2-(1-Adamantyl)-2-hydroximinoacetonitrile Oxide (IV). A solution of $K_3Fe(CN)_6$ (7.4 g, 22.5 mmole) and KOH (1.26 g, 22.5 mmole) in water (67 ml) was added dropwise with stirring to a solution of glyoxime Ia (2 g, 9 mmole) in ether (60 ml). The reaction mixture was stirred for 2 h at 25°C, the ether layer separated, wahsed with water, and dried. After removal of ether the residue was washed with pentane to give IV (1.4 g) which was chromatographed using CCl_4-acetone (6:1) [7].

4-(1-Adamantyl)-3-aminofuroxan (VIa). A 25% solution of ammonia (200 ml) and chloroform (100 ml) was added to IV (1 g, 4.5 mmole) and refluxed with stirring for 2 h and cooled to 0°C. The precipitated solid (0.6 g) was filtered off, transferred to a three necked flask, ether (50 ml) added, and a solution of $K_3Fe(CN)_6$ (1.66 g, 5 mmole) in ammonia solution (2%, 50 ml) added dropwise with stirring at 0°C over 15 min. Stirring was continued for 2 h at 0°C and a further 1 h at 20°C. The ether layer was separated, washed with water and dried. After removal of ether the residue was chromatographed on a silica gel column using CCl_4-acetone (6:1).

4-(1-Adamantyl)-3-methylaminofuroxan (VIb) was obtained similarly using a methylamine solution (33%, 60 ml) and compound IV (1 g).

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SYNTHESIS OF MACROHETEROCYCLES — ANALOGS OF DIBENZO-CROWN COMPOUNDS.

2.* 18-MEMBERED DIOXADIAZA-CROWN COMPOUNDS

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Macrocyclic diamides were synthesized by condensation of bridged 1,7-bis(2-aminophenyl)-1,7-dioxaheptanes that contain an additional donor oxygen or nitrogen atom in the bridge with glutaric, diglycolic, and N-tosyliminodiacetic acid dichlorides under high-dilution conditions. Subsequent reduction with boron hydride leads to 18-membered dibenzodiaza-crown-4-6 compounds. The structural assigments were made using the IR, ^1H and ^{13}C NMR, and mass spectra.

The replacement of some of the oxygen atoms in the crown ether molecule by other donor atoms, particularly by nitrogen atoms, leads to a significant change in the character of the complexing of such aza-crown ethers [2]. Aliphatic aza analogs of crown ethers have been studied in relatively great detail; however, aza-crown compounds with aromatic rings condensed with the macroheteroring have been studied to a much smaller extent [3, 4]. The presence of aromatic rings imparts a number of useful properties to aza-crown compounds: it increases their lyophilicity, it permits the possibility of diverse chemical modifications

*See [1] for Communication 1.

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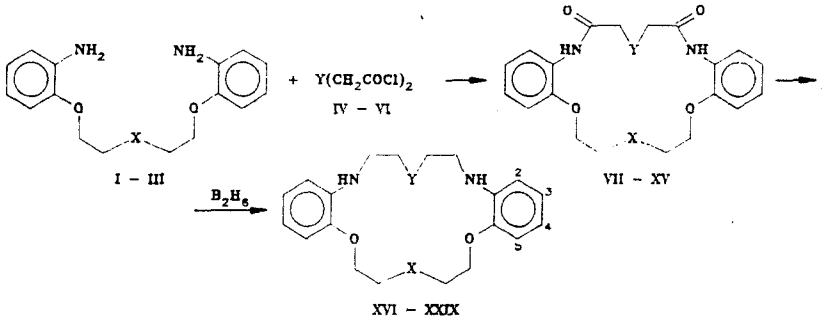
of the macrocycle without substantial distortion of the geometry of the coordination node, etc. (for example, see [5]).

We have previously described the synthesis of diaza analogs of dibenzo-15-crown-5 compounds [1]; some of them have proved to be promising extractants for mercury(II) and silver(I) [6].

Continuing our search for new highly selective macrocyclic extractants we have synthesized a series of 18-membered dioxadiaza-crown compounds of the 8,9;17,18-dibenzo-1,7-dioxa-10,16-diazacyclooctadecane system that contain additional donor nitrogen and/or oxygen atoms in the 4 and 13 positions of the macroheterocycle (XVI-XXIX).



I, IV X,Y=CH_2; II, V X,Y=O; III, VI X,Y=NTs; VII, XVI X=Y=CH_2; VII, XVII X=CH_2, Y=O; IX, XVIII X=CH_2, Y=NTs; X, XIX X=O, Y=CH_2; XI, XX X=Y=O; XII, XXI X=O, Y=NTs; XIII, XXII X=NTs, Y=CH_2; XIV, XXIII X=NTs, Y=O; XV, XXIV X=Y=NTs; XXV X=CH_2, Y=NH; XXVI X=O, Y=NH; XXVII X=NH, Y=CH_2; XXVIII X=NH, Y=O; XXIX X=NH, Y=NH

For the synthesis we used a scheme that includes acylation of bridged aromatic diamines I-III with dicarboxylic acid dichlorides IV-VI under high-dilution conditions. The resulting macrocyclic diamides VII-XV were reduced with boron hydride to macrocylic amines XVI-XXIV. Compounds XXV-XXIX were obtained from the corresponding N-tosyl derivatives after removal of the protective group.

Only XX [5, 7, 8] and XXVIII and XXIX [8] have been described in the literature; a sequence of reactions in which lithium aluminum hydride serves as the reducing agent was used for the synthesis of XX [5, 7]. Another approach [8] is based on the alkylation of N-mesyl (for XX) or N-tosyl (for XXVIII and XXIX) derivatives of bridged aromatic amines II and III with diethylene glycol ditosylate (XX, XXVII) or diethanolamine tritosylate (in the case of XXIX). The low overall yields of XX (28.4%), XXVIII (44.3%), and XXIX (6.0%) should be included among the inadequacies of this approach.

Starting aromatic amines I-III were obtained by reduction of the the corresponding nitro compounds; the latter, in turn, were obtained by the reaction of o-nitrophenol with 1,5-dibromopentane, sym-dichloroethyl ether, and diethanolamine tritosylate in the presence of potassium carbonate in DMF. Hydrazine hydrate was used for the reduction of the nitro compounds [8]; however, the reduction requires a long time (up to 50 h) and large excess amounts of the reducing agent, which hinders purification of the desired diamines. On the basis of [9] we developed a method for the reduction of the nitro compounds with sodium borohydride that made it possible to obtain I-III in high yields in 3-6 h and did not require further purification.

Diamides VII-XV, which were characterized by the results of TLC and elementary analysis (Table 1) and IR and ^{1}H NMR spectral data (Table 2), were obtained by acylation of bridged aromatic diamines I-III with glutaric (IV), diglycolic (V), and N-tosylmimnodiacetic (VI) acid dichlorides under high-dilution conditions in benzene in the presence of pyridine.

Absorption bands at 3170-3410 cm^{-1}, which are characteristic for the stretching vibrations of free and associated NH groups of secondary amines, intense bands of a carbonyl group at 1650-1690 cm^{-1}, and bands at 1580-1600 cm^{-1} ("amide II") and 1275-1280 cm^{-1} ("amide III") are present in the IR spectra of VII-XV. Bands of asymmetrical (1325-1340 cm^{-1}) and symmetrical (1150-1160 cm^{-1}) stretching vibrations of a sulfonyl group are observed in the spectra of IX and XII-XV, which contain a tosyl group. In addition to this, bands at 1110-1140 and 1200-1260 cm^{-1}, which are characteristic for C–O–C_{al} and C–O–C_{ar} vibrations, respectively, are observed in the IR spectra of all of the synthesized amides.

