which each portion was added only after gas evolution from the previous portion had ceased. The mixture was stirred at room temperature for 3-4 h, after which the acid layer was separated and poured into 350 ml of water containing ice. The aqueous mixture was neutralized with sodium bicarbonate and extracted with five 100-ml portions of ethyl acetate. The extract was washed with water and dried over calcined magnesium sulfate. The solvent was removed, and the product was purified by crystallization.

<u>1-(2-Aminoethyl)-3-nitro-1,2,4-triazole Hydrochloride (VI)</u>. Concentrated HCl (20 ml) was added to 3 g (15.5 mmole) of amide III, and the mixture was refluxed for 6 h. It was then evaporated to dryness on a steam bath, and the residue was crystallized from methanol to give 2.1 g (69%) of a product with mp 209-210°C. IR spectrum: 840 s, 435 w, 1030 m, 1110 m, 1185 m, 1240 w, 1310 s, 1390 w, 1340 m, 1415 m, 1460 m, 1495 s, 1540 m, 1555 m, 1600 w, 2800 w, 2880 w, 2450 w, 3070 w, and 3120 w cm<sup>-1</sup>. Found: C 24.6; H 4.4; Cl 18.0; N 36.1%; M 190 by ebullioscopy, from acetone.  $C_4H_8ClN_5O_2$ . Calculated: 24.8; H 4.1; Cl 18.4; N 36.2%; M 193.5.

 $\frac{2-\text{Nitro-}5,6-\text{dihydro-}1\text{H-imidazo}[2,3-\text{b}]-1,2,4-\text{triazole (VIII)}.}{1000} \text{ A } 2-\text{g} (8 \text{ mmole}) \text{ sample of amide V was added to 10 ml of 10\% H_2SO_4, and the mixture was refluxed for 6 h. It was then made alkaline to pH 8 with so-dium bicarbonate and extracted with three 25-ml portions of ethyl acetate. The extract was then washed with water and dried over calcined magnesium sulfate. The solvent was removed, and the residue was crystallized from ethanol to give 0.62 g (51\%) of a product with mp 177-178°C. IR spectrum: 815 w, 860 w, 880 m, 940 w, 1100 w, 1240 s, 1270 s, 1300 s, 1350 w, 1410 w, 1440 m, 1460 m, 1500 s, 1535 s, 1620 s, 2850 w, 2920 m, and 3200-3400 m cm<sup>-1</sup>. Found: C 30.8; H 4.0; N 45.4\%; M 153 by ebullioscopy, from acetone. C<sub>4</sub>H<sub>5</sub>N<sub>5</sub>O<sub>2</sub>. Calculated: C 30.9; H 3.2; N 45.1\%; M 153.$ 

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## SYNTHESIS OF NEW CONDENSED HETEROCYCLIC SYSTEMS

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UDC 547.785'792.07:543.422.4

Two new diamines - [1,3-bis(5-phenyl-1,2,4-triazol-3-yl)-4,6-diamino]benzene and [1,3-di-(2-benzimidazolyl)-4,6-diamino]benzene - were synthesized from 4,6-dinitroisophthalic acid. New heterocyclic systems - 3,5,9,11-tetraphenyl[benzo[1,2-a;4,5-a']bis(1,2,4-triazolo[4,3-c]pyrimidine)] and 2,16-diphenyl[benzo[1,2-a;4,5-a']bis(pyrimido[1,6-a]benzimidazole)] - were obtained by reaction of the diamines with benzoyl chloride and subsequent cyclization.

Continuing our study of heterocyclic compounds that model "ladder" polymers [1, 2], we synthesized previously undescribed diamines that contain benzimidazole and sym-triazole rings in the ortho positions relative to the amino groups and new heterocyclic compounds from them. The starting diamines were obtained from 4,6-dinitroisophthalic acid anhydride (I) in conformity with scheme 1. The structures of the intermediate and final reaction products (II-VII) were confirmed by the results of elementary analysis (Table 1) and the IR spectral data. Thus the reaction of I with benzamidrazone gave (4,6-dinitroisophthaloyl)dibenzamidrazone (II), the IR spectrum of which contains absorption maxima at 1350, 1530 (NO<sub>2</sub>); 1680 (amide CO); and 3200 and  $3490 \text{ cm}^{-1}$  (NH and NH<sub>2</sub>). The cyclodehydration of II to [1,3-bis(5-phenyl-1,2,4-triazol-3-yl)-4,6-dinitro]ben-

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow 117312. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1274-1277, September, 1977. Original article submitted June 30, 1976; revision submitted December 13, 1976.

