3-Cyclopropylcarbonyl-4,6-dinitroanthranil (IVd) was obtained by method (B) from 0.16 g (1 mmole) of $CH_2{=}C(OSiMe_3){-}\underbrace{CHCH_2CH_2}$. After addition of CuBr, CCl_4, and α,α'-bipyridyl the mixture was stirred for 5 days. Yield 0.15 g (54%), mp 110-112°C.

Oxidation of a Mixture of σ-Complexes of 3,5-Dinitrobenzyl Trifluoride with Methyl Ethyl Ketone (B). A mixture of 0.48 g (2 mmole) of 3,5-dinitrobenzyl trifluoride, 0.28 g (2 mmole) of Me_3SiCH_2COEt, 0.53 g (2 mmole) of 18-crown-6, and 0.12 g (2.1 mmole) of KF in 10 ml of MeCN was stirred for 3 h. The mixture was filtered, and the filtrate was treated with 5 ml of CCl_4, 0.03 g (0.2 mmole) of CuBr, and 0.03 g (0.2 mmole) of α,α'-bipyridyl and stirred for 1 day. Then 10 ml of 10% HCl was added and the mixture was extracted with benzene. The extracts were washed with water and dried with $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a column of SiO_2 (40/100). The yield of the mixture of (V) and (VI) ($C_{11}H_9F_3N_2O_5$) was 0.38 g (63%). The PMR spectrum indicates formation of two isomeric alkylation products. PMR spectrum (in CD_3CN), ppm (J, Hz): 9.05 d (J = 2); 8.61 d (J = 2) and 8.55 s (2H); 4.48 s and 4.45 s (2H); 2.75 q (2H, J = 7.3), 1.15 t (3H, J = 7.3).

LITERATURE CITED

1. S. V. Kovalenko, G. A. Artamkina, I. P. Beletskaya, and O. A. Reutov, Metallorg. Khim., No. 1, 125 (1988).
2. G. A. Artamkina, S. V. Kovalenko, I. P. Beletskaya, and O. A. Reutov, J. Organomet. Chem., 329, 189 (1987).
3. K. H. Wünch, Adv. Heterocycl. Chem., 8, 303 (1967).
4. J. C. Splitter and M. Calvin, J. Org. Chem., 20, 1086 (1955).
5. R. A. Khmel'nitskii and P. B. Terent'ev, Usp. Khim., 48, 854 (1979).
6. S. S. Gitis and A. Ya. Kaminskii, Zh. Obshch. Khim., 32, 3277 (1963).
7. M. I. Kalinkin, Z. H. Parnes, V. E. Puzanova, A. D. Khmelinskaya, S. N. Shein, and D. N. Kursanov, Zh. Org. Khim., 9, 2354 (1973).

SYNTHESIS AND STRUCTURE OF DERIVATIVES OF AZADITHIAPENTALENEANTHRONE AND ISOTHIAZOLEANTHRONE

M. V. Gorelik, R. A. Alimova, V. Ya. Shteiman,
T. Kh. Gladysheva, V. A. Tafeenko, and S. V. Medvedev

UDC 547.673'738'788.6.
07:543.422:548.737

The reaction of N,N'-dialkyl- or N,N'-diaryl-1,5-diaminoanthrones with sulfur in a polar aprotic solvent in the presence of a base leads to the formation of 4-alkyl(aryl)amino-9-alky(aryl)-5H-anthra[1,9,8-bcde]-9-aza-1,10λ^4-dithiapentalen-5-ones. The reaction of the 1,5-diaminoanthrone, followed by methylation, leads to 7-amino-10-methylthio- and 7-amino-8,10-dimethylthio-6H-anthra[9,1-cd]isothiazol-6-ones. The structures of the last two compounds and of 4-methylamino-9-methylazadithiapentaleneanthrone were studied by x-ray crystallography. Elimination of the amino group occurs in each series. The structural features and the spectral characteristics of the new heterocyclic systems are discussed.

Compounds of 1,6,7λ^4-trithiapentalene and its heteroanalogs have been investigated intensively in connection primarily with the problem of aromaticity and "no bond—single bond" resonance of the I ↔ I' ↔ I" type [1-5]. Together the known data show that trithiapentalene is an aromatic 10π-electron system similar to naphthalene. Condensed compounds containing the bicycle (I) have been investigated to a significantly lesser degree.

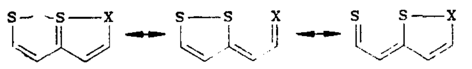
Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 417-425, March, 1990. Original article submitted January 28, 1988.

TABLE 1. The Azadithiapentaleneanthrones (IIIb, VIa-d, X) and Isothiazoleanthrones (VII, VIII, XI)

Compound	Molecular formula	mp, °C*	IR spectrum, ν_{CO}, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	M$^+$, m/z
IIIb	$C_{20}H_{17}NOS_2$	255...257	1645	351 (3,72), 443 (3,70), 467 (3,78), 637 (4,05)	351
VIa	$C_{16}H_{12}N_2OS_2$	350	1612	337 (3,67), 385 sh (3,85), 415 (3,95), 466 sh (3,38), 692 (4,41)	312
VIb	$C_{26}H_{28}N_2OS_2$	258...259	1612	338 (3,73), 390 sh (3,85), 419 (3,95), 476 sh (3,30), 700 (4,40)	448
VIc	$C_{26}H_{16}N_2OS_2$	268...269	1612	338 (3,73), 390 sh (3,85), 419 (3,98), 439 sh (3,90), 698 (4,72)	436
VId	$C_{28}H_{20}N_2O_3S_2$	288...289	1612	395 sh (3,83), 420 (3,94), 442 sh (3,90), 704 (4,39)	—
VII	$C_{15}H_{10}N_2OS_2$	229...230	1625	236 (4,42), 334 (3,77), 528 (3,86)	298
VIII	$C_{16}H_{12}N_2OS_3$	193...193,5	1625	237 (4,12), 336 (3,60), 535 (3,73)	344
X	$C_{20}H_{18}N_2OS_2$	234...236	1620	336 (3,59), 376 (3,75), 400 (3,76), 470 (3,40), 677 (4,27)	366
XI	$C_{15}H_9NOS_2$	198...198,5	1662	238 (4,51), 319 (4,04), 441 (4,02)	283

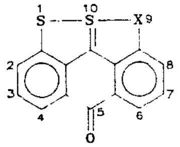
*Compounds (IIIb, VIc, VII, X) were recrystallized from toluene, (VIa) from chlorobenzene, and (VIb, d, VIII) from a mixture of benzene and hexane, (XI) from ethanol.

5H-Anthra[1,9,8-bcde]-1,9,10λ^4-trithiapentalen-5-one [trithiapentaleneanthrone (II)], formed in the reaction of 1,8-dichloroanthraquinone with sodium sulfide in DMFA, and some of its derivatives were synthesized from 9,10-anthraquinone derivatives [6, 7]. The present work is devoted to the synthesis of derivatives of the aza analogs of trithiapentaleneanthrone — the previously unknown 5H-anthra[1,9,8-bcde]-9-aza-1,10λ^4-dithiapentalen-5-one system* [azadithiapentaleneanthrone (III)].



I I' I''

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



II, III

For the synthesis of azadithiapentaleneanthrone derivatives we chose the method of direct introduction of sulfur atoms at the unsubstituted peri positions of the anthracene ring by the action of elemental sulfur on N,N'-disubstituted 1,5-diaminoanthrones (IV), which are obtained with good yields by the reduction of the respective 1,5-diaminoanthraquinones (V). When N,N'-alkyl- or N,N'-diaryl-1,5-diaminoanthrones (IVa-d) are heated with sulfur in a polar aprotic solvent (DMFA, DMSO, N-methylpyrrolidone, sulfolane, etc.) in the presence of a base (tertiary amines, alcoholates, potassium carbonate, potassium hydroxide), 4-alkyl(aryl)amino-9-alkyl(aryl)azadithiapentaleneanthrones (VIa-d) are formed as green substances, which can be isolated in the pure form from the solution (with yields of about 50%) (Table 1). The reaction of 1,5-diaminoanthrone (IVe), which contains primary amino groups, with sulfur under the same conditions leads to products having acidic characteristics. After their methylation both in alkaline and in a neutral medium not even traces of the green $N_{(9)}$-methyl derivative of azadithiapentaleneanthrone (VIe) were found, but 7-amino-10-methylthio- and 7-amino-8,10-dimethylthio-6H-anthra[9,1-cd]isothiazol-6-ones (VII) and (VIII) (2.5:1) were isolated as cherry-red compounds, which were derivatives of another previously undescribed system.† The elemental compositions, molecular masses, and NMR and IR spectra of (VI-VIII) correspond to the given formulas. In addition, the structures of the azadithiapentaleneanthrone (VIa) and of the isothiazoleanthrones (VII, VIII) were proved by the x-ray crystallographic method (Fig. 1).

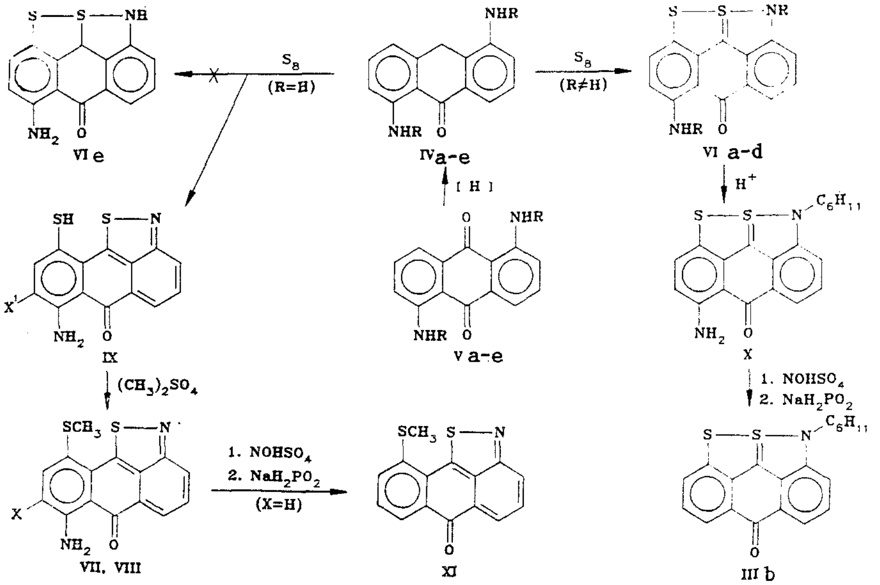
---

*Alternative name: 5H-benzo[cd][1,2]benzodithiolo[4,3,2-ghi][1,2]benzo[cd][1,2]isothiazol-$10S^{IV}$-5-one.

†For the previous communication, see [8].

Thus, two sulfur atoms enter at the unoccupied peri positions both in the reaction of the N,N'-disubstituted 1,5-diaminoanthrone and in the reaction of the unsubstituted compound. If there is a secondary amino group adjacent to the sulfur atom, the azadithiapentalene bicycle is formed, and if there is a primary amino group the isothiazole ring is closed and a mercapto group [compound (IX)], which is then easily methylated, remains at the α position of the end ring. As a side reaction a second mercapto group enters at the ortho position to the primary amino group. In the absence of a base the reaction does not go either in DMFA or in other solvents. The base evidently activates the substrate as a result of enolization to the anthranol [9] or deprotonation to the anthranolate anion, where each of the attacked protons has an electron-donating substituent (the amino and the hydroxy or oxide group) at the para position. The ability of aromatic amines and phenols to react with elemental sulfur at the ortho and para positions is well known [10]. The activation of the reagent by the base is less likely as a determining factor, since when the process is conducted in DMFA traces of dimethylamine present in the solvent are usually sufficient for activation of the sulfur [11].

In order to pass to the azadithiapentaleneanthrone not containing substituents in the anthracene fragment we converted the cyclohexylamino group in (VIb) into a primary amino group by dealkylation by heating in a mineral acid by analogy with the dealkylation of α-alkylaminoanthraquinones [12]. The obtained 4-amino derivative (X) was deaminated to 9-cyclohexylazadithiapentaleneanthrone (IIIb) by diazotization and reduction of the diazonium salt with sodium hypophosphite. 10-Methylthioisothiazoleanthrone (XI) was obtained similarly by the deamination of (VII).



IV—VI a $R=CH_3$, b $R=C_6H_{11}$, c $R=C_6H_5$, d $R=4\text{-}CH_3OC_6H_4$, e R=H; VII X=H;
VIII $X=SCH_3$; IX X'=H,SH

The synthesized representatives of the new condensed systems, i.e., azadithiapentaleneanthrone (IIIb, VIa-d, X) and isothiazoleanthrone (VII, VIII, XI), contain the same heteroatoms S...S...N at the peri positions of the anthrone ring, but a hydrocarbon substituent is at the nitrogen atom in the former and at the sulfur atom in the latter. If the presence of the substituent in the amino group (VIa) is disregarded, compounds (VIa) and (VII) can be regarded as the N- and S-methyl isomers. It seemed of interest to study the effect of this difference on the geometry and electronic structure of the molecules. Such a possibility is presented by x-ray crystallographic determination of the bond lengths and angles in 4-methylamino-9-methylazadithiapentaleneanthrone (VIa) (Fig. 1a) and in the methylthio derivatives of 7-aminoisothiazoleanthrone (VII, VIII) (Fig. 1b) and by the data from the electronic, IR, and NMR spectra.

All the atoms of the rings in (VIa, VII, VIII) and the heteroatoms attached to them and also the $N-CH_3$ bonds in (VIa) lie in practically the same plane, the $S-CH_3$ bonds in (VII) are rotated in relation to the plane by an angle of 102.0°, and in (VIII) they are

