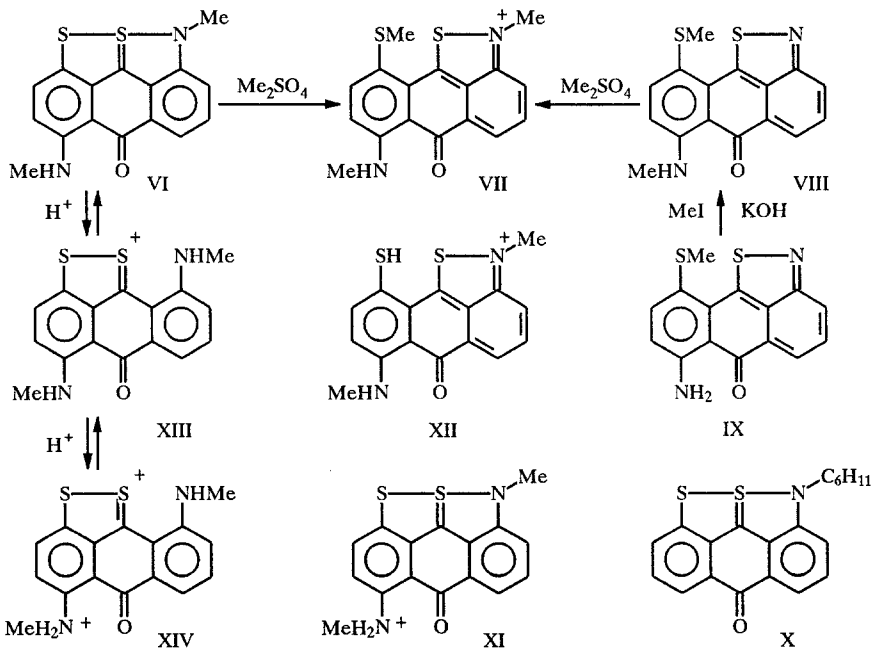


Fig. 1. Electronic absorption spectra (in ethanol): 1) dithiaazapentaleneanthrone VI; 2) anthraisothiazolium VII perchlorate; 3) anthraiso=-thiazolium XVa perchlorate; 4) anthraisothiazole VIII; 5) anthraisothiazole XVIa; 6) pseudobase XVIII.

VII by quaternization of 7-methylamino-10-methylthio-6H-anthra[9,1-cd]isothiazol-6-one (VIII), as well as by the formation of the latter and other products containing a methylthio group by the action of bases on salt VII. Compound VIII was obtained by methylation at the amino group of 7-amino-10-methylthio-6H-anthra[9,1-cd]isothiazol-6-one (IX), the structure of which was established by x-ray diffraction analysis [1].



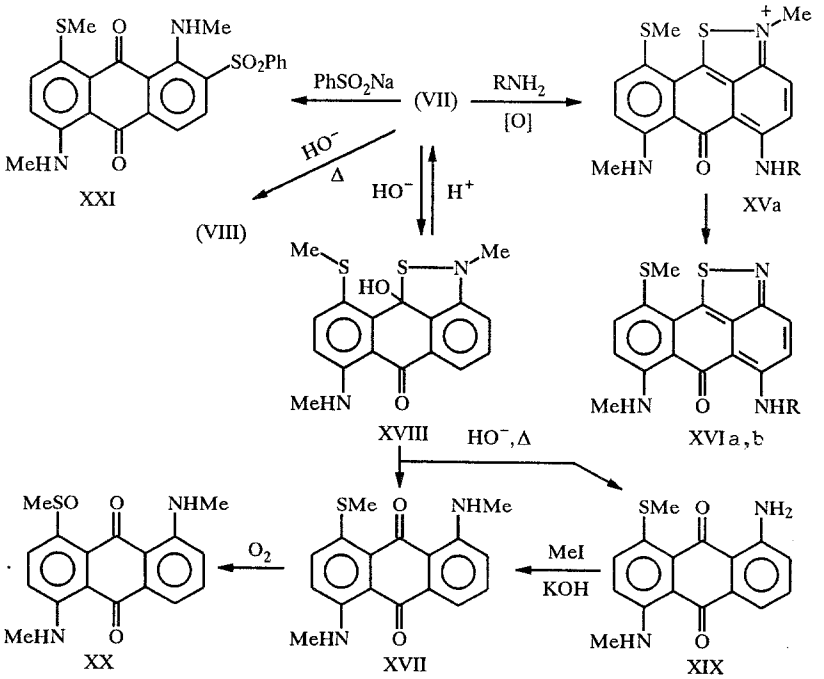
The transformation of dithiaazapentaleneanthrone VI to anthraisothiazolium cation VII is accompanied by an ≈60 nm hypsochromic shift of the long-wave maximum and a decrease in the absorption intensity (Fig. 1, curves 1 and 2). A similar change in the spectrum is observed in the case of monoprotonation. However, one cannot draw a conclusion regarding the