Com- pound	mp <b>, °</b> C	Method of purification	F <b>ound</b> , %			Emp <b>irical</b>	Calc., %			UV spec- tra*		70
			с	н	N	formula	с	n	N	λ <sub>m a x</sub> . nm	8 8	Yield,
II	338—340	Recrystalliza- tion [DMF-	53.6	3,9	23,0	$C_{22}H_{18}N_8O_6$	53,9	3,6	22,8	247	4,60	72
ш	345—346	Recryst. (iso-	58,1	3,3	24,6	$C_{22}H_{14}N_8O_4$	58,1	3,1	24,7	247	4,73	62
IV	335—336	Recrystalliza- tion (ethanol)	66,3	4,8	28,8	$C_{22}H_{18}N_8$	67,0	4,5	28,4	275	4,72	77
v	256—257	Recrystal. [DMF-water	48,5	3,3	16.6	$C_{20}H_{12}N_6O_{10}$	48,4	3,4	17,0	231	4,75	63
VI	280-282	(3:1)] Extraction with	61.7	5,9	21,8	$C_{20}H_{20}N_6O_2$	63.8	5,3	22,3			90
VII	412-413	Sublimat. at	70,6	4,9	24,5	$C_{20}H_{14}N_6$	70,6	4,7	24.7	305	4,51	80
VIII	367	10 <sup>-4</sup> mm Recrystalliza- tion [DMF-	69,0	4,9	17,9	$C_{36}H_{26}N_8O_2$	71.8	4,3	18,6	263	4,86	73
IX	400402	Sublimat. at 350-360°C/	76,0	4,0	20,2	$C_{36}H_{22}N_8$	76,3	3,9	19,8	$\frac{260}{322}$	4,71 4,41	86
x	365 - 366	Recrystalliza-	74,5	4,4	15,1	$C_{34}H_{24}N_6O_2$	74,4	4,4	15,3	265	4,66	70
хі	436-440	Sublimat. at 300-350°C/	78,6	4,()	16,3	$C_{34}H_{20}N_6$	79,7	3,9	16,4	235 267	4,49 4,43 4,20	90
		10 <sup>-4</sup> mm and recrystalliza- tion (DMF)	ſ							340 427 452	$3.17 \\ 4.51 \\ 4.52$	

TABLE 1. Some Properties of the Synthesized Compounds

\* The UV spectra were recorded from  $10^{-5}$  mole/liter solutions of the compounds in 98% H<sub>2</sub>SO<sub>4</sub>.

zene (III) was accompanied by disappearance of the absorption maxima characteristic for the amide CObond and NH and  $NH_2$  groups and by the appearance of absorption maxima at 1615 (triazole C = N) and 3100-3400 cm<sup>-1</sup> (triazole NH).



Reduction of III gave [1,3-bis (5-phenyl-1,2,4-triazol-3-yl)-4,6-diamino] benzene (IV), the IR spectrum of which does not contain the absorption maxima characteristic for nitro groups but does contain the absorption maxima characteristic for the triazole C = N bond (1615 cm<sup>-1</sup>) and for amino groups (3380 cm<sup>-1</sup>). On the other hand, the reaction of I with

o-nitroaniline gave 4,6-dinitroisophthalic acid bis (o-nitroanilide) (V), the IR spectrum of which contains absorption maxima at 1350, 1530 (NO<sub>2</sub>); 1690 (amide CO); and 3300-3380 cm<sup>-1</sup> (amide NH). The reduction of V to 4,6-diaminoisophthalic acid bis (o-aminoanilide) (VI) was accompanied by disappearance of the absorption maxima characteristic for nitro groups, a shift of the absorption maximum of an amide CO group to 1650 cm<sup>-1</sup>, and the appearance of absorption maxima at 1260 and 1320 cm<sup>-1</sup> (amine C-N) and 3460 and 3490 cm<sup>-1</sup> (NH<sub>2</sub>). The cyclodehydration of VI to [1,3-di(2-benzimidazolyl-4,6-diamino]benzene (VII) was accompanied by disappearance of the absorption maxima characteristic for amide group CO and NH bonds and the appearance of absorption maxima at 1460, 1600, 1625, and 3000-3400 cm<sup>-1</sup> (benzimidazole).

New heterocyclic systems -3,5,9,11-tetraphenyl[benzo[1,2-a;4,5-a']bis(1,2,4-triazolo[4,3-c]pyrimidine)] (IX) and 2,16-diphenyl[benzo[1,2-a;4,5-a']bis(pyrimido[1,6-a]benzimidazole)] (XI) (Scheme 2) - were obtained by reaction of diamines IV and VII with benzoyl chloride and subsequent cyclocondensation of the resulting dibenzamides VIII and X.

Scheme 2



The structures of the intermediate and final reaction products (VIII-XI) were confirmed by the results of elementary analysis (Table 1) and IR spectral data. The benzoylation of IV was accompanied by the disappearance of the absorption maxima characteristic for amino groups and by the appearance of the absorption maxima characteristic for amide CO and NH bonds (1660 and 3200 cm<sup>-1</sup>), which attests to the formation of [1,3-bis(5-phenyl-1,2,4-triazol-3-yl)-4,6-dibenzamido]benzene (VIII). Absolutely analogous changes in the spectral characteristicswere observed in the benzoylation of VII, which leads to [1,3-di(2-benzimidazolyl)-4,6-dibenzamido]benzene (X). The cyclodehydration of VIII and X was accompanied by the disappearance of the absorption maxima characteristic for amide CO and NH bonds and triazole and benzimidazole NH bonds; at the

same time the IR spectra of the cyclization products contained absorption maxima at 1380 (-N-) and 1620 cm<sup>-1</sup>, which confirm the structures of the desired heterocyclic systems -3,5,9,11-tetraphenyl[benzo[1,2-*a*; 4,5-*a*']bis(1,2,4-triazolo[4,3-c]pyrimidine)] (IX) and 2,16-diphenyl[benzo[1,2-*a*;4,5-*a*']bis(pyrimido[1,6-*a*]benzimidazole)] (XI).

## EXPERIMENTAL

<u>Starting Compounds.</u> 4,6-Dinitroisophthaloyl dichloride (I), with mp 104-105°C (mp 107°C [3]), was obtained (in 65% yield) and purified by the method in [3]. Benzamidrazone, with mp 74.5-76°C (mp 75-76°C [4]), was synthesized (in 55% yield) and purified by the method in [4].

<u>(4,6-Dinitroisophthaloyl)dibenzamidrazone (II)</u>. A 2.70-g (0.02 mole) sample of benzamidrazone was placed in a 100-ml three-necked flