SYNTHESIS AND IR SPECTRA OF SOME DERIVATIVES OF PHENANTHRIDINE AND 4, 9-DIAZAPYRENE

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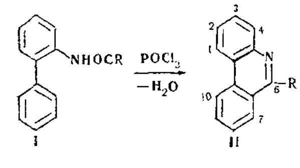
A number of acylamino- and diacylaminobiphenyls and the corresponding derivatives of phenanthridine and 4, 9-diazapyrene, including the previously unknown 2, 2'-dipropionamidobiphenyl, 5, 10-diethyl-4, 9-diazapyrene, 2, 4-dibenzamidobiphenyl, and 3-benzamido-6-phenylphenanthridine, have been synthesized. The IR spectra of all the compounds have been studied and a group of bands characteristic for the phenanthridine ring in the 1570–1620 cm^{-1} region and a group of five bands characteristic for the 4, 9-diazapyrene ring in the 1330–1640 cm^{-1} region have been identified. The nature of the IR spectra of phenanthridine derivatives containing unsubstituted amide groups has also been established.

At the present time, one of the main directions in the chemistry of high-molecular-weight compounds is the creation of heat-stable polymers. The majority of heat-stable polymers synthesized have a cyclic-linear structure with various aromatic and heteroaromatic rings in the main chain (polyimides, polybenzazoles, polyazines, etc.). Such polymers contain, in addition to aromatic nuclei, five- and six-membered heteroaromatic rings, which are responsible for the high stability of these polymers to various types of aggressive attacks.

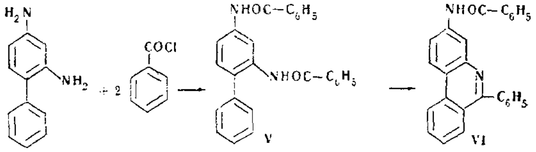
In polymers that we have synthesized, phenanthridine and diazapyrene rings are formed by a polycyclodehydration reaction [1, 2]. We have been unable to find in the literature any information on the IR spectra of phenanthridine derivatives, while 4, 9-diazapyrene and a few of its derivatives have been synthesized only recently and have been little studied [3, 5]. Consequently, as model compounds we have synthesized derivatives of phenanthridine and of 4, 9-diazapyrene the structures of which correspond to the structures of the elementary units of the polymeric chains, and we have studied their IR spectra.

The phenanthridine derivatives were synthesized by the Morgan-Walls reaction [6], by the dehydration of 2-acylaminobiphenyls under the action of phosphorus oxychloride:



Thus, from 2-aminobiphenyl and carboxylic acid chlorides, via the corresponding amides, we synthesized 6-ethylphenanthridine (II, R = C_2H_5) and 6-phenylphenanthridine (II, R = C_6H_5); 1, 4-bis(phenanthridin-6-yl)butane (IV) was synthesized by the cyclodehydration of N, N'-bis(biphenyl-2-yl)adipamide (III).

We also considered it necessary to study the nature of the IR spectra of compounds simultaneously containing phenanthridine rings and amide groupings. For this purpose, we synthesized 3-benzamido-6-phenylphenanthridine (VI) and 10-benzamido-6-phenylphenanthridine (VII).



4, 9-Diazapyrene, in which biphenyl is condensed with two pyridine nuclei, is formed under more severe conditions. In particular, all the 4, 9-diazapyrene derivatives were synthesized from 2, 2'-diacylaminobiphenyls (VIII) using a mixture of aluminum chloride at 240–250° C as the cyclodehydrating medium:

Table 1

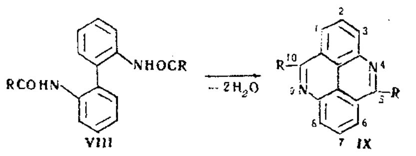
Characteristics of the Amides Used for the Synthesis of the Phenanthridine and 4, 9-Diazapyrene Derivatives