A weak-field signal of an amide proton at 8.1-8.9 ppm is observed in the ^{1}H NMR spectra of amides VII-XV. The aromatic protons in the ortho position relative to the amide group are

TABLE 1. Yields, Constants, and Results of Elementary Analysis of Macrocyclic Amides VII-XV

Compound	mp, °C	R_f ($CHCl_3$)	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
VII	242—243	0,29	69,0	6,8	7,2	$C_{22}H_{26}N_2O_4$	69,1	6,8	7,3	83
VIII	162—163	0,61	65,6	6,2	7,2	$C_{21}H_{24}N_2O_5$	65,6	6,3	7,3	88
IX	216—217	0,74	62,6	5,8	7,8	$C_{28}H_{31}N_3O_6$	62,5	5,8	7,8	92
X	237—238	0,53	65,7	6,3	7,2	$C_{21}H_{24}N_2O_5$	65,6	6,3	7,3	88
XII	141—142	0,51	60,0	5,4	7,9	$C_{27}H_{29}N_3O_7S$	60,1	5,4	7,8	78
XIII	244—246	0,22	62,6	5,8	7,8	$C_{28}H_{31}N_3O_6S$	62,5	5,8	7,8	90
XIV	191—193	0,83	60,1	5,4	7,7	$C_{27}H_{29}N_3O_7S$	60,1	5,4	7,8	94
XV	222—224	0,26	59,0	5,2	8,2	$C_{34}H_{36}N_4O_8S_2$	58,9	5,2	8,1	87

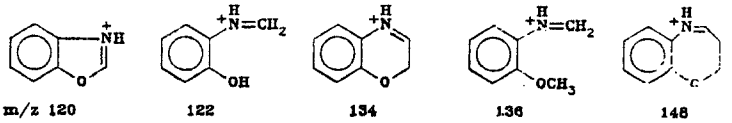
appreciably (0.5-0.9 ppm) deshielded as compared with the other aromatic protons; this is due to the magnetic anisotropy of the carbonyl group. The observed deshielding increases by 0.4-0.6 ppm when an $O_{(13)}$ atom is introduced; this constitutes evidence for drawing together of the ortho protons of the aromatic ring with the amide group on passing from VII and X to VIII and XI. An N-tosyl group in the 13 position gives rise to a similar effect, although it is somewhat smaller in magnitude (0.2-0.3 ppm). In the spectra of VII-IX all of the protons of the $-CH_2-X-CH_2-$fragment (X = CH_2) give a weakly resolved six-proton multiplet centered at ~1.8 ppm. A singlet of a methyl group and two weak-field doublets, which are characteristic for a tosyl group, are observed in the spectra of IX and XII-XV.

Macrocyclic amines XVI-XXIV were obtained by reduction of the corresponding amides with a solution of boron hydride in THF or dimethoxyethane and were characterized by the results of TLC and elementary analysis (Table 3) and by the mass, IR, ^1H NMR (Table 4), and ^{13}C NMR (Table 5) spectra. Removal of the tosyl group in XVIII and XXII-XXIV by the action of hydrogen bromide in acetic acid leads to XXV and XXVII-XXIX, respectively. It is interesting to note that XXI is resistant to hydrolytic cleavage by the action of a refluxing 30% solution of hydrogen bromide in acetic acid in the course of 24 h. The protective group could be removed only by the action of sodium in refluxing n-butyl alcohol, which leads to macrocyclic amide XXVI. Compounds XXV-XXIX were also characterized by spectral and necessary analytical data (Tables 3-5).

In the IR spectra of XVI-XXIX a band of ν_{NH} vibrations is observed at 3280-3410 cm^{-1}. The significant shift (by 100-130 cm^{-1}) of this band on passing from XVI and XVII to XIX and XX is evidently associated with a strong hydrogen bond between the proton of the NH group and the $O_{(4)}$ atom. Additional confirmation was obtained from the IR spectra of XXVI and XXVIII: the ν_{NH} frequency is 3310 cm^{-1} for XXVI, in which the oxygen atom occupies the $O_{(4)}$ position; in XXVIII with the same set of heteroatoms but an oxygen atom in the 13 position ν_{NH} is 3410 cm^{-1}.