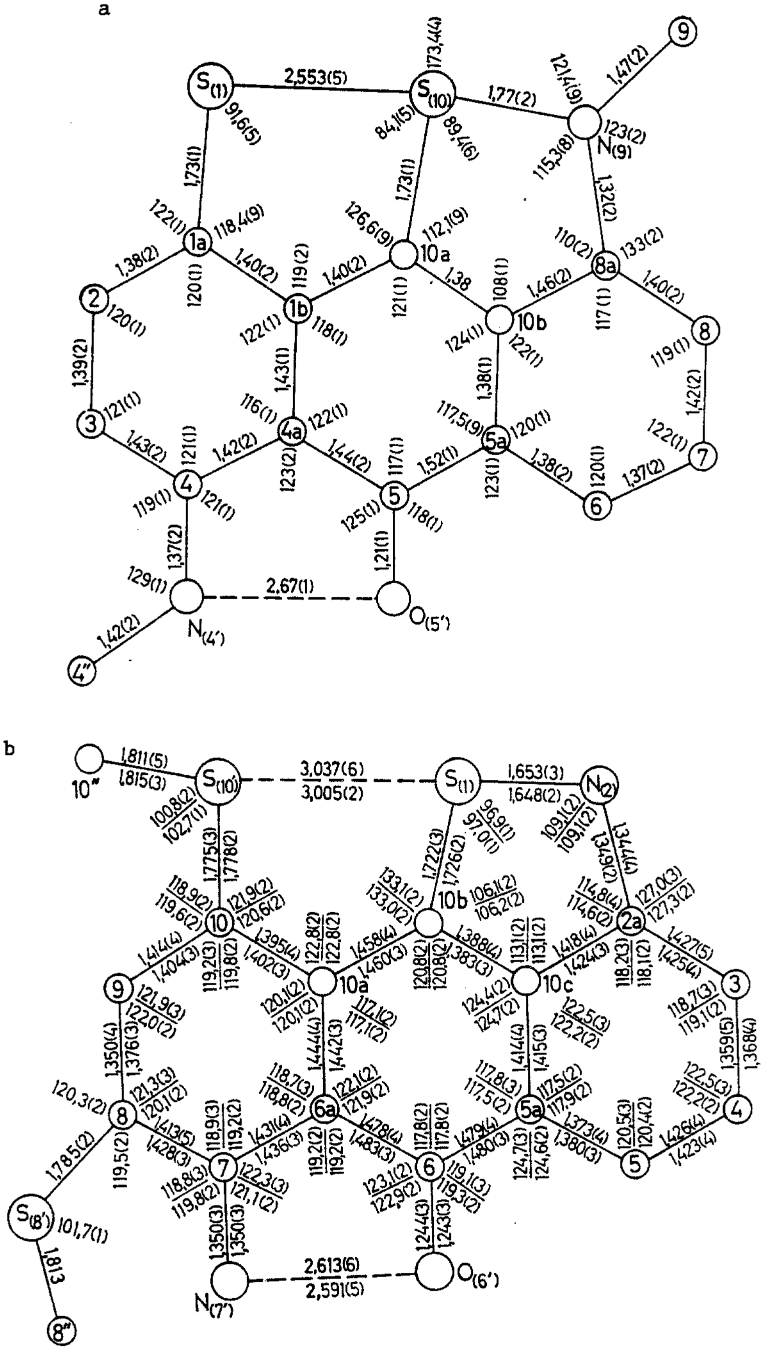


Fig. 1. The molecular structures of N,N'-dimethylazadithiapentalene-anthrone (VIa) (a) and 7-amino-10-methylthioisothiazoleanthrones (VII) (above the line) and (VIII) (b).

rotated by 92.4° [at $C_{(10)}$] and 101.8° [at $C_{(8)}$] on different sides. In the isothiazole-anthrones (VII, VIII) (Fig. 1b) the length of the S...S bond (3.00-3.04 Å) is significantly longer than that of the normal S—S bond (2.05 Å [10]), but it is less than the sum of the van der Waals radii (3.40-3.60 Å [2, 3]). The last fact and also the absence of a deflection of the S atoms from the plane and the value of the $S_{(10')}$—$C_{(10)}$—$C_{(10a)}$ angle, close to 120°, indicate specific bonding interaction between the sulfur atoms. The parameters of the isothiazole ring in compounds (VII, VIII) differ little from those in 5-chlorobenzo[c]-isothiazole (XII) [13]. An exception is the length of the C—S bond, which is 0.06 Å larger, and also the angles at the $C_{(10c)}$ and $C_{(10b)}$ atoms, belonging at the same time to the anthrone ring, which are 3.5° larger and smaller, respectively, as a result of annellation.

In the transition from the S-methyl derivative [methylthiaisothiazoleanthrone (VII), Fig. 1b] to the N-methyl derivative [azadithiapentaleneanthrone (VIa), Fig. 1a] the length of the S...S bond is reduced by 0.50 Å, remaining 0.50 Å greater than the length of the normal single S—S bond, while the S...N distance is increased by 0.13 Å. During comparison of the 2,4,6- and 2,5,6-triphenyl-substituted azadithiapentalenes (I) (X = Ph) [14, 15] with (VIa) the $S_{(1)}...S_{(10)}$ bond in (VIa) is 0.11-0.15 Å longer, the $S_{(10)}...N_{(9)}$ bond is 0.09-0.10 Å shorter, while the total length of the $S_{(1)}...N_{(9)}$ bond remains approximately the same. This is due to the annellation of the anthrone ring, which gives rise to a decrease of the angle at the $C_{(10a)}$ atom, common to the heterocycles, by 4-7° compared with the angles of the bicyclic azadithiapentalenes and to a simultaneous increase of the angle in the dithiole ring at the same atom, i.e., deflection of the $C_{(10a)}—S_{(10)}$ bond toward the $N_{(9)}$ atom. Both C—S bonds are shorter (1.73 Å) than the C—S single bond [1.78-1.81 Å in the methylthio groups of compounds (VII, VIII)] but longer than the C=S double bond (1.61 Å [16]), and they are identical, which underlines the arbitrary nature of the formulas of type (I-III) and their names with designation of the nonequivalent divalent and tetravalent (λ^4) sulfur atoms [2-4]. The lengths of the C—C bonds in the dithiole ring (1.40 Å), equal to the length of the aromatic bond, are also identical. The approach of the sulfur atoms during the transition from the isothiazoleanthrone (VII) (Fig. 1b) to the azadithiapentaleneanthrone (VIa) (Fig. 1a) leads to a reduction of the angles included in the dithiole ring (VIa) and to shortening of the $C_{(1a)}—C_{(10a)}$ bond in the azadithiapentaleneanthrone. In the isothiazole ring of the azadithiapentaleneanthrone (VIa) the angles at the $C_{(10a)}$, $N_{(9)}$ atoms are increased by 5-7° and the angles at the $C_{(8a)}$, $S_{(10)}$ atoms are increased in comparison with the angles in the isothiazoleanthrones (VII, VIII). Apart from the S—N bond the length of the $C_{(8a)}—C_{(10b)}$ bond is increased by 0.04 Å, but the $C_{(8a)}—N_{(9)}$ bond is shorter than in 5-chlorobenzisothiazole (XII) or isothiazoleanthrones (VII, VIII), although it is shown as a single bond in the formula (VI) and as a double bond in the formulas (VII, VIII, XII).

In the carbocycles of azadithiapentaleneanthrone (VIa) the deviations of the C—C bond lengths from the average value of 1.40 Å do not alternate, but in the isothiazoleanthrones (VII, VIII), as in benzoisothiazole (XII) [13], there is (although to a lesser degree) an ortho-quinonoid distribution of the bonds in the ring adjacent to the heterocycle. Thus, in the isothiazoleanthrone (VII) the $C_{(3)}—C_{(4)}$ (1.359 Å) and $C_{(5)}—C_{(5a)}$ (1.373 Å) bonds are shortened, while the $C_{(4)}—C_{(5)}$ (1.426 Å) bond is elongated; in the benzisothiazole (XII), the analogous bonds have lengths of 1.341, 1.348, and 1.410 Å [13]. According to [17], in the formally also 1,10-anthraquinonoid system containing not an isothiazole but a pyrrole ring annellated with the anthrone ring [the pyrroleanthrone (XIII)] the bonds in the ring adjacent to the heterocycle are almost completely equalized. (The lengths of these bonds are 1.380, 1.405, and 1.382 Å.) The equalization was attributed to the transfer of electron density from the electron-donating π-excess heterocycle to the carbonyl group [a contribution from the resonance structure (XIII)], confirmed by the decrease in the frequency of the C=O stretching vibration in the IR spectrum to 1645 cm^{-1}. The absence of such bond delocalization in the isothiazoleanthrone system is consistent with the lower electron-donating character of the isothiazole ring compared with the pyrrole ring and the "normal" frequency of the C=O vibrations [1662 cm^{-1} in the isothiazoleanthrone (XI)]. At the same time the carbonyl group in the azadithiapentaleneanthrone (IIIb) is polarized (ν_{CO} 1645 cm^{-1}), as in the pyrroleanthrone (XIII). The absence of polarization in trithiapentaleneanthrone (ν_{CO} 1660 cm^{-1} [7]) indicates that the polarization in (IIIb) is due to the presence of the isothiazole and not the dithiole ring. The difference in the electronic effects of the isothiazole ring in the isothiazoleanthrone and azadithiapentaleneanthrone systems is determined by the different roles of the heteroatoms. In the isothiazoleanthrones the nitrogen atom of pyridine type supplies one electron to the aromatic π system while the sulfur atom supplies two electrons, whereas the nitrogen atom of the pyrrole type in azadithiapentaleneanthrones supplies two electrons while the sulfur atom supplies one electron. The pyridine nitrogen atom in the isothiazoleanthrones has an electron-withdrawing effect, while the pyrrole nitrogen atom in the azadithiapentaleneanthrones has an electron-donating effect. Experimental evidence for the latter is obtained from the increase in the screening of the carbon nuclei at the para and ortho positions to the nitrogen atom, which indicates an increase in the electron density. Thus, in the transition from trithiapentaleneanthrone (II) to azadithiapentaleneanthrone (IIIb) the signals of the $C_{(6)}$ and $C_{(8)}$ nuclei in the ^{13}C NMR spectra are shifted upfield by 11.3 and 11.6 ppm, while the signals for the protons of these atoms in the PMR spectra are shifted by 0.36 and 0.50 ppm, respectively.

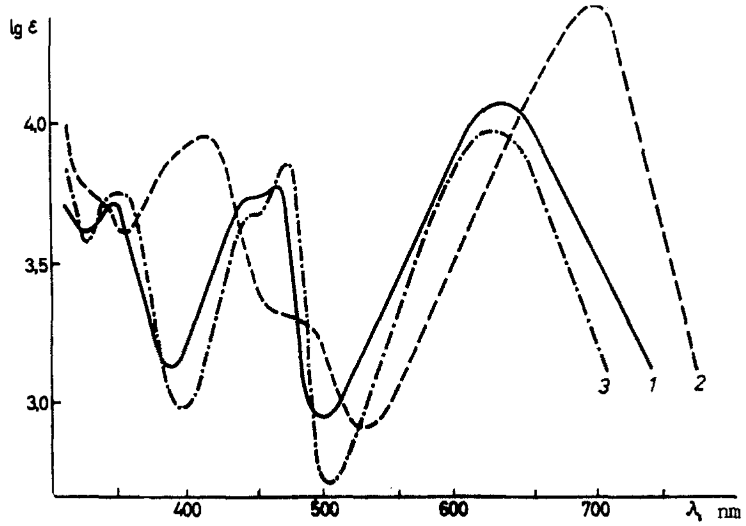
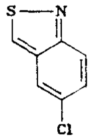
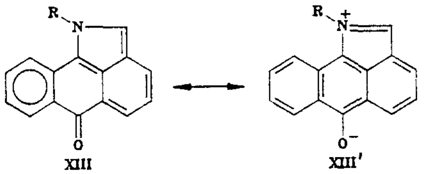


Fig. 2. The electronic absorption spectra (in chlorobenzene): 1) azadithiapentaleneanthrone (IIIb); 2) 4-cyclohexylaminoazadithiapentaleneanthrone (VIc); 3) trithiapentaleneanthrone (II).