Compound	Name	Mp, °C (solvent)	Empirical formula	Found, %			Calculated, %			Amide bands in the IR spectrum, cm^{-1}	Mp, °C, according to the literature
				C	H	N	C	H	N		
I, R=C_2H_5	2-Propionamidobiphenyl	66.3–67.2 (aqueous ethanol)	$C_{15}H_{15}NO$	80.29	6.96	6.32	79.97	6.71	6.21	1660; 1530; 1280	65 [15]
I, R=C_6H_5	2-Benzamidobiphenyl	86.0–86.5 (aqueous ethanol)	$C_{19}H_{15}NO$	83.04	5.18	5.34	83.49	5.53	5.12	1650; 1525; 1305	88 [12]
III	N,N'-Bis(biphenyl-2-yl)adipamide	172.5 (ethanol)	$C_{30}H_{28}N_2O_2$	80.50	6.21	6.51	80.20	6.28	6.23	1650; 1520; 1305	174 [13]
V	2,4-Dibenzamidobiphenyl	189 (ethanol)	$C_{26}H_{20}N_2O_2$	79.29	5.19	7.31	79.59	5.11	7.13	1650; 1525; 1310	—
VIII, R=C_2H_5	2,2'-Dipropionamidobiphenyl	156 (ethanol)	$C_{18}H_{20}N_2O_2$	73.55	6.78	9.04	72.94	6.76	9.45	1665; 1525; 1285	—
VIII, R=C_6H_5	2,2'-Dibenzamidobiphenyl	189.8 (methanol)	$C_{26}H_{20}N_2O_2$	79.09	5.11	7.27	79.59	5.11	7.13	1650; 1515; 1300	190–191 [16]

Table 2

Compounds Synthesized and Their Properties

Compound	Name	Mp, °C (solvent)	Empirical formula	Found, %			Calculated, %			Characteristic bands in the IR spectrum of the heterocycles, cm^{-1}	Mp, °C, according to the literature
				C	H	N	C	H	N		
II, $R=C_2H_5$	6-Ethylphenanthridine	55.5—56.0 (petroleum ether)	$C_{15}H_{13}N$	87.13	6.49	6.91	86.95	6.31	6.75	1615; 1580	56.5[12]
II, $R=C_6H_5$	6-Phenylphenanthridine	106 (ethanol)	$C_{19}H_{13}N$	89.58	5.56	4.34	89.34	5.15	5.50	1615; 1565	106[12]
IV	1,4-Bis(phenanthridin-6-yl)butane	216 (pyridine)	$C_{30}H_{24}N_2$	88.00	6.34	6.72	87.34	5.86	6.79	1610; 1580	215[13]
VI	3-Benzamido-6-phenylphenanthridine	231.0—231.6 (ethanol)	$C_{26}H_{18}N_2O$	83.39	4.75	7.30	83.67	4.84	7.47	1615; 1575	—
VII	10-Benzamido-6-phenylphenanthridine	211—212 (ethanol)	$C_{26}H_{18}N_2O$	83.51	4.53	7.07	83.67	4.84	7.47	1605; 1580	214[14]
IX, $R=C_2H_5$	5,10-Diethyl-4,9-diazapyrene	188—189 (methanol)	$C_{18}H_{16}N_2$	83.29	6.28	10.66	83.03	6.19	10.75	1640; 1570; 1490; 1450; 1345	—
IX, $R=C_6H_5$	5,10-Diphenyl-4,9-diazapyrene	322—323 (chlorobenzene)	$C_{26}H_{16}N_2$	87.75	4.70	7.68	87.61	4.52	7.86	1635; 1565; 1475; 1445; 1335	320—32[15]



2,2'-Dipropionamidobiphenyl (VIII, R = C_2H_5) and 2,2'-dibenzamidobiphenyl (VIII, R = C_6H_5) were obtained as intermediates, their cyclodehydration leading, respectively, to 5,10-diethyl-4,9-diazapyrene (IX, R = = C_2H_5) and 5,10-diphenyl-4,9-diazapyrene (IX, R = = C_6H_5).