In the ^1H NMR spectra of XVI-XXIX (Table 4) the signals of the aromatic protons are shifted by 0.2-0.3 ppm to strong field as compared with the atomatic protons of the corresponding amides VII-XV; this is most likely associated with an increase in the electron-donor character of the substituents. The protons of the three methylene groups (the $-CH_2-X-CH_2-$ fragment, X = CH_2) in XVI-XVIII and XXV give a weakly resolved multiplet centered at ~1.8 ppm in the ^1H NMR spectra. Similarly, the protons of the $-CH_2-Y-CH_2-$fragment (Y = CH_2) give a broad six-proton multiplet centered at ~1.6 ppm in the spectra of XVI, XIX, XXII, and XXVII.

The molecular masses of the synthesized macrocylic amides were determined by mass spectrometry. The introduction of heteroatoms in the 4 and 13 positions sharply decreases the stability of the molecular ion due to the development of new fragmentation pathways. A significant part of the total ion current goes into the fragment with m/z 120, 122, 134, 136, and 148, the peaks of which are observed in the mass spectra of all of the compounds (Table 4). According to the high-resolution mass-spectrometric data,* these fragments evidently have the following structures:



*The authors thank B. S. Subbotin for his assistance in this research.

TABLE 2. Data from the ^{1}H NMR and IR Spectra of Macrocyclic Amides VII-XV

Compound	Chemical shifts of the protons, δ, ppm ($CDCl_3$)							IR spectrum, ν_{NH}, cm^{-1}
	CH_2—O, m	CH_2—X, m	X, m	CH_2—Y, s	Y, m	NH, br. s	Ar	
VII	4,03	1,82	1,82	2,50*2	2,42	8,16	7,80 (2H), 6,65—7,30 (6H)	3330
VIII	4,05	1,80	1,80	4,22	—	8,62	8,03—8,33 (2H) 6,72—7,12 (6H)	3410
IX	4,00	1,82	1,82	3,88	2,40*1, 3H, 7,1—7,8	8,83	7,80—8,16 (2H) 6,55—7,06 (6H)	3400
X	4,10	3,91	—	2,53*2	2,42	8,25	7,73 (2H), 6,70—7,13 (6H)	3170
XI	4,13	3,82	—	4,20	—	8,08	8,08—8,30 (2H), 6,68—7,15 (6H)	3300
XII	4,03	3,84	—	3,92	2,32*1, 3H, 7,2—7,9	8,76	7,70 (2H), 6,60—6,95 (6H)	3260
XIII	3,95	3,61	2,43*1, 3H 7,1—7,7	2,26*2	2,26	8,25	6,30—7,15 (6H)	3240
XIV	4,20	3,70	2,43*1, 3H 7,2—7,8	4,28	—	8,77	8,21—8,43 (2H), 6,71—7,23 (6H)	3410
XV	4,11	3,77	2,41*1, 3H 7,5—8,4	3,88	2,34*1, 3H, 7,5—8,4	8,90	6,45—7,00 (6H)	3270

*1 Singlet.
*2 Multiplet.

An interesting peculiarity of the mass spectra of macrocyclic amines XVIII and XXI-XXIV consists in the fact that the N-tosyl group is readily split out from the 13 position (XVIII and XXI), whereas it virtually does not split out from the 4 position in the isomeric XXII and XXIII. This is confirmed by the mass spectrum of XXIV, in which the peak of the $[M - Ts]^+$ ions is 7% of the overall ion current and is due to the elimination of a tosyl group only from the 13 position.

The ^{13}C NMR spectra (Table 5) confirm the structures of the synthesized XVI-XXIX. The signals at 67.0-69.5 ppm were assigned to methylene groups attached to $O_{1(7)}$ atoms. Similarly, the signals at 42.6-43.7 ppm were assigned to the signals of methylene groups attached to $N_{10(16)}$ atoms.

The assignment of the remaining strong-field signals was made on the basis of an analysis of the ^{13}C NMR chemical shifts of related systems [1], the relative intensities of the signals, and their multiplicities in the spectra without proton decoupling. The assignment of the signals of the aromatic carbon nuclei was made taking into account the increments of the alkoxy and alkylamino groups [10]. The assignment of the signals of the aromatic carbon nuclei with close chemical shifts at 109.4-112.7 ppm to the C^2 and C^5 carbon atoms (the numbering of the carbon atoms in the aromatic rings is given in the scheme) is difficult because of the insufficient accuracy of the additivity scheme used.

EXPERIMENTAL

The IR spectra of solutions of the compounds in $CHCl_3$ in NaCl cuvettes with thicknesses of 0.156 and 0.623 mm were recorded with a Specord IR-71 spectrometer. The ^{1}H NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with Tesla BS-467 (60 MHz) and Bruker AC-250 (250 MHz) spectrometers with tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectra of solutions (0.2 M) of the compounds in $CDCl_3$ were recorded with Bruker HX-270 and Bruker AC-250 spectrometers. The mass spectra were obtained with an MKh-1303 spectrometer at an ionizing voltage of 12-50 eV. Thin-layer chromatography and preparative chromatography were carried out on Brockmann activity II neutral Al_2O_3 with development by iodine vapors. The compositions of the eluents are indicated in Tables 1 and 3.

1,7-Bis(2-nitrophenyl)-1,7-dioxaheptane (XXX). A mixture of 15.2 g (0.11 mole) of anhydrous potassium carbonate, 30.0 g (0.216 mole) of o-nitrophenol, and 25.3 g (0.11 mole) of 1,5-dibromopentane in 40 ml of dry DMF was refluxed for 2 h, after which it was cooled and poured into 300 ml of water. The precipitate was separated, washed with 10% KOH solution and water, dried, and crystallized from acetone to give 31.6 g (83%) of a product with mp 86-87°C. Found: C 58.9; H 5.2; N 8.0%. $C_{17}H_{18}N_2O_6$. Calculated: C 58.9; H 5.2; N 8.1%.

1,7-Bis(2-aminophenyl)-1,7-dioxaheptane (I). A 15.0-g (0.37 mole) sample of sodium borohydride was added in small portions to a stirred suspension of 31.0 g (0.09 mole) of XXX and 0.5 g of 10% palladium on carbon in 500 ml of methanol. At the end of the addi-

TABLE 3. Yields, Constants, and Results of Elementary Analysis of Macrocyclic Amines XVI-XIX and XXI-XXVII

Compound	mp, °C	R_f ($CHCl_3$)	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
XVI	205—206	0,40*1	74,6	8,5	8,0	$C_{22}H_{30}N_2O_2$	74,5	8,5	7,9	77
XVII	215—216	0,32*1	70,8	8,0	7,9	$C_{21}H_{28}N_2O_3$	70,8	7,9	7,9	74
XVIII	191—192	0,67	66,0	6,9	8,2	$C_{28}H_{35}N_3O_4S$	66,0	6,9	8,1	85
XIX	168—169	0,52*2	70,7	7,9	7,9	$C_{21}H_{28}N_2O_3$	70,8	7,9	7,9	88
XXI	153—154	0,35	63,3	6,5	8,0	$C_{27}H_{33}N_3O_5S$	63,4	6,5	8,2	90
XXII	241—242	0,90	66,1	6,9	8,0	$C_{28}H_{35}N_3O_4S$	66,0	6,9	8,2	95
XXIII	178—179	0,71	63,6	6,5	8,0	$C_{27}H_{33}N_3O_5S$	63,4	6,5	8,2	86
XXIV	262—263	0,35	61,1	6,0	8,1	$C_{34}H_{40}N_4O_6S_2$	61,4	6,1	8,4	77
XXV	207—208	0,51	71,1	8,2	11,5	$C_{21}H_{29}N_3O_2$	70,9	8,2	11,8	71
XXVI	180—181	0,53*3	67,0	7,6	11,6	$C_{20}H_{27}N_3O_3$	67,2	7,6	11,8	67
XXVII	166—167	0,80*4	71,1	8,2	11,6	$C_{21}H_{29}N_3O_2$	70,9	8,2	11,8	60

*1Benzene.
*2Benzene—chloroform (1:1).
*3Benzene—ethanol (95:5).
*4Chloroform—ethanol (97:3).

tion the mixture was refluxed for 1 h, the precipitate was removed by filtration, and the filtrate was evaporated. The residue was extracted with chloroform (three 100-ml portions), the extract was dried with sodium sulfate, and the solvent was evaporated to give 23.1 g (91%) of a product with mp 60-61°C. ^1H NMR spectrum: 1.77 (m, 6H), 3.70 (m, 4H, NH_2), 3.95 (m, 4H, CH_2—O), 6.70 ppm (m, 8H, C_6H_4). Found: C 71.2; H 7.7; N 9.9%. $C_{17}H_{22}N_2O_2$. Calculated: C 71.3; H 7.7; N 9.8%.