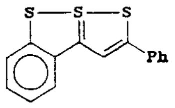
The transmission of the electron-donating effect of the CO group in the azadithiapentaleneanthrones is evidently realized not directly through the adjacent carbocycle but through the dithiole ring and the adjacent benzene ring. This is indicated by the large difference in the lengths of the bonds linking the CO group in the azadithiapentaleneanthrone molecule (VIa) to the benzodithiole fragment (1.44 Å) and the benzoisothiazole fragment (1.52 Å). In the pyrroleanthrone (XIII), where polarization of the CO group is realized, the length of the bond directed toward the heterocycle is 1.45 Å, while the length of the other is 1.51 Å, whereas in the isothiazoleanthrones (VII, VIII), where polarization is absent, both bonds have an identical length of 1.48 Å. In the anthrone ring of the azadithiapentaleneanthrone (VIa) and isothiazoleanthrones (VII, VIII) the "withdrawing" action of the isothiazole ring leads to distortion of the angles by 2-4° (Fig. 1a, b) less than in the pyrroleanthrone (XIII), since the angle in the heterocycle, which is at the same time the external angle of the anthrone ring, is larger in isothiazole than in pyrrole.



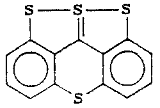
XII



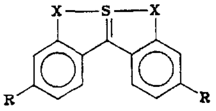
XIII XIII'



XIV



XV



XVI, XVII

XVI X=NCH_3, R=H; XVII X=O, R=OH

The electronic spectra of the isothiazoleanthrones and azadithiapentaleneanthrones differ substantially (Table 1). The isothiazoleanthrone (XI), which does not contain an amino group, gives one absorption band in the visible region with a maximum at 440 nm, whereas azadithiapentaleneanthrone (IIIb) gives two bands with maxima at about 470 and 635 nm, the combination of which gives rise to the green color of the compound. In the presence of the amino group in the molecules the bathochromic shift of the long-wave maximum of the azadithiapentaleneanthrone (X) in relation to the absorption maximum of the isothiazoleanthrone (VII) amounts to 150 nm. The introduction of the alkylamino (VIa, b) or arylamino (VIb, c) group at position 4 of the azadithiapentaleneanthrone gives rise to a bathochromic shift of the long-wave band by 55-65 nm and an increase of more than twice its intensity. In the short-wave region here at the position of the minimum a new band appears at about 420 nm, while the band at 470 nm is transformed into a shoulder or merges with the new band. The electronic spectra of the azadithiapentaleneanthrone (IIIb) and trithiapentaleneanthrone (II) are close to each other (Fig. 2). The maximum of the long-wave band in the spectrum of (IIIa) undergoes a slight bathochromic shift, while the short-wave band undergoes a hypsochromic shift in relation to the maxima in the spectrum of (II). The position of the short-wave band in the visible spectra of (II) and (IIIb) coincides with the position of the band in the spectra of the bicyclic derivatives of trithiapentalene (I) (X = S) [2] and azadithiapentalene (I) (X = NPh) [18, 19], which belongs to the $\pi\pi^*$ transition directed along the long axis of the molecule [3]. It can be supposed that this band in the spectra of (II) and (IIIa) also belongs to an electronic transition localized in the π system of the heterocycles, whereas the long-wave band belongs to a new chromophoric system formed as a result of annellation of the anthrone ring. In itself benzannellation along the C–C bond of trithiapentalene and its heteroanalogs does not lead to deepening of the color. All the described mono- and dibenzo derivatives represent red substances, e.g., compounds XIV [20], XV [7], XVI [21], XVII [22] ($\lambda_{max} \leq 520$ nm). The appearance of the absorption band with $\lambda_{max} \geq 630$ nm in the azadithiapentaleneanthrone and trithiapentaleneanthrone (II, III) is due to the presence of the carbonyl group linking the benzene rings. This gives reason to suppose that the electronic transition responsible for the long-wave absorption of systems (II, III) is realized with the transfer of charge from the heterocycles to the CO group in the excited state. It would be advisable to check this idea by a quantum-chemical calculation.

EXPERIMENTAL

The IR spectra were measured in tablets with potassium chloride on a Perkin-Elmer 598 instrument. The electronic spectra were obtained on Specord M-40 spectrophotometer in chlorobenzene. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-400 instrument with TMS as internal standard. The mass spectra were obtained on an MS-702 instrument. Column chromatography was conducted on silica gel L100/160 (Czech). The reactions and the purity of the obtained substances were monitored by TLC on Silufol-254 plates in the 10:1 toluene–acetone system.

The characteristics of the synthesized compounds are given in Table 1. The data from elemental analysis for C, H, N, and S for compounds (IIIb, Va, c, VIa-d, VII, VIII, X, XI) correspond to the calculated data.