site of protonation on the basis of the electronic spectra, since a model of the form protonated at the amino group (XI) — dithiaazapentaleneanthrone X [1] — has absorption in the same region as anthraisothiazolium salt VII — a model of the form protonated at the sulfur atom (XIII) — while a model of the form protonated at the heterocyclic nitrogen atom (XII) is not available. The problem of the structure of the protonated form was solved by means of the PMR spectra.

The location of the singlet of the protons of the $N_{(4')}$—CH_3 group (δ = 3.27 ppm) does not change when trifluoroacetic acid, which causes monoprotonation, is added to a solution of dithiaazapentaleneanthrone VI in $CDCl_3$, while the signal of the $N_{(9)}$—CH_3 group is shifted to strong field (δ = 3.42-3.84 ppm). This indicates that the $N_{(9)}$ atom is protonated to give the 5,10-bis(methylamino)-6-oxo-6H-anthra[1,9-cd]dithiolium cation (XIII), since in the case of protonation at the $S_{(1)}$ or $N_{(4')}$ atom to give an isothiazolium (XII) or ammonium (XI) cation one would observe a shift of the signal of the protons of the $N_{(9)}$—CH_3 or $N_{(4')}$—CH_3 group to weak field. Judging from the increase in the chemical shifts of the aromatic protons, the positive charge in anthradithiolium cation XIII is delocalized not only in the ring adjacent to the heteroring, as in anthraisothiazolium cation VII, but also in the remote outer ring. The presence of protonated forms XI and XII is not detected within the limits of sensitivity of the method. Thus the protonation of the 4-amino derivative of dithiaazapentaleneanthrone, which is controlled by thermodynamic factors, as in the protonation of dithiaazapentalenes IIIa [5], takes place at the heterocyclic nitrogen atom, while methylation, which is kinetically controlled, takes place at the sulfur atom in the 1 position.

In concentrated sulfuric acid one observes diprotonation of dithiaazapentaleneanthrone VI with a change in the color to red and merging (in the PMR spectrum in D_2SO_4) of the singlets of both methyl groups (δ = 3.60 ppm), i.e., a shift of the signal of the $N_{(9)}$—CH_3 group to strong field and a shift of the signal of the $N_{(4')}$—CH_3 group to weak field. Consequently, the diprotonated form has the anthradithiolium cation XIV structure containing an ammonium group.

In a study of the reaction of anthraisothiazolium cation VII with primary amines it was found that, in contrast to the reaction of monocyclic IV, the hydrogen atom in the ring adjacent to the heteroring rather than the methylthio group is replaced by an amine residue. A salt of the 5-phenylamino derivative of anthraisothiazolium cations XVa was obtained in ≈90% yield as a result of treatment of anthraisothiazolium VII methylsulfate with aniline at room temperature. Demethylation with conversion to the 5-phenylamino derivative of anthraisothiazole XVIa occurs when salt VII or XVa is heated in aniline or the latter is heated with NaOH in aqueous dimethyl sulfoxide. Cyclohexylamine, which is a harder nucleophilic reagent than aniline [6], attacks not only the benzene ring adjacent to the heteroring but also the heteroring, leading to its opening. 5-Cyclohexylamino-substituted anthraisothiazole XVIb and 1,5-bis(methylamino)-4-methylthioanthraquinone (XVII) are formed in the reaction with cyclohexylamine in dimethyl sulfoxide at 20°C. Evidence for the incorporation of a phenylamino group and a cyclohexylamino group in the 5 position is provided by the presence in the PMR spectra of XVIa, b of four doublets of protons of an anthrone ring and shifting of the signal of the proton of the incorporated amino group far to weak field, which indicates participation of this proton in an intramolecular hydrogen bond.



The amination of anthraisothiazolium cation VII in the 5 position is evidently 1,4-addition to a chain including the C=O group and the $C_{(5a)}$—$C_{(5)}$ bond, which has increased multiplicity, with subsequent oxidation by air oxygen. The o-quinoid distribution of the bonds in the ring of the isothiazoloanthrone that is adjacent to the heteroring was confirmed by x-ray diffraction data in the case of IX [1]. Quaternization of the heteroring intensifies the electron-acceptor effect of the carbonyl group, thereby ensuring successful amination of anthraisothiazolium cation VII. In the absence of a positive charge, amination in anthraisothiazole VIII does not occur under comparable conditions. Substitution of the methylthio group in anthraisothiazolium cation VII, like substitution in 5-(methylthioethenyl)isothiazolium cation IVa, is hindered by the presence of an electron-donor methylamino group in the para position and the lower effectiveness of transmission of the activating effect of the isothiazolium ring through the aromatic C—C bond in cation VII than through the double bond in cation IVa.

The introduction of a phenylamino group in the 5 position of both the anthraisothiazolium cation and the anthraisothiazole molecule on passing from VII and VIII to phenyl-substituted XVa and XVIa, respectively, leads to a bathochromic shift of 13-25 nm in the electronic spectra and an increase in the intensity (ε_{max}) by a factor of approximately two (see Fig. 1).

Intensification of the electron-acceptor effect of the heteroring as a result of quaternization on passing from anthraisothiazoles VIII and XVIa to anthraisothiazolium cations gives rise to a bathochromic shift of 74-86 nm without a change in the intensity of the long-wave band, which is evidently the charge band that is typical for amino derivatives of anthraquinone and anthrone [7]. The fact that methylation of dithiaazapentaleneanthrone VI with conversion to anthraisothiazolium cation VII and protonation with conversion to anthradithiolium cation XIII are accompanied not by a bathochromic shift but rather by a hypsochromic shift of 65-80 nm with a decrease in the intensity by a factor of two to three (see Fig. 1) emphasizes the specificity of the chromophore system of dithiaazapentaleneanthrone.

Attack on anthraisothiazolium cation VII by a hard nucleophile — the hydroxide anion — is directed to the heteroring. A precipitate of pseudobase XVIII is formed when NaOH is added to an aqueous solution of VII methylsulfate. The band of the anthraisothiazolium cation at 625 nm vanishes in the electronic spectrum when alkali is added to an ethanol solution of the VII salt, and a new band of XVIII with maxima at 470-520 nm develops (see Fig. 1). Upon acidification, the initial spectrum is restored completely, from which it follows that the forward and reverse reactions proceed quantitatively. In the PMR spectrum of XVIII formed by the action of alkali the signals of the protons attached to the $C_{(4)}$ and $C_{(8)}$ atoms are shifted 1.3-1.4 ppm as compared with the spectrum of starting cation VII. This is in agreement with addition of the hydroxide ion to the carbon atom bonded in the para positions relative to the indicated atoms and makes it possible to assign the 10b-hydroxy-2-methyl-7-methylamino-10-methylthio-2,10b-dihydro-6H-anthra[9,1-cd]isothiazol-6-one (XVIII) structure to the pseudobase.

Refluxing an aqueous solution of VII methylsulfate with NaOH leads to the formation of 1,5-bis(methylamino)-4-methylthioanthraquinone (XVII), as well as anthraisothiazole VIII as a result of nucleophilic attack by the hydroxide ion of the $N_{(2)}$-methyl group in cation VII, which exists in equilibrium with pseudobase XVIII. Heating salt VII with NaOH in aqueous dimethyl sulfoxide leads to a mixture of 1,5-bis(methylamino)-4-methylthioanthraquinone (XVII) and 5-amino-1-methylamino-4-methylthioanthraquinone (XIX), which is converted to XVII by N-methylation. Splitting out of the methyl group during the formation of XIX occurs in one of the intermediate steps involved in opening of the heteroring, since 1,5-bis(methylamino)-4-methylthioanthraquinone (XVII) is not demethylated under the same conditions, and anthraisothiazole VIII does not cleave the heteroring.

The methylthio group in XVII and XIX is readily oxidized by air oxygen in organic solvents. Thus passing air into a solution of XVII in dimethylformamide with heating (including in the dark) leads to 1,5-bis(methylamino)-4-methylsulfinylanthraquinone (XX) in 95% yield. The easy oxidation of the sulfide grouping to a sulfoxide grouping by air is unexpected, since it usually requires photochemical initiation (singlet oxygen) or the presence of a catalyst [8]. The structure of methylsulfinyl derivative XX was confirmed by x-ray diffraction analysis.*

The reaction of an anthraisothiazolium VII salt with sodium benzenesulfinate in dimethylformamide or dimethyl sulfoxide without heating leads to a mixture of products, from which 1,5-bis(methylamino)-4-methylthioanthraquinone (XVII) and 1,5-bis(methylamino)-2-phenylsulfonyl-4-methylthioanthraquinone (XXI) were isolated. The absence in the PMR spectrum of the strong-field signal of the proton in the ortho position relative to the methylamino group at 6.94 ppm that is present in the spectrum of XVII constitutes evidence for the location of the phenylsulfonyl group in XXI. Phenylsulfonyl derivative XXI

*The authors thank V. A. Tafeenko for determining the molecular structure of XX; the results of the x-ray diffraction analysis will be published separately.

is evidently formed via nucleophilic 1,6-addition to the conjugated chain in cation VII, which includes the carbonyl group, and subsequent transformations of the adduct. 1,4-Addition with attack by the benzenesulfinate anion in the 5 position of cation VII is evidently prevented by steric hindrance.

EXPERIMENTAL

The IR spectra of KCl pellets of the compounds were obtained with a Perkin—Elmer 598 spectrometer. The electronic spectra were recorded with a Specord M-40 spectrophotometer. The NMR spectra were obtained with Bruker WP 200 SY and Bruker AM 400 spectrometers with tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with a Kratos MS 25 RFA spectrometer. Thin-layer chromatography was accomplished on Silufol UV-254 plates in CH_2Cl_2 or in butanol—acetic acid—water (11:4:4) in the case of VII and XV; chromatographic separation of the substances was accomplished with columns packed with silica gel 40/100 μm. The melting points were determined with a microheating stage. The identification of the compounds synthesized by the various methods was carried out by TLC, mixed-melting-point determinations, and comparison of the IR spectra. The results of elementary analysis for C, H, Cl, N, and S were in agreement with the calculated values.