Both the phenanthridine and the 4,9-diazapyrene rings are extremely resistant to the action of the majority of oxidizing agents. The phenanthridine ring cannot be destroyed by such oxidizing agents as chromic acid, potassium permanganate, and nitric acid [7]. The 4,9-diazapyrene nucleus is also very stable to oxidation. 4,9-Diazapyrene is not oxidized under the conditions of the oxidation of quinoline; it is not nitrated and is not brominated in sulfuric acid solution [4].

The IR spectra of all the initial amides exhibited the well-studied bands characteristic for secondary amides at 1650–1670 cm^{-1} (amide I), 1520–1530 cm^{-1} (amide II), and about 1300 cm^{-1} (amide III) [8]. The disappearance or weakening of the amide bands in the spectra of the compounds of the phenanthridine and 4,9-diazapyrene series was regarded as a proof of the formation of the above-mentioned rings as the result of the cyclodehydration of the corresponding amides. At the same time, the appearance of new groups of bands was identified with the phenanthridine and 4,9-diazapyrene rings. The characteristics of the spectra of the initial amides and the corresponding phenanthridine and 4,9-diazapyrene derivatives in the 400–1800 cm^{-1} region are given in Tables 1 and 2 and in the figure.

The formation of phenanthridine and diazapyrene rings is also confirmed by the disappearance of the characteristic bands in the 3200–3400 cm^{-1} region corresponding to the stretching vibrations of the —N—H group in secondary amides.

It may be concluded from an analysis of the IR spectra of the amides synthesized and the corresponding heterocyclic compounds that the system of five bands in the 1330–1640 cm^{-1} region observed for the 4,9-diazapyrene ring and the two bands in the 1570–1620 cm^{-1} region observed for the phenanthridine ring will permit the identification of compounds of this type, and this, together with the disappearance or weakening of the amide bands, will make it possible to show the presence of these heterocycles in high-molecular-weight compounds.

EXPERIMENTAL

2-Aminobiphenyl and 2,2'-diaminobiphenyl were obtained by the reduction of the corresponding nitro derivatives—2-nitrobiphenyl and 2,2'-dinotrobiphenyl—with hydrazine hydrate in the presence of Raney nickel by a published method [9]. Mp of the 2-aminobiphenyl, 49–50° C, which corresponds to literature data [10]; mp of the 2,2'-diaminophenyl, 79–80° C, according to the literature [11], 81° C.

2,4-Diaminobiphenyl was synthesized as we have described previously [2].

All the acylamino- and diacylaminobiphenyls were synthesized by the Schotten-Baumann reaction from the above-mentioned amines of biphenyl and propionyl, adipoyl, and benzoyl chlorides. The constants of the acylamino- and diacylaminobiphenyls synthesized are given in Table 1.