X-Ray Crystallographic Analysis. Single crystals of azadithiapentaleneanthrone (VIa) were obtained from chlorobenzene, and single crystals of the isothiazoleanthrones (VII, VIII) were obtained from toluene. The unit cell parameters were as follows. Compound (VIa), $a = 15.231(3)$, $b = 13.345(3)$, $c = 6.659(2)$ Å, $Z = 4$, space group P_{nma}; compound (VII), $a = 7.569(2)$, $b = 10.011(2)$, $c = 11.315(2)$ Å, $Z = 88.22(1)$, $\alpha = 92.57(2)$, $\beta = 110.42(2)°$, $\gamma = 2$, space group $P\overline{1}$, its centrosymmetric form was established during the interpretation process; compound (VIII), $a = 7.706(1)$, $b = 13.782(2)$, $c = 13.928(2)$ Å, $\alpha = 92.06(2)°$, $Z = 4$, space group $P2_1/n$. Compound (VII) cocrystallizes with toluene, and the two molecules of (VII) and the molecule of toluene were determined independently. The investigation was conducted on a CAD-4 four-circle diffractometer (λ_{MoK_α}, graphite monochromator, ω scan). For compounds (VIa, VII, VIII) in the region of $\theta \leq 25°$ we obtained 1297, 2640, and 2449 unique reflections. Of these reflections, 482, 2140, and 2137, the values of which were greater than 3σ, were used for refinement of the position and thermal parameters of the molecule, the structures of which were determined by the direct method using the MULTAN program. The refinements were made in full-matrix anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms were revealed by a Fourier difference synthesis and were refined isotropically. The final R values were 0.048 (VIa), 0.037 (VII), and 0.028 (VIII). The polycyclic fragment in all three molecules is planar, and the angles between the rings do not exceed 1.6°. The bond lengths and angles are given in Fig. 1a, b.

N,N'-Disubstituted 1,5-Diaminoanthrones (IVa-d). To a suspension of 0.01 mole of the respective N,N'-dialkyl(aryl)-1,5-diaminoanthraquinone (Va-d) in 50 ml of acetic acid we added a solution of 10 g of $SnCl_2 \cdot 2H_2O$ in 25 ml of concentrated hydrochloric acid, and we boiled the mixture for 2 h. On cooling the yellow precipitate was filtered off, washed with water, and dried. The yield was 90-98%. The compounds were used without further purification.

1,5-Di(methylamino)anthrone (Va) ($C_{16}H_{16}N_2O$). mp 203-205°C (from benzene).

1,5-Di(phenylamino)anthrone (Vc) ($C_{26}H_{20}N_2O$). mp 207-208.5°C (benzene—hexane).

N,N'-Disubstituted 4-Amino-5H-anthra[1,9,8-bcde]-9-aza-1,10λ^4-dithiapentalen-5-ones (VIa-d). A mixture of the respective diaminoanthrone (IVa-d) [obtained from 0.01 mole of diaminoanthraquinone (Va-d)], 0.8 g (0.025 mole) of sulfur, 100 ml of DMFA, and 1.5 ml of triethylamine was boiled for 30 min. The green crystals were separated on cooling and washed with DMFA and with water. The yield was 48-51% calculated on the diaminoanthraquinone. PMR spectrum of (VIb) (deuterochloroform): 8.07 (1H, dd, 6-H); 7.93 (1H, 2 dd, 8-H); 7.86 (1H, t, 7-H); 7.63 (1H, d, 2-H); 7.30 (1H, d, 3-H); 4.38 (1H, m, 9'-H); 3.83 (1H, m, 4"-H); 1.45-2.38 ppm (20H, m, cyclohexane).

4-Amino-9-cyclohexyl-5H-anthra[1,9,8-bcde]-aza-1,10λ^4-dithiapentalen-5-one (X). A solution of 0.90 g (2 mmole) of (VIb) in 80 ml of orthophosphoric acid was heated at 120°C for 4 h, poured into 350 ml of water, and extracted with benzene (4 × 75 ml). The organic layer was separated, washed with water (2 × 150 ml), concentrated to 70 ml, and chromatographed on a column of silica gel (3 × 40 cm) with benzene as eluant. We obtained 0.40 g (43%) of (X) in the form of green crystals. PMR spectrum (DMSO-d_6): 8.02 (1H, dd, 6-H); 7.97 (1H, dd, 8-H); 7.94 (1H, t, 7-H); 7.79 (1H, d, 8-H); 7.23 (1H, d, 3-H); 4.58 (1H, m, 9'-H); 1.35-2.30 ppm (10H, m, cyclohexane).

9-Cyclohexyl-5H-anthra[1,9,8-bcde]-9-aza-1,10λ^4-dithiapentalen-5-one (IIIb). To a solution of 0.18 g (0.5 mmole) of (X) in 7 ml of concentrated sulfuric acid we added 0.5 ml of 1 N $NOHSO_4$ in sulfuric acid. The mixture was stirred at 20°C for 1 h and slowly added to a suspension of 2 g of NaH_2PO_2 in 3 ml of 50% sulfuric acid while the temperature was kept at 40-45°C. When the release of nitrogen had stopped the mixture was diluted with 50 ml of water, the precipitate was filtered off, and after column chromatography (3 × 30 cm) with chloroform as eluant 0.031 g (17%) of the green (IIIb) was obtained. PMR spectrum (deuterochloroform): 8.22 (1H, dd, 4-H); 8.13 (1H, dd, 6-H); 8.09 (1H, dd, 2-H); 7.83 (1H, t, 7-H); 7.76 (1H, dd, 8-H); 7.60 (1H, t, 3-H); 4.42 (1H, m, 9'-H); 1.85-2.37 ppm (10H, cyclohexane). ^{13}C NMR spectrum (deuterochloroform): 134.75 (4-C); 132.71 (2-C); 128.54 (3-C); 124.18 (7-C); 121.58 (6-C); 118.33 ppm (8-C). ^{13}C NMR spectrum of 5H-anthra[1,9,8-bcde]-1,9,10λ^4-trithiapentalen-5-one (II) [6] (deuterochloroform): 129.92 ($C_{(2)}$, $C_{(8)}$); 132.91 ($C_{(4)}$, $C_{(6)}$); 125.87 ppm ($C_{(3)}$, $C_{(7)}$).