2-Methyl-7-methylamino-10-methylthio-6-oxo-6H-anthra[9,1-cd]isothiazolium (VII) Salts. A solution of 1.87 g (6 mmole) of VI and 5.6 ml (60 mmole) of dimethyl sulfate in 200 ml of chlorobenzene was refluxed for 30 min, after which it was cooled, and the precipitated VII methylsulfate was removed by filtration, washed with benzene, and dried. For conversion to the perchlorate all of the precipitate was dissolved in 300 ml of distilled water, 5 ml of 30% $HClO_4$ was added, and the precipitate was removed by filtration and washed with water to give 2.52 g (98% based on VI) of **VII perchlorate ($C_{17}H_{15}ClN_2O_5S_2$)**, which did not melt up to 350°C after recrystallization from water. The very same salt was synthesized as a result of the reaction of isothiazoloanthrone VIII with dimethyl sulfate under similar conditions. IR spectrum: 1623 cm^{-1} (C=O). UV spectrum (90% ethanol), λ_{max} (log ε): 340 (4.11), 385 (3.69), 428 (3.84), 625 nm (3.91). PMR spectrum (CD_3OD): 10.61 (1H, s, 7-NH), 8.23 (3H, m, 3-5-H), 7.96 (1H, d, J = 9.8 Hz, 9-H), 7.34 (1H, d, J = 9.8 Hz, 8-H), 4.39 (3H, s, 2-CH_3), 3.30 (3H, s, 7-NCH_3), 2.65 ppm (3H, s, SCH_3).

The addition of an aqueous solution of 15 mmole of $NaBF_4$ or KI to an aqueous solution of VII methylsulfate gave, respectively, **VII tetrafluoroborate ($C_{17}H_{15}BF_4N_2OS_2$)** or **VII iodide ($C_{17}H_{15}IN_2OS_2$)**, which were recrystallized from water.

Protonation of 4-Methylamino-9-methyl-5H-anthra[1,9,8-bcde]-1,10λ^4-dithia-9-azapentalen-5-one (VI).*

Compound VI. UV spectrum (50% ethanol), λ_{max} (log ε): 243 (4.30), 276 (4.37), 342 (3.75), 393 sh (3.94), 423 (4.00), 691 nm (4.40). PMR spectrum ($CDCl_3$): 11.25 (1H, d, 4-NH), 8.08 (1H, d, 6-H), 7.98 (1H, d, 2-H), 7.89 (1H, t, 7-H), 7.58 (1H, d, 8-H), 7.30 (1H, d, 3-H), 3.84 (3H, s, 9-CH_3), 3.27 ppm (3H, d, 4-NCH_3).

Monoprotonated form XIII. UV spectrum (30% H_2SO_4 in 50% ethanol), λ_{max} (log ε): 265 (4.85), 365 (4.08), 612 nm (4.13). PMR spectrum (mixture of $CDCl_3$ and CF_3CO_2H, with a 20-fold molar excess of the latter): 8.38 (1H, d, 2-H), 8.32 (1H, d, 6-H), 8.04 (1H, t, 7-H), 7.85 (1H, d, 3-H), 7.81 (1H, d, 8-H), 3.42 (3H, d, 9-CH_3), 3.24 ppm (3H, d, 4-NCH_3).

Diprotonated form XIV. UV spectrum (100% H_2SO_4), λ_{max} (log ε): 345 (4.13), 372 (4.11), 498 (4.11), 536 nm (4.20). PMR spectrum (D_2SO_4): 3.60 ppm (6H, methyl groups).

7-Methylamino-10-methylthio-6H-anthra[9,1-cd]isothiazol-6-one (VIII, $C_{16}H_{12}N_2OS_2$). A. This compound was obtained under the conditions in [9] by the reaction of 30 mg (0.1 mmole) of IX in 5 ml of sulfolane, 30 mg of KOH, and 0.3 ml of CH_3I at 40°C for 8 h. At the end of the reaction (monitoring by TLC) the solution was poured into 30 ml of 3% HCl. The resulting precipitate was removed by filtration, washed with water, dried, and chromatographed by elution with CH_2Cl_2. The yield was 13 mg (42%).