1,7-Bis(2-aminophenyl)-1,4,7-trioxaheptane (II). This compound was similarly obtained in 88% yield and had mp 63-64°C (mp 64°C [8]).

1,7-Bis(2-aminophenyl)-4-tosyl-1,7-dioxa-4-azaheptane (III). This compound was obtained in 90% yield as described above and had mp 146-147°C (mp 147-148°C [8]).

N-Tosyliminodiacetic Acid (XXXI). A 26.6-g (0.2 mole) sample of iminodiacetic acid was added to 400 ml of 2 N NAOH (0.8 mole). After all of the solid had dissolved, a solution of 60.0 g (0.312 mole) of p-toluenesulfonyl chloride in 300 ml of ether was added in the course of 2 h, and the mixture was stirred for 4 h. The ether layer was discarded, the aqueous layer was acidified to pH ~ 1 with concentrated HCl, and the precipitate was separated, dried, and crystallized from water to give 34.8 g (61%) of a product with mp 193-194°C.

N-Tosyliminodiacetic Acid Dichloride (VI). A 41-ml sample of thionyl chloride and 0.1 ml of DMF were added to a suspension of 18.4 g (64 mmole) of XXXI in 80 ml of dry benzene, and the mixture was stirred at 35°C until the solid had dissolved completely. The solvent was evaporated in vacuo to give 20.7 g (98%) of a product with mp 92°C.

General Method for Obtaining Macrocyclic Amides VII-XV. Solutions of 10 mmole of diamine I, II, or III in 50 ml of dioxane (in the case of diamines I and II) or pyridine (in the case of diamine III) and 10 mmole of the corresponding dichloride in 50 ml of dioxane were added simultaenously in the course of 6 h to a heated (to 75°C) solution of 8 ml of dry pyridine in 800 ml of dry benzene, after which the solvent was evaporated in vacuo, and the residue was washed with 100 ml of 0.1 N HCl or chromatographed. The characteristics of VII-XV are presented in Tables 1 and 2. Compound XI was obtained in 90% yield and had mp 170-171°C [5, 11± and R_f 0.43 ($CHCl_3$).

General Method for the Reduction of Amides VII-XV to Amines XVI-XXIV. We have previously described this method [1]. Compound XXI was reduced in dimethoxyethane. The characteristics of XVI-XXIV are presented in Tables 3-5. Compound XX was obtained in 60% yield and had mp 204-205°C [5-8] and R_f 0.30 [benzene—$CHCl_3$ (1:1)]. Compound XXVIII was obtained in 59% yield and had mp 200-201°C [8] and R_f 0.74 ($CHCl_3$). Compound XXIX was obtained in 50% yield and had mp 182-183°C [8] and R_f 0.47 ($CHCl_3$).

General Method for Splitting Out of the Protective Group. A mixture of 10 mmole of XVIII or XXII-XXIV and 9.4 g of phenol was reflected for 6 h in 100 ml of a 33% solution of hydrogen bromide in acetic acid, after which the mixture was evaporated to dryness, and the residue was treated with 50 ml of dry ether. The precipitate was washed with 50 ml of dry ether and suspended in 150 ml of 10% NaOH solution, and the suspension was extracted

TABLE 4. Data from the ^{1}H NMR, IR, and Mass Spectra of Macrocyclic Amines XVI-XXIX