7-Amino-10-methylthio- and 7-Amino-8,10-dimethylthio-6H-anthra[9,1-cd]isothiazol-6-one (VII) and (VIII). A solution of 2.24 g (0.01 mole) of 1,5-diaminoanthrone (Ve) [22], 0.90 g (0.028 mole) of sulfur, and 0.6 ml of triethylamine in 90 ml of DMFA was boiled for 15 min, quickly filtered, and mixed with 250 ml of 4% aqueous sodium hydroxide and 7 ml of dimethyl sulfate. After 1 h the precipitate was separated, washed to a neutral reaction with water, dried, and extracted successively with toluene (2 × 70 ml) and methylene chloride (2 × 70 ml). The solution was concentrated to 50 ml and chromatographed on a column of silica gel (3 × 40 cm), and 0.46 g (15%) of (VII) and a mixture of (Ve) and (VIII) were eluted with toluene. The mixture was separated by chromatography on aluminum oxide (3 × 25 cm) with toluene as eluant. The yield of (VIII) was 0.23 g (6.5%); R_f 0.50.

Compound (VII). R_f 0.32. PMR spectrum (DMSO-d_6): 8.02 (1H, dd, 3-H); 7.99 (1H, dd, 5-H); 7.83 (1H, t, 4-H); 7.65 (1H, d, 9-H); 6.90 (1H, d, 8-H); 2.30 ppm (3H, s, $S—CH_3$). ^{13}C NMR spectrum (DMSO-d_6): 139.28 (9-C); 129.98 (4-C); 125.80 (3-C); 124.02 (5-C); 119.36 (8-C); 118.95 ($S—CH_3$).

10-Methylthio-6H-anthra[9,1-cd]isothiazol-6-one (XI). The compound was obtained from 0.15 g (0.5 mmole) of the amine (VII) by analogy with the method described for (IIIb). It was purified by chromatography on silica gel with chloroform as eluant. The yield was 0.12 g (85%).

LITERATURE CITED

1. E. Klingsberg, Q. Rev., 23, 537 (1969).
2. N. Lozach, Adv. Heterocycl. Chem., 13, 161 (1971).
3. R. Gleiter and R. Gygax, Topics Curr. Chem., 63, 51 (1976).
4. C. T. Pedersen, Sulfur Rep., 1, 1 (1980).
5. N. Lozach, Comprehensive Heterocyclic Chemistry (editors A. R. Katritzky and C. N. Rees), Pergamon, Oxford (1984), Vol. 6, p. 1049.

6. N. R. Ayyangar, S. R. Purao, and B. D. Tilak, Indian J. Chem., 16B, 673 (1978).
7. S. Davidson, T. J. Grinter, D. Leaver, and J. H. Steven, J. Chem. Res. (M), No. 7, 3172 (1980).
8. M. V. Gorelik, R. A. Alimova, V. A. Tafeenko, S. V. Medvedev, and V. Ya. Shteiman, Zh. Org. Khim., 24, 231 (1988).
9. H. Baba and T. Takamura, Tetrahedron, 24, 4779 (1968).
10. S. Oae, Chemistry of Organic Compounds of Sulfur [Russian translation], Khimiya, Moscow (1975), p. 512.
11. J. P. Brown and M. J. Thompson, J. Chem. Soc. Perkin I, No. 8, 863 (1974).
12. French Patent No. 1405673, W. Brawn and M. Ruske; Chem. Abs., 63, 15020 (1965).
13. M. Davis, M. F. Mackay, and W. A. Denne, J. Chem. Soc., Perkin II, No. 5, 565 (1972).
14. F. Leung and S. C. Nyburg, Can. J. Chem., 50, 324 (1972).
15. M. M. Borel and A. Leclaire, Acta Cryst., B33, 2940 (1977).
16. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, Determination of Geometric Structure of Free Molecules [in Russian], Khimiya, Leningrad (1978), p. 181.
17. G. V. Gridunova, V. E. Shklover, Yu. T. Struchkov, R. A. Alimova, and M. V. Gorelik, Khim. Geterotsikl. Soedin., No. 4, 485 (1988).
18. E. Klingsberg, J. Org. Chem., 33, 2915 (1968).
19. H. Behringer and J. Falkenberg, Chem. Ber., 102, 1580 (1969).
20. H. Behringer, M. Ruff, and R. Wiedemann, Chem. Ber., 97, 1732 (1964).
21. D. M. McKinnon, K. A. Duncan, A. M. McKinnon, and P. A. Spevack, Can. J. Chem., 63, 882 (1985).
22. W. Bradley and R. F. Maisey, J. Chem. Soc., No. 1, 274 (1954).