B. Refluxing 300 mg (0.70 mmole) of VII methylsulfate in 70 ml of water with 1 ml of 40% NaOH for 1.5 h gave a precipitate, which was removed by filtration, washed with water, dried, and extracted with chloroform (3 × 50 ml). The extract was concentrated and chromatographed by elution with toluene to give 40 mg (37%) of XVII and 20 mg (18%) of VIII with mp 196.5-197.5°C [CCl_4—hexane (1:1)]. IR spectrum: 1620 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 236 (4.49), 407 (3.79), 551 nm (3.94). PMR spectrum ($CDCl_3$): 10.50 (1H, d, 7-NH), 8.09 (1H, d, J = 6.5 Hz, 5-H), 8.00 (1H, d, J = 8.5 Hz, 3-H), 7.66 (1H, d, J = 9.2 Hz, 9-H), 7.65 (1H, t, J = 6.5 Hz, 8.5 Hz, 4-H), 6.74 (1H, d, J = 9.2 Hz, 8-H), 3.05 (3H, d, 7-NCH_3), 2.45 ppm (3H, s, SCH_3). M^+ 312.

*The same numbering of the atoms as that used for base VI was adopted for the protonated forms.

2-Methyl-7-methylamino-10-methylthio-6-oxo-5-phenylamino-6H-anthra[9,1-d]isothiazolium (XVa) Perchlorate ($C_{23}H_{20}ClN_3O_5S_2$). When 300 mg (0.70 mmole) of VII methylsulfate was stirred in 10 ml of aniline for 2 h at 20°C, the color of the solution changed from green to blue. Monitoring by TLC provided evidence that the starting substance had vanished. The aniline was removed by steam distillation, and 1 ml of 30% $HClO_4$ was added to the aqueous solution, or the reaction mixture was poured into 350 ml of 5% $HClO_4$. The precipitated perchlorate was removed by filtration and washed with water. For analysis, the substance was crystallized from water. IR spectrum: 1623 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 263 (4.48), 369 (4.14), 498 (3.81), 650 nm (4.23). PMR spectrum (DMSO-D_6): 12.30 (1H, s, 5-NH), 10.08 (1H, d, 7-NH), 8.03 (1H, d, J = 9.8 Hz, 3-H), 7.93 (1H, d, J = 9.8 Hz, 4H), 7.85 (1H, d, J = 9.0 Hz, 9-H), 7.43-7.61 (5H, m, Ph), 6.96 (1H, d, J = 9.0 Hz, 8-H), 4.31 (3H, s, 2-CH_3), 2.96 (3H, d, 7-NCH_3), 2.39 ppm (CD_3CN) (3H, s, SCH_3). The yield was 330 mg (89%).

7-Methylamino-10-methylthio-5-phenylamino-6H-anthra[9,1-cd]isothiazol-6-one (XVIa, $C_{22}H_{17}N_3OS_2$). **A.** A 260-mg (0.5 mmole) sample of XVa was refluxed in 10 ml of aqueous DMSO (1:1) with 1 ml of 40% NaOH for 5 h, after which the mixture was cooled, and the resulting precipitate was removed by filtration, washed with water, dried (120 mg), and extracted with benzene; 40 mg (15%) of starting salt XVa remained. The benzene solution was concentrated and chromatographed by elution with benzene to give 58 mg (29%) of XVIa.

B. When 215 mg (0.5 mmole) of VII methylsulfate was refluxed in 10 ml of aniline for 15 min, 35 mg (16%) of starting salt VII methylsulfate was recovered. Chromatography yielded 64 mg (32%) of XVIa with mp 255-256°C (benzene). IR spectrum: 1619 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 233 (4.49), 280 (4.32), 360 (4.14), 447 (3.78), 564 nm (4.25). PMR spectrum ($CDCl_3$): 12.53 (1H, s, 5-NH), 10.45 (1H, d, J = 4.9 Hz, 7-NH), 7.78 (1H, d, J = 9.7 Hz, 3-H), 7.73 (1H, d, J = 8.8 Hz, 9-H), 7.51 (1H, d, J = 9.7 Hz, 4-H), 7.26-7.45 (5H, m, Ph), 6.61 (1H, d, J = 8.8 Hz, 8-H), 2.98 (3H, d, J = 5.0 Hz, 7-NCH_3), 2.38 ppm (3H, s, SCH_3). M^+ 403.