Compound	Chemical shifts of the protons, δ, ppm ($CDCl_3$)*1								IR spectrum, ν_{NH}, cm^{-1}	M		Mass spectrum, intensities of the peaks that characterize the fragment ions					
	CH_2—O	CH_2—X	X	CH_2—N	CH_2—Y	Y	NH br. s	Ar		found	calc.	120	122	134	136	148	[M—Ts]
XVI	4,05	1,82	1,82	3,18	1,65	1,65	4,23	6,4—7,0	3430	354	354,5	5,8	6,0	2,5	1,3	2,8	—
XVII	3,93	1,78	1,78	3,25	3,73	—	4,52	6,4—7,0	3410	356	356,5	16,8	6,9	7,6	3,4	2,5	—
XVIII	4,03	1,85	1,85	3,35	3,35	2,37 s, 3H 7,1—7,8	4,81	6,3—6,9	3420	509	509,7	5,2	5,0	3,4	2,2	1,6	4,8
XIX	4,13	3,88	—	3,17	1,65	1,65	4,33	6,4—7,0	3320	356	356,5	5,9	3,4	2,0	1,7	4,9	—
XX*2	4,10	3,94	—	3,27	3,76	—	4,30	6,4—7,0	3280	358	358,4	10,6	3,7	3,5	2,5	8,2	—
XXI	4,00	3,85	—	3,25	3,25	2,30 s, 3H 7,0—7,8	4,86	6,3—6,9	3410	511	511,6	5,1	3,4	3,0	2,3	4,8	10,6
XXII	4,10	3,82	2,37 s, 3H 7,1—7,7	3,15	1,53	1,53	4,65	6,4—7,0	3350	509	509,7	4,3	2,5	2,2	1,4	4,3	—
XXIII	4,08	3,66	2,37 s, 3H 7,1—7,8	3,33	3,58	—	4,62	6,4—7,0	3400	511	511,6	6,3	3,7	3,2	2,7	5,9	—
XXIV	4,15	3,70	2,37 s, 3H 7,1—7,7	3,22	3,22	2,37 s, 3H 7,1—7,7	4,83	6,2—6,8	3420	664	664,8	2,5	2,8	2,5	1,6	7,1	7,0
XXV	4,02	1,86	1,86	3,20	3,02	4,76	4,76	6,6—7,1	3400	355	355,5	4,8	5,9	3,3	2,3	1,5	—
XXVI	4,10	3,74	—	3,15	2,80	4,72	4,72	6,6—7,1	3310	...	...	...	...	...	...	...	...
XXVII	4,11	3,11	4,20	3,11	1,65	1,65	4,20	6,4—7,0	3430	355	355,6	3,5	4,1	1,8	2,0	3,3	—
XXVIII	4,11	3,10	3,28	3,10	3,75	—	4,41	6,4—7,0	3410	357	357,4	5,4	4,8	1,4	4,9	4,3	—
XXIX	4,11	3,08	1,65	3,08	3,08	1,65	4,65	6,4—7,0	3400	356	356,5	3,1	5,0	2,6	3,2	6,2	—

*1 With the exception of the indicated cases, all of the signals are weakly resolved multiplets.

*2 Literature data [5]: PMR spectrum ($CDCl_3$): 4.15, 3.92, 3.29, 3.77, 4.72, 6.53-6.96 ppm; IR spectrum ($CHCl_3$): 3422, 3385 cm^{-1}.

TABLE 5. ^{13}C NMR Spectra, Chemical Shifts of the Carbon Nuclei, δ, ppm ($CDCl_3$)*1

Compound	CH_2—O	CH_2—N	CH_2—X	CH_2—Y	C^1	C^3	C^4	C^2; C^5	C^6	Other nuclei
XVI	67,0	42,7	29,7	28,6	138,4	121,0	116,0	109,7; 109,4	146,1	24,6; 24,3 (CH_2)
XVII	67,2	43,6	29,5	70,0	138,3	120,9	116,6	109,8; 109,7	146,5	28,9 (CH_2)
XVIII	67,2	43,3	29,5	49,4	137,7	120,9	116,5	110,2; 109,5	146,4	23,1 (CH_2)
XIX	67,1	42,6	69,8	28,1	138,3	121,4	115,9	110,0; 109,7	145,7	24,4 (CH_2)
XX	67,7	43,6	69,8*2	69,7*2	138,5	121,5	116,5	110,7; 110,1	146,4	—
XXI	68,5	43,1	69,5	49,5	138,7	121,8	116,1	110,1; 112,6	146,6	—
XXII	67,8	43,0	49,1	25,4	138,7	122,1	116,2	110,1; 111,3	145,4	24,2 (CH_2); 143,4; 129,7; 127,0; 138,9; 21,2 (Ts)
XXIII	69,5	43,7	48,8	69,9	138,8	122,1	116,8	110,8; 112,7	146,2	144,6; 130,1; 127,4; 138,6; 21,2 (Ts)
XXIV	68,5	43,2	50,1	43,8	137,9	121,8	116,7	110,1; 111,3	145,8	143,4; 129,7; 127,0; 135,9; 21,2 (Ts)
XXV	67,2	43,3	29,5	49,1	138,4	121,0	116,3	109,7; 109,7	146,5	23,9 (CH_2)
XXVI*3	67,0	43,2	69,3	48,7	138,8	121,3	115,9	109,5; 109,7	146,2	—
XXVII	67,5	42,6	49,2	28,3	138,3	121,4	116,1	109,9; 109,7	146,1	24,3 (CH_2)
XXVIII	67,2	43,3	48,7	69,5	138,0	121,2	116,2	109,8; 109,8	146,2	—
XXIX	67,0	43,1	48,7*2	48,8*2	138,0	121,2	116,5	109,8; 109,5	146,1	—

*1 With tetramethylsilane as the internal standard.

*2 The assigments can be interchanged.

*3 For a solution in d_5-pyridine.

with chloroform (three 100-ml portions). The extract was dried with sodium sulfate, the solvent was evaporated, and the residue was chromatographed in chloroform. The characteristics of XXV and XXVII-XXIX are presented in Tables 3-5.

8,9;17,18-Dibenzo-1,4,7-trioxa-10,13,16-triazacyclooctadecane (XXVI). A 5.0-g (0.217 mole) sample of sodium was added in the course of 2 h to a heated (to 100°C) solution of 3.82 g (7.47 mmole) of XXI in 100 ml of n-butyl alcohol. After the sodium had dissolved completely, the solution was cooled and washed with water (three 100-ml portions), and 120 ml of 20% HCl solution was added to the butanol layer. After prolonged shaking, the butanol layer was separated and discarded, and the aqueous layer was made alkaline with 30% KOH solution to pH ~ 12 and cooled. The precipitate was separated, washed with 200 ml of water, and dried in vacuo to give 1.78 g (67%) of product. The characteristics are presented in Tables 3-5.

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SYNTHESIS AND PROPERTIES OF SOME DERIVATIVES OF 2-THIONOINDENO[1,2-d]-PYRIMIDINE AND INDENO[1,2-d][3,1]THIAZINE

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Derivatives of 2-thiono-5-oxo-2,3,4,5-tetrahydroindeno[1,2-d]pyrimidine and 5-oxo-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine are formed in the cyclocondensation of 2-arylideneindan-1,3-diones with thiourea and N-monomethylthiourea, while only derivatives of indeno[1,2-d]-pyrimidine are formed in the reaction with N,N-dimethylthiourea. S- and $N_{(3)}$-Alkylation occur in the alkylation of 2-thiono-4-phenyl-5-oxo-2,3,4,5-tetrahydroindeno[1,2-d]pyrimidine, while only the N-methyl derivative is formed in the alkylation of 2,5-dioxo-4-phenyl-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine.

It is known [1, 2] that 2-oxoindeno[1,2-d]pyrimidines are formed in the condensation of urea with derivatives of indan-1-one or indan-1,3-dione. In the opinion of Benera and Nayak [3], the condensation of 2-arylideneindan-1,3-diones with thiourea leads to 2-thiono-4-aryl-5-oxo-2,3,4,5-tetrahydroindeno[1,2-d]-pyrimidines, although only the results of elementary analysis for sulfur are presented for confirmation of the structures of the reaction products. From 2-benzylideneindan-1,3-indole and thiourea we obtained a substance with a

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