to a solution of 1.5 g (4.3 mmoles) of trichloroethyl 6-α-hydroxypenicillanate in 50 ml of dry methylene chloride, and the resulting solution was maintained at room temperature for 48 h. The solvent was then removed at reduced pressure, and the residue was dissolved in 20 ml of ethanol. The ethanol solution was filtered and poured with stirring into 500 ml of petroleum ether, and the resulting precipitate was removed by filtration and dried in a vacuum desiccator to give 0.8 g (47%) of a product with R_f 0.96 $[\alpha]_D^{20}$ + 31° (c 1, DMSO), and M^+ 406. IR spectrum: 1760 and 1740 cm^{-1}. PMR spectrum: 1.53 (3H, s, 2-CH_3), 1.69 (3H, s, 2-CH_3), 4.23 (1H, s, 3-H), 4.77 (2H, s, CH_2CCl_3), 5.24 (1H, d, J = 1 Hz, 5-H), 5.36 (1H, d, J = 1Hz, 6-H), and 8.41 ppm (2H, s, H_2NCS).

6-α-Thiocarbamoyloxypenicillanic Acid (IX, X = S, R^1 = H). A 0.6-ml (4.3 mmoles) sample of triethylamine was added to a suspension of 0.93 g (4.3 mmoles) of 6-α-hydroxypenicillanic acid in 40 ml of methylene chloride, the mixture was then cooled to 0°C, and a solution of 1.1 g (4.3 mmoles) of tetraisocyanatosilane in 10 ml of methylene chloride was added. The solution was maintained at room temperature for 48 h, after which the solvent was evaporated at reduced pressure, and the residue was dissolved in 20 ml of ethanol. The ethanol solution was filtered and poured with stirring into 500 ml of diethyl ether. The resulting precipitate was removed by filtration and dried *in vacuo* to give 0.65 g (48%) of a product with R_f 0.92 and $[\alpha]_D^{20}$ + 89° (c ~1, DMSO). IR spectrum: 1740 and 1600 cm^{-1}.

LITERATURE CITED

1. T. Naito, S. Nakagawa, J. Okumura, M. Konishi, and U. Kawaguchi, J. Antibiot., 18, 786 (1965).
2. N. Oi, B. Aoki, T. Shinozaki, K. Moro, I. Matsunaga, T. Noto, T. Nebasi, J. Harada, and H. Endo, Japanese Patent No. 79,106,486: Chem. Abstr., 92, 94386 (1980).
3. R. D. G. Cooper, US Patent No. 3,956,292; Chem. Abstr., 95, 94372 (1982).
4. L. N. Petrulyanis, G. A. Veinberg, L. I. Kononov, I. V. Dipan, and É. Lukevits, Khim. Geterotsikl. Soedin., No. 6, 786 (1983).
5. F. Roberts, USSR Inventor's Certificate No. 608,477; Byull. Izobret., No. 19, 172 (1978).
6. D. Hauser and H. P. Stigg, Helv. Chim. Acta, 50, 1327 (1967).
7. J. H. Sheehan, Y. S. Lo, J. Loliger, and C. C. Podewell, J. Org. Chem., 39, 1444 (1974).

SYNTHESIS OF 3,4,7,8-BIS(3-R-BENZO)-2,6-DITHIA-1,5-DIAZA-2,6-DIHYDROANTHRACENE 2,6-DIOXIDES

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UDC 547.869.07

Derivatives of a new heterocyclic quinoid system, viz., 3,4,7,8-bis(3-R-benzo)-2,6-dithia-1,5-diaza-2,6-dihydroanthracene 2,6-dioxide, were synthesized by the oxidation of 3,4,7,8-bis(3-R-benzo)-2,6-dithia-1,5-diaza-1,2,5,6-tetrahydroanthracene 2,6-dioxides with lead tetraacetate in acetic acid or with phenyliodoso diacetate in benzene.

N,N'-Diarylsulfonylquinonediimines are valuable intermediates in the synthesis of several indole derivatives [1]. It is known that in the indole series there exist compounds with high biological activity and medicinal preparations. Several dibenzo [c,e] [1, 2]-thiazine 5,5-dioxides also display biological activity [2]. In a continuation of our research [3] in order to find new biologically active substances that combine dibenzothiazine and indole rings we have synthesized heterocyclic quinoneimines of the 3,4,7,8-bis(3-R-benzo)-2,6-dithia-1,5-diaza-2,6-dihydroanthracene 2,6-dioxide (Va,b) series.

N,N'-Bis(arylsulfonyl)-1,4-phenylenediamines (Ia,b) were synthesized by the action of the corresponding arenesulfonyl chlorides on 1,4-phenylenediamine by the method in [4]:

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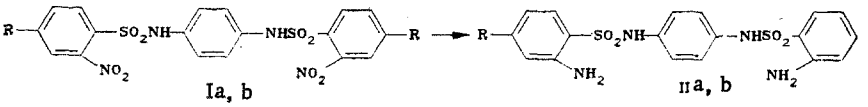
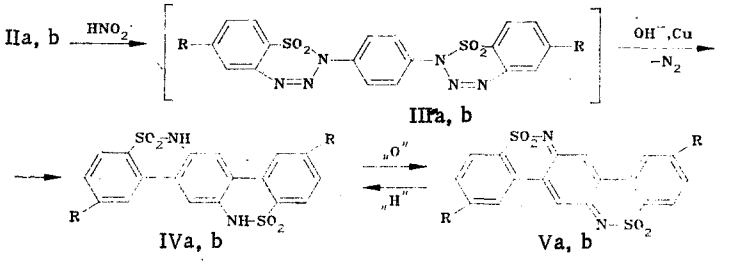


I,II a R=H; b R=Cl

Peaks of the absorption of N–H bonds (3280 and 3315 cm^{-1}), sulfonyl groups (1170 and 1365-1370 cm^{-1}), and nitro groups (1550-1560 cm^{-1}) are present in the IR spectra of nitro compounds Ia,b. N,N'-Bis(4-R-2-aminophenylsulfonyl)-1,4-phenylenediamines (IIa,b) were obtained by reduction of nitro compounds Ia,b with stannous chloride in alcohol or with zinc in acetic acid. The IR spectra of these compounds contain absorption peaks that are characteristic for NH and SO_2 groups, as well as for amino groups (3380-3450 cm^{-1}). In addition, amines IIa,b give a positive reaction for an amino group with p-dimethylaminobenzaldehyde [5]. Compounds Ia and IIa have been previously described [6]; in the latter paper these compounds were reported to have mp 112-114°C and 192-194°C, respectively. However, these products were evidently not purified sufficiently, since the determination of the molecular masses of the compounds that we synthesized by titration with alkali gave values of 475.2 (Ia) and 413.7 (IIa) (calculated values 478.4 and 418.5, respectively).

Under the influence of nitrous acid diamines IIa,b form thiatriazines IIIa,b (we did not isolate these products, and their structures were postulated in analogy with the Ullmann–Gross synthesis of dibenzo[c,e][1,2]thiazine 5,5-dioxides [7]), which, in an alkaline medium in the presence of copper powder, give 3,4,7,8-bis(3-R-benzo)-2,6-dithia-1,5-diaza-1,2,5,6-tetrahydroanthracene 2,6-dioxides (IVa,b).

The IR spectra of IVa,b contain peaks of absorption of an N–H bond (3220 and 3330 cm^{-1}) and a sulfonyl group (1180 and 1330-1335 cm^{-1}); however, the absorption bands of amino groups are absent. In the PMR spectrum of IVb the protons of the central benzenoid ring give a singlet at δ = 7.46 ppm, and the protons of the extreme rings constitute an AXB system: 7.28 ($2H^1$, d, J_{1-2} = 1.9 Hz), 7.74 ($2H^2$, q, J_{2-3} = 8.4 Hz), and 8.01 ppm ($2H^3$, d). In the spectrum of IVa one observes the signal of the protons of the central benzenoid ring (7.35 ppm); the protons of the extreme rings form a complex multiplet at 7.4-8.1 ppm.



III–V a R=H; b R=Cl

3,4,7,8-Bis(3-R-benzo)-2,6-dithia-1,5-diaza-2,6-dihydroanthracene 2,6-dioxides (Va,b) were obtained by oxidation of IVa,b with lead tetraacetate in acetic acid or phenyliodoso acetate in benzene. The IR spectra of these compounds do not contain absorption above 3100 cm^{-1}, which indicates the absence of N–H bonds; however, peaks corresponding to the stretching vibrations of the C=N bond (1575 cm^{-1}) [8] do appear, and the vibrations of the sulfonyl groups (1180-1185 and 1340-1355 cm^{-1}) are retained. The retention of the molecular skeleton in quinoneimines Va,b is confirmed by the fact that in the case of their reduction with zinc in acetic acid they are converted quantitatively to starting dihydro compounds IVa,b. Absorption peaks at 493 and 469 nm, which are absent in the spectra of dihydro compounds IVa,b and are characteristic for the quinoneimine structure [9], appear in the UV spectra of quinoneimines Va,b. It is interesting to note that dioxane solutions of dihydro compounds IVa,b have blue fluorescence, whereas alkaline solutions have green fluorescence.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in isopropyl alcohol (IVa,b) and acetonitrile (Va,b) were recorded with a Specord M-40 spectrophotometer. The PMR spectra of 5% solutions of the compounds in deuterodimethyl sulfoxide were recorded with a Jeol JNM-60H radiospectrometer with tetramethylsilane (TMS) as the internal standard.

The characteristics of the synthesized compounds are presented in Table 1.

TABLE 1. Properties of the Synthesized I-V

Compound	mp, °C (dec.)	UV spectrum, λ_{max}, nm (log ε)	Found			Empirical formula	Calc.			Yield, %
			N, %	S, %	M		N, %	S, %	M	
Ia	261—263		11,7	13,5	475,2	$C_{18}H_{14}N_4O_8S_2$	11,7	13,4	478,4	77
Ib	265—267*		10,2	11,9	546,3	$C_{18}H_{12}Cl_2N_4O_8S_2$	10,2	11,7	547,3	72
IIa	253—254		13,5	15,2	413,7	$C_{18}H_{18}N_4O_4S_2$	13,4	15,3	418,5	76
IIb	250—252		11,4	13,0	507,3	$C_{18}H_{16}Cl_2N_4O_4S_2$	11,5	13,2	487,4	76
IVa	340	242 (4,54), 316 (4,09), 358 (3,74)	7,2	16,7	394,5	$C_{18}H_{12}N_2O_4S_2$	7,3	16,7	384,4	26
IVb	330	247 (4,48), 290 (4,04), 367 (3,71)	6,2	13,9	453,9	$C_{18}H_{10}Cl_2N_2O_4S_2$	6,2	14,1	453,3	11
Va	330	238 (4,47), 334 (4,24), 493 (3,65)	7,5	16,6	—	$C_{18}H_{10}N_2O_4S_2$	7,3	16,8	—	60
Vb	310	244 (4,61), 338 (4,19), 469 (3,66)	5,8	14,0	—	$C_{18}H_8Cl_2N_2O_4S_2$	6,2	14,2	—	65

*Without decomposition.

N,N'-Bis(2-aminophenylsulfonyl)-1,4-phenylenediamine (IIa). A 19-g (90 mmoles) sample of stannous chloride dihydrate was added at 50-60°C to a suspension of 5.0 g (10 mmoles) of dinitro compound Ia in 50 ml of isopropyl alcohol, after which 18 ml of 36% hydrochloric acid was added dropwise in the course of 0.5 h. The mixture was stirred at 60°C for 3 h, after which it was cooled, and the resulting precipitate was removed by filtration, reprecipitated from 100 ml of 10% sodium hydroxide solution, and crystallized from isopropyl alcohol.

N,N'-Bis(2-amino-4-chlorophenylsulfonyl)-1,4-phenylenediamine (IIb). A solution of 5.5 g (10 mmoles) of nitro compound Ib in 100 ml of acetic acid with 10 g of zinc dust was refluxed for 4 h until it became colorless. It was then diluted with 300 ml of water and worked up as in the case of Ia.

3,4,7,8-Bis(3-chlorobenzo)-2,6-dithia-1,5-diaza-1,2,5,6-tetrahydroanthracene 2,6-Dioxide (IVb). A 3.8-g (56 mmoles) sample of sodium nitrite was added to a solution of 11.6 (28 mmoles) of diamine IIb in 100 ml of 2% sodium hydroxide solution, and the resulting solution was added dropwise at −2°C to −6°C to 230 ml of 5% hydrochloric acid. The reaction mixture was then stirred at −2°C to 3°C for 1 h, after which 100 ml of a 15% solution of sodium acetate was added. The precipitated thiatriazine IIIb was removed by filtration and washed with water. The entire crude precipitate obtained was suspended in 200 ml of 1.5% sodium hydroxide solution, and 5 g of copper was added immediately. The mixture was stirred until the thiatriazine IIIb had dissolved completely, after which the mixture was filtered, and the filtrate was acidified with hydrochloric acid. The precipitated dihydro compound IVb was removed by filtration, reprecipitated from 100 ml of 10% sodium hydroxide solution by the addition of acetic acid, and crystallized successively from toluene and acetic acid.

3,4,7,8-Dibenzo-2,6-dithia-1,5-diaza-1,2,5,6-tetrahydroanthracene 2,6-Dioxide (IVa). This compound was similarly obtained.

3,4,7,8-Dibenzo-2,6-dithia-1,5-diaza-2,6-dihydroanthracene 2,6-Dioxide (Va). A suspension of 0.6 g (1.8 mmoles) of phenyliodoso diacetate and 0.5 g (1.3 mmoles) of dihydro compound IVa in 10 ml of benzene was stirred at 50-60°C for 2.5 h, and the resulting precipitate was removed by filtration and dissolved in 200 ml of chloroform. The solution was filtered, the solvent was removed by vacuum distillation, and the residue was crystallized from benzene.

3,4,7,8-Bis(3-chlorobenzo)-2,6-dithia-1,5-diaza-2,6-dihydroanthracene 2,6-Dioxide (Vb). A 0.3-g (0.66 mmole) sample of dihydro compound IVb was added with stirring to a solution of 0.3 g (0.7 mmole) of lead tetraacetate in 15 ml of acetic acid, and the mixture was stirred at 20°C for 2 h. The precipitate was removed by filtration and crystallized from benzene.

Reduction of Quinoneimine Va. A 64-mg (1 mmole) sample of zinc dust was added to a solution of 0.1 g (0.22 mmole) of quinoneimine Va in 10 ml of acetic acid, after which the solution was refluxed for 20 min and then diluted, while still hot, with 40 ml of water. The resulting precipitate was removed by filtration to give a product (98% yield), which, according to the IR spectrum, TLC, and melting point, was identical to dihydro compound IVa.

Compound IVb was similarly obtained in 97% yield from quinoneimine Vb.

LITERATURE CITED

1. R. Adams and W. Reifschneider, Bull. Soc. Chim. France, No. 1, 23 (1958).
2. J. R. Geigy, French Patent No. 1,377,693; Chem. Abstr., 63, 16361 (1965).
3. K. S. Burmistrov, S. I. Burmistrov, and M. S. Malinovskii, Khim. Geterotsikl. Soedin., No. 11, 1503 (1977).
4. E. A. Titov, A. P. Avdeenko, and V. F. Rudchenko, Zh. Org. Khim., 8, 2546 (1972).
5. S. I. Burmistrov, Zh. Anal. Khim., 1, 265 (1946).
6. M. L. Shevchenko and Ya. P. Berkman, Nauchn. Zap. L'vovsk. Politekh. Inst. Ser. Khim. Tekhnol., 50, 89 (1958).
7. F. Ullmann and C. Gross, Ber., 43, 2694 (1910).
8. E. A. Titov and G. A. Podobuev, Zh. Org. Khim., 7, 335 (1971).
9. I. M. Issa, A. K. El-Shafei, S. H. Etaiw, and H. S. El-Kashef, J. Prakt. Chem., 320, 557 (1978).

1-SUBSTITUTED AZIRIDINE-2,2-DICARBOXYLIC ACID ESTERS

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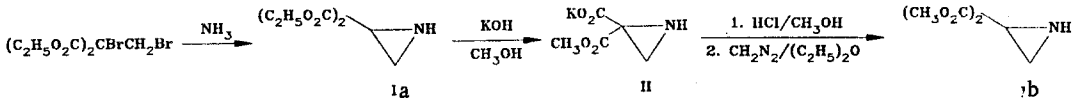
The synthesis and chemical properties of aziridine-2,2-dicarboxylic acid esters were investigated. The activation parameters of the inversion of the nitrogen atom in 1-substituted aziridine-2,2-dicarboxylic acid esters were determined. The σ_{inv} values of a number of substituents attached to the nitrogen atom were established.

1-Substituted aziridine-2,2-dicarboxylic acid esters are among the most suitable subjects for the investigation of the inversion of the nitrogen atom [1]. However, because of the lack of a method for the synthesis of aziridine-2,2-dicarboxylic acid ester, many of the 1-substituted derivatives have been virtually inaccessible. Attempts to obtain aziridine 2,2-dicarboxylic acid ester under conditions similar to those in the known syntheses of esters of 1-alkoxy-, 1-methyl-, and 1-phenylaziridine-2,2-dicarboxylic acids [1] from α,β-dibromomethylmalonic acid ester and ammonia under various temperature conditions were unsuccessful. However, carrying out the reaction in absolute ethanol at 20°C for 2 days made it possible to obtain, for the first time, diethyl aziridine-2,2-dicarboxylate (Ia) [2]:



Ia II Ib

The transesterification of aziridine Ia was carried out in order to remove the very small amounts of bromo derivative impurities that catalyze the decomposition of aziridines at high temperatures and interfere with the determination of the activation parameters of the inversion of the nitrogen atom, as well as to ensure the more accurate determination of the coalescence temperatures (T_c) from the singlet signals of the protons of the methoxycarbonyl groups.

Aziridine Ia is readily acylated by acid chlorides, phenyl isocyanate, and pheny isothiocyanate:

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