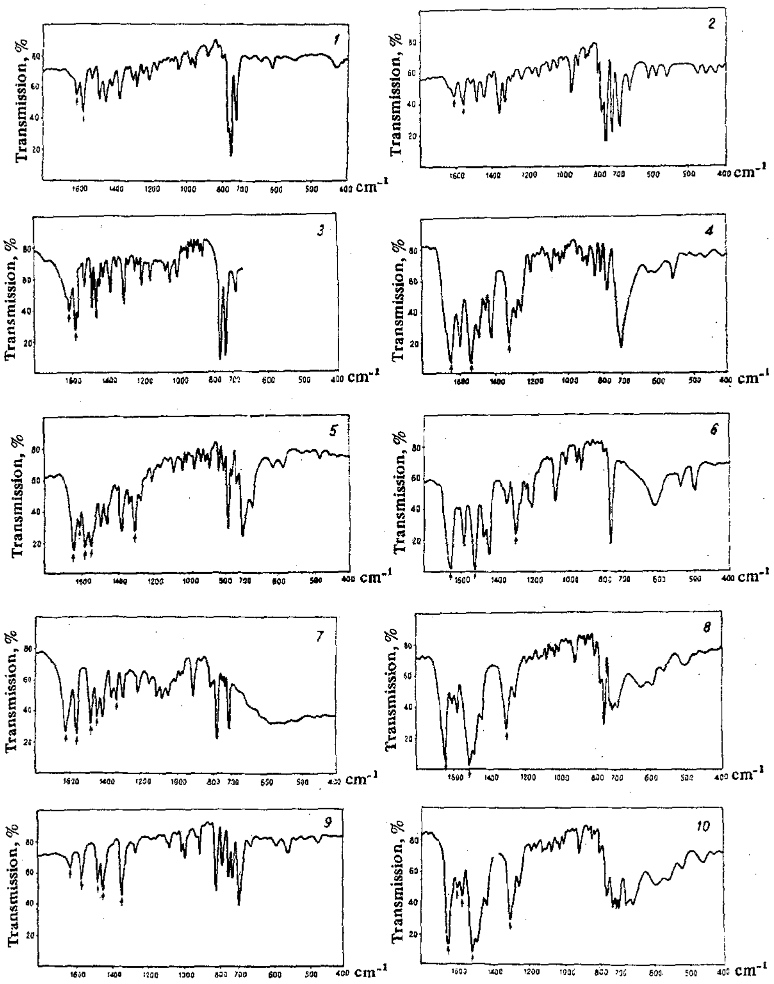
6-Ethylphenanthridine. The amide I (R = C_2H_5) was subjected to cyclodehydration with phosphorus oxychloride [12].

6-Phenylphenanthridine (II, R = C_6H_5) was synthesized by a method similar to that given by Morgan and Walls [12]. Compound IV and the starting material for its synthesis, III, were obtained as recommended by Hollingsworth and Petrow [13].

3-Benzamido-6-phenylphenanthridine (VI). A mixture of 4 g of the amide V and 8 g of freshly-distilled $POCl_3$ was heated to a gentle boil in a current of dry nitrogen for 1 hr. The yellow precipitate that deposited after the cooling reaction mixture had been treated with hot water was filtered off, washed with water, and dried. The dry substance was dissolved in 15 ml of hot pyridine, and the solution was poured into 30 ml of hot water. The pale yellow precipitate that deposited was filtered off, washed with water, and dried. The VI was crystallized from ethanol to form pale yellow crystals.

10-Benzamido-6-phenylphenanthridine (VII) was obtained by the cyclodehydration [14] of the amide VIII (R = C_6H_5).

5,10-Diethyl-4,9-diazapyrene. The amide VIII (R = C_2H_5) was subjected to cyclodehydration by the action of a mixture of NaCl and



IR spectra: 1) 6-ethylphenanthridine; 2) 6-phenylphenanthridine; 3) 1,4-bis(phenanthridin-6-yl)butane; 4) 2,4-dibenzamidobiphenyl; 5) 3-benzamido-6-phenylphenanthridine; 6) 2,2'-dipropionamidobiphenyl; 7) 5,10-diethyl-4,9-diazapyrene; 8) 2,2'-dibenzamidobiphenyl; 9) 5,10-diphenyl-4,9-diazapyrene; 10) 10-benzamido-6-phenylphenanthridine.

$AlCl_3$ at 250° C. The reaction product was treated and isolated as in the case of 4, 9-diazapyrene [5].

5,10-Diphenyl-4,9-diazapyrene (IX, R = C_6H_5) was synthesized from the amide VIII (R = C_6H_5) by a similar method [5].

The melting points and elementary analyses of all the phenanthridine and 4, 9-diazapyrene derivatives synthesized are given in Table 2.

The IR spectra of all the compounds (see figure) were obtained in a UR-10 infrared spectrometer in the region from 400 to 4000 cm^{-1}. The substances were investigated in the solid state in the form of tablets with KBr (5 mg to 1 g of KBr).

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