SYNTHESIS AND INVESTIGATION OF SOME BISBENZIMIDAZOLOQUINAZOLINES

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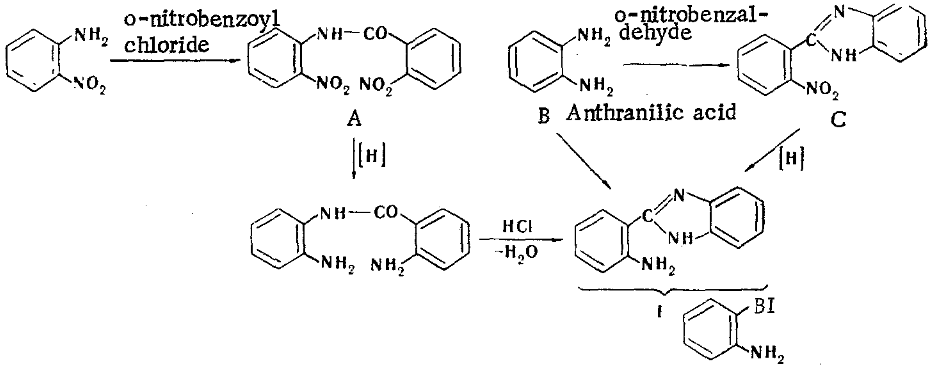
A number of previously undescribed bisbenzimidazoloquinazolines were obtained by reaction of 2-(2-aminophenyl)benzimidazole with dicarboxylic acids or their derivatives and also by reaction of bis[2-(2-aminophenyl)-6-benzimidazolyls] with benzoic acid or its derivatives. It is shown that benzimidazoloquinazolones fall into the category of the highest-melting and most heat-resistant heterocyclic systems.

Polybenzimidazoloquinazolines have received relatively little study but constitute an extremely promising class of "block-ladder" polymers. The principal method used to prepare them is the reaction of aromatic diamines containing benzimidazole rings with aromatic dicarboxylic acids or their derivatives in the ortho positions relative to the amino groups [1]. In order to determine the optimum conditions for the synthesis of polybenzimidazoloquinazolines and their identification, we synthesized a number of individual compounds that model the structure of the macromolecules of these polymers and studied the principal spectral and thermal characteristics of these products. The starting 2-(2-aminophenyl)benzimidazole (I) for the synthesis of a number of model compounds was obtained by three different routes in conformity with the following general scheme:



The simplest model compound — 6-phenylbenzimidazolo[1,2-c]quinazoline (III) was obtained by reaction of I with benzoic acid in polyphosphoric acid (PPA) or with benzoyl chloride in amide aprotic solvents with subsequent cyclization of the resulting 2-(2-benzamidophenyl)benzimidazole (II):

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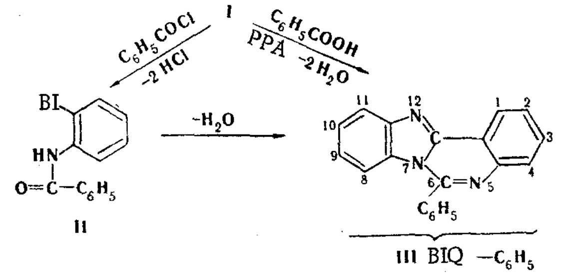
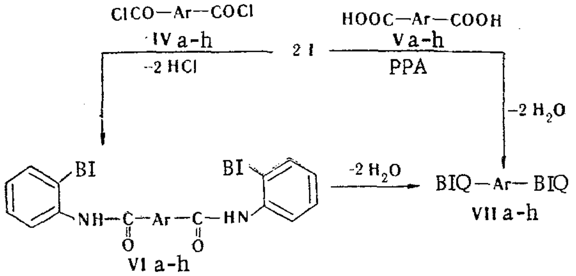


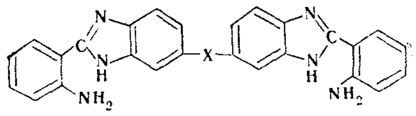
The cyclodehydration of amide II to III was accompanied by the disappearance of the absorption maxima at 1610-1670 cm^{-1}, which are ascribed to the carbonyl groups of amide bonds, and at 2800-3200 cm^{-1}, which are related to the vibrations of amide NH groups and the benzimidazole ring; at the same time, the appearance of a new maximum at 1380 cm^{-1}, which is characteristic for benzimidazoloquinazoline ring with a tertiary nitrogen atom, appears.

Model compounds of more complex structures were obtained by reaction of amine I with aromatic dicarboxylic acids dichlorides in amide solvents and subsequent thermal cyclodehydration of the resulting bis[2-(2-benzimidazolyl)anilido]arylenes (VIa-h); bis(benzimidazolo[1,2-c]quinazol-6-yl)arylenes (VIIa-h) of similar structure were obtained by reaction of amine I with dicarboxylic acids or their derivatives in PPA:



IV—VII a p-phenylene, b m-phenylene c p,p'-diphenylene, d 2,6-naphthylene, e 2,6-pyridylene f p,p'-hydroxydiphenylene g p,p'-diphenyleneketone, h p,p'-diphenylenesulfone

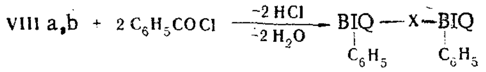
Model compounds with different structures were obtained from bis[2-(2-aminophenyl)benzimidazol-6-yls] and benzoic acid or its derivatives. The starting bis[2-(2-aminophenyl)benzimidazol-6-yls] can be obtained by any of the three methods used for the preparation of I, but the most efficient method is method A, in accordance with which the corresponding (3,3'-dinitro-4,4'-diamino)arylenes were treated with 2 moles of o-nitrobenzoyl chloride to give tetranitrodiamides, the subsequent reduction of which to tetraaminodiamides and catalytic cyclization of the latter give bis[2-(2-aminophenyl)benzimidazol-6-yls] (VIIIa,b):



VIII a,b

VIII a X=— ; b X=—O—

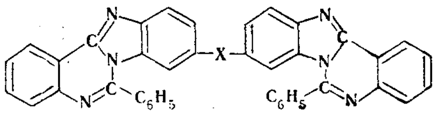
The synthesis of bis[(6-phenyl)benzimidazolo[1,2-c]quinazol-9-yls] (IXa,b) was accomplished by acylation of VIIIa,b with benzoyl chloride in amide solvents with subsequent thermal cyclodehydration of the resulting bis[2-(2-benzamidophenyl)benzimidazol-6-yls]:

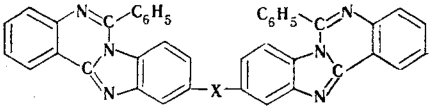


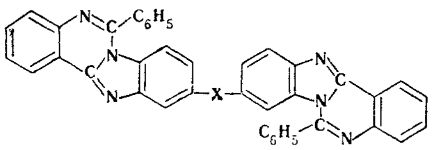
$$\text{VIII a,b} + 2\,C_6H_5COCl \xrightarrow[-2\,H_2O]{-2\,HCl} \underset{C_6H_5}{\text{BIQ}}—X—\underset{C_6H_5}{\text{BIQ}}$$

IX a X=— ; b X=—O— IX a,b

The principal characteristics of the synthesized model compounds are presented in Table 1. One's attention is drawn to the fact that bis(benzimidazolo[1,2-c]quinazol-6-yl)arylenes VIIa-h are characterized by high and distinct melting points, while bis[(6-phenyl)benzimidazolo[1,2-c]quinazol-9-yls] IXa,b melt at relatively low temperatures and over a rather broad range. The observed difference is probably explained by the fact that, in contrast to VIIa-h, IXa,b are not individual compounds but rather mixtures of isomers of the following types:







An investigation of the thermal stabilities of the model compounds by the methods of differential thermal analysis and thermogravimetric analysis showed that these compounds begin to undergo intensive destruction at temperatures above 400°. Judging from the results of differential thermal analysis, the destruction of the products takes place in two steps, and the temperatures of the maximum rates of decomposition for these compounds are considerably higher than the corresponding temperatures for the previously described bis(N-phenyl)benzimidazoles [2] and bis(triazoloquinazolines) [3].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The thermal characteristics of the compounds obtained were determined with the derivatograph of the Paulik—Paulik—Erdey system in air at a temperature-rise rate of 4.5°/min.

2-(2-Aminophenyl)benzimidazole (I). A) A solution of 10 g of 2-nitrobenzoic acid 2-nitroanilide in 100 ml of dimethylformamide (DMFA) was hydrogenated over Raney nickel in a rotating autoclave at 25° and a pressure of 100 atm. After absorption of ~40 atm, the reaction mixture was filtered to remove the Raney nickel, and ~800 ml of distilled water was added. The resulting light-gray precipitate was recrystallized from aqueous methanol. The yield of anthranilic acid 2-aminoanilide with mp 127° (mp 129-130° [4]) was 90%. A solution of 5 g of anthranilic acid 2-aminoanilide in 50 ml of 4 N HCl was refluxed for 2 h. The precipitate was treated with ammonium hydroxide and washed with water until the wash waters were neutral. The resulting solid was sublimed at 150° (10^{-4} mm) to give 2-(2-aminophenyl)benzimidazole with mp 211-212° (mp 211° [5]) in 70% yield.

B) 2-Nitrobenzaldehyde was added in portions to a heated (to 50°) solution of 4.3 g of o-phenylenediamine [6] in 50 ml of dimethylsulfoxide (DMSO). The temperature was raised to 80°, and the mixture was stirred at this temperature for 12 h. The cooled mixture was poured into water, and the aqueous mixture was worked up to give 2-(2-nitrophenyl)benzimidazole with mp 266-268° (from ethanol) (mp 263° [7]) in 85% yield. Hydrazine hydrate (20 ml) and Raney nickel were added to a solution of 4.4 g of 2-(2-nitrophenyl)benzimidazole in 90 ml of ethanol. The mixture was stirred and refluxed for 5 h, after which, without cooling, it was filtered away from the Raney nickel. Cooling of the filtrate gave crystals of 2-(2-aminophenyl)benzimidazole with mp 211-212°.

Bis[2-(2-aminophenyl)benzimidazol-6-yl] Oxide (VIIIb). A 13.2-g sample of 2-nitrobenzoyl chloride was added dropwise to a solution of 8.7 g of 3,3'-dinitro-4,4'-diaminodiphenyl oxide, obtained by the method in [8], in 80 ml of N-methyl-2-pyrroli-

TABLE 1. Principal Characteristics of Mono- and Bisbenzimidazoloquinazolines

Compound	mp, °C*	Empirical formula	Found, %			Calc., %			UV spectra†		Thermal characteristics‡	
			C	H	N	C	H	N	λ_{max}	log ε	T_1	T_2
III	240—241 (242[4])	$C_{20}H_{13}N_3$							241 272	4,4 4,6	455	485
VIIa	415 (>350[4])	$C_{34}H_{20}N_6$							243 274	4,6 4,8	520	600
VII b	332	$C_{34}H_{70}N_6$	80,1	3,9	16,6	79,7	3,9	16,4	244 293	4,5 4,9	515	570
VII c	438	$C_{40}H_{24}N_6$	82,1	4,0	14,4	81,6	4,1	14,3	243 275	4,5 4,8	520	625
VII d	472	$C_{38}H_{22}N_6$	80,8	3,9	13,9	81,0	4,0	14,9	222 243 300	4,9 4,7 4,9	540	620
VII e	355	$C_{33}H_{19}N_7$	77,7	3,8	19,7	77,2	3,7	19,1	245 299	4,7 5,0	525	615
VII f	372	$C_{40}H_{24}N_6O$	79,7	3,8	13,8	79,4	4,0	13,9	243 293	4,7 4,8	545	615
VII g	370	$C_{41}H_{24}N_6O$	79,8	3,9	13,6	79,9	3,9	13,6	243 296	4,7 5,1	540	625
VII h	405	$C_{40}H_{24}N_6O_2S$	73,6	3,9	13,1	73,6	3,7	12,9	243 294	4,5 4,9	545	610
IX a	370—380 (>250[4])	$C_{40}H_{24}N_6$							250 306	4,6 4,8	550	635
IX b	270—315	$C_{40}H_{24}N_6O$ ·	79.3	4.1	13,8	79,4	4,0	13,9	246 305	4,7 4,9	560	640

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*The literature melting points are presented in parentheses.
†The spectra in H_2SO_4 with c = 10^{-5} mole/liter were recorded.
‡Symbols: T_1 is the temperature of the maximum rate of decomposition in the first stage of destruction, and T_2 is the temperature of the maximum rate of decomposition in the second stage of destruction.

done at 25° with vigorous stirring, after which the mixture was stirred for 20 h. The resulting solution was poured into water, and the aqueous mixture was worked up to give 3,3'-dinitro-4,4'-di(2-nitrobenzamido)diphenyl oxide with mp 277° (DMFA—water) in 65% yield. Found: C 52.5; H 2.7; N 14.3%. $C_{26}H_{16}N_6O_{11}$. Calculated 53.1; H 2.7; N 15.3%. A solution of 10 g of the compound obtained above in 100 ml of DMFA was hydrogenated as in the preceding experiment. After 7 h, the hydrogen pressure fell to 40 atm; the mixture was then separated from the Raney nickel, and the filtrate was poured into 500 ml of water. The resulting powder was removed by filtration, washed with water, and, without additional purification, refluxed with 100 ml of 4 N HCl for 6 h. The precipitate was removed by filtration, treated with ammonium hydroxide, washed with water to neutrality, vacuum dried at 50° (5 mm), and sublimed at 270-310° (10^{-4} mm) to give a product with mp 296-298° (mp 295-297° [9]).

Bis[2-(2-aminophenyl)benzimidazol-6-yl] (VIIIa). This compound was similarly obtained from 3,3'-dinitrobenzidine, obtained by the method in [10]. The yield of 3,3'-dinitro-4,4'-di(2-nitrobenzamido)diphenyl with mp 365° (from DMFA) was 68%. Found: C 54.6; H 2.5; N 14.6%. $C_{26}H_{16}N_6O_{10}$. Calculated: C 54.5; H 2.8; N 14.7%. Compound VIIIa was sublimed at 330-350° (10^{-4} mm); the yield of product with mp 364-366° (mp 372-373° [9]) was 50% based on the starting 3,3'-dinitro-4,4'-di(2-nitrobenzamido)diphenyl. Found: C 75.2; H 4.9; N 20.2%. $C_{26}H_{20}N_6$. Calculated: C 75.0; H 4.8; N 20.2%.

2-(2-Benzamidophenyl)benzimidazole (II). This compound was obtained by reaction of equimolar amounts of amine I and benzoyl chloride in freshly distilled dry N,N-dimethylacetamide (DMA). The reaction mixture was poured into water, and the aqueous mixture was filtered and worked up to give a product with mp 252-254° (from ethanol) (mp 251° [1]) in 90% yield.

6-Phenylbenzimidazolo[1,2-c]quinazoline (III). This compound was obtained by heat treatment of II at 250° (1 mm) for 6 h or by reaction of I with benzoic acid in PPA at 210-220° for 10 h. The product was purified by recrystallization from ethanol or by sublimation at 220° (1 mm) to give a product with mp 240-241° (mp 242° [11]) in 90% yield.

Bis(benzimidazolo[1,2-c]quinazol-6-yl)arylenes (VIIa-h). These compounds were obtained by reaction of I with aromatic dicarboxylic acid dichlorides in DMFA. The reaction solutions were poured into water to obtain precipitates of the corresponding bis[2-(benzimidazol-2-yl)anilido]arylenes (VIa-h), which were dried and, without additional purification, subjected to heat treatment at 300-350° (10^{-4} mm). The yields were 70-80%. The melting points and results of elementary analysis of VIIa-h are presented in Table 1.

Bis[(6-phenyl)benzimidazolo[1,2-c]quinazol-9-yls] (IXa, b). These compounds were obtained by reaction of VIIIa and VIIIb with benzoyl chloride in DMFA. As in the preceding experiment, the corresponding bis[2-(2-benzamidophenyl)benzimidazol-6-yls] were isolated; without additional purification, the latter were subjected to heat treatment at 300-350° (10^{-4} mm). The resulting IXa, b were purified by sublimation at 350-380° (10^{-4} mm) or by recrystallization from DMFA to give the products in 70-80% yields. The melting points and results of elementary analysis are presented in Table 1.

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