7-Methylamino-10-methylthio-5-cyclohexylamino-6H-anthra[9,1-cd]isothiazol-6-one (XVIb, $C_{22}H_{23}N_3OS_2$). A mixture of 300 mg (0.70 mmole) of VII methylsulfate, 1 ml (8 mmole) of cyclohexylamine, and 10 ml of DMSO was stirred for 4 h at 20°C, after which it was poured into 100 ml of 15% $HClO_4$. The precipitate was removed by filtration, washed with water, and dried (205 mg). After extraction with benzene, 85 mg (28%) of undissolved starting VII remained. The benzene extract was concentrated and chromatographed in benzene to give successively 30 mg (19%) of XVII and 55 mg (27%) of XVIb with mp 258-260°C [benzene—hexane (1:1)]. IR spectrum: 1623 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 234 (4.50), 300 (3.84), 346 sh (4.16), 438 (3.62), 559 nm (4.22). PMR spectrum ($CDCl_3$): 11.22 (1H, d, J = 7.2 Hz, 5-NH), 10.59 (1H, d, J = 4.3 Hz, 7-NH), 7.85 (1H, d, J = 9.9 Hz, 3-H), 7.76 (1H, d, J = 8.7 Hz, 9-H), 7.26 (1H, d, J = 9.9 Hz, 4-H), 6.63 (1H, d, J = 8.7 Hz, 8-H), 3.78 (1H, m, 5-NCH), 3.00 (3H, d, 7-NCH_3), 3.00 (3H, d, 7-NCH_3), 2.37 (3H, s, SCH_3), 1.66-2.10 ppm (10H, m, cyclohexane). M^+ 409.

10b-Hydroxy-2-methyl-7-methylamino-10-methylthio-2,10b-dihydro-6H-anthra[9,1-cd]isothiazol-6-one (XVIII). Compound XVIII (200 mg) precipitated when 1 ml of 40% NaOH solution was added to a solution of 300 mg (0.70 mmole) of VII methylsulfate in 50 ml of water. The substance was not purified to the analytically pure state. The UV spectrum was measured after the addition of 1 N NaOH solution to a solution of VII perchlorate in 90% ethanol [λ_{max} (log ε)]: 360 (4.05), 378 (4.20), 444 sh (3.88), 470 (4.15), 500 nm (4.16). The spectrum of the VII salt was reproduced quantitatively when a 1 N solution of acid was added. The PMR spectrum was obtained by the addition of a solution of KOD in D_2O to a solution of the VII salt in DMSO-D_6: 7.48 (1H, d, J = 8.3 Hz, 5-H), 7.45 (1H, d, J = 7.8 Hz, 9-H), 6.87 (1H, t, J = 8.3 Hz, J = 7.0 Hz, 4-H), 6.56 (1H, d, J = 7.0 Hz, 3-H), 5.88 (1H, d, J = 7.85 Hz, 8-H), 3.32 (3H, s, 2-CH_3), 2.83 (3H, s, 7-NCH_3), 2.18 ppm (3H, s, SCH_3).

1,5-Bis(methylamino)-4-methylthioanthraquinone (XVII, $C_{17}H_{16}N_2O_2S$) and 5-Amino-1-methylamino-4-methylthioanthraquinone (XIX, $C_{16}H_{14}N_2O_2S$). A mixture of 300 mg (0.70 mmole) of VII methylsulfate, 10 ml of DMSO, and a solution of 1 g of NaOH in 6 ml of H_2O was heated for 5 h at 80°C, after which it was poured into 50 ml of 15% HCl, and the precipitate was removed by filtration, washed with water, dried, and extracted with benzene (3 × 20 ml). The benzene extract was concentrated and chromatographed in benzene to give successively 54 mg (25%) of XVII and 66 mg (32%) of XIX.

Compound XVII had mp 277.5-278.5°C [benzene—hexane (1:1)]. IR spectrum: 1612 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 226 (4.57), 313 (4.03), 574 nm (4.17). PMR spectrum ($CDCl_3$): 9.96 (1H, d, NH), 9.53 (1H, d, NH), 7.53 (1H, d, 3-H), 7.52 (2H, m, 7-H, 8-H), 7.05 (1H, d, 2-H), 6.94 (1H, d, 6-H), 3.02 (3H, d, NCH_3), 3.01 (3H, d, NCH_3), 2.50 ppm (3H, s, SCH_3). M^+ 312.

Compound XIX had mp 277-278°C [benzene—hexane (1:1)]. IR spectrum: 1638 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 242 (4.56), 310 (4.01), 555 nm (4.16). M^+ 298.

A 59-mg sample of KOH and 0.3 ml of CH_3I were added to 30 mg (0.1 mmole) of XIX in 5 ml of sulfolane, and the mixture was stirred for 4 h at 40°C. The solution was poured into 30 ml of 3% HCl, and the precipitate was separated, washed with water, dried, and chromatographed in benzene to give 12 mg (38%) of XVII.

1,5-Bis(methylamino)-4-methylsulfinylanthraquinone (XX, $C_{17}H_{16}N_2O_3S$). A solution of 156 mg (0.5 mmole) of XVII in 15 ml of DMF was heated for 3 h at 140°C as air was bubbled through it. After the starting compound had vanished (monitoring by TLC), the mixture was poured into 100 ml of water, and the resulting precipitate was separated, washed with water, and dried to give 155 mg (95%) of XX with mp 254-255°C (benzene). IR spectrum: 1612 (C=O), 1048 cm^{-1} (S=O). UV spectrum (ethanol), λ_{max} (log ε): 234 (4.51), 312 (4.04), 538 nm (4.02). PMR spectrum ($CDCl_3$): 9.87 (1H, d, NH), 9.29 (1H, d, NH), 8.41 (1H, d, J = 9.3 Hz, 3-H), 7.53 (1H, t, 7-H), 7.49 (1H, d, 8-H), 7.13 (1H, d, J = 9.3 Hz, 2-H), 6.93 (1H, d, 6-H), 3.05 (3H, d, NCH_3), 3.01 (3H, d, NCH_3), 2.87 ppm (3H, s, SCH_3). M^+ 328.

1,5-Bis(methylamino)-8-methylthio-2-phenylsulfonylanthraquinone (XXI, $C_{23}H_{20}N_2O_4S$). A 200-mg (1 mmole) sample of sodium benzenesulfinate was added to a solution of 109 mg (0.25 mmole) of VII methylsulfate in 10 ml of DMSO, after which the mixture was stirred for 6 h at 20°C and then poured into water. The precipitate was separated, washed with water, and chromatographed in benzene to give 8 mg (10%) of XVII and 17 mg (15%) of XXI with mp 225-226°C [benzene—hexane (1:1)]. IR spectrum: 1623 cm^{-1} (C=O). UV spectrum (ethanol), λ_{max} (log ε): 236 (4.61), 319 (4.01), 586 nm (4.11). PMR spectrum ($CDCl_3$): 9.80 (1H, d, NH), 8.60 (1H, d, NH), 8.10 (1H, d, J = 8.3 Hz, 3-H), 7.50-7.90 (5H, m, Ph), 7.60 (1H, d, J = 8.2 Hz, 4-H), 7.40 (1H, d, 7-H), 7.0 (1H, dd, J - 9.5 Hz, 6-H), 3.02 (3H, d, NCH_3), 2.96 (3H, d, NCH_3), 2.43 ppm (3H, s, SCH_3). M^+ 452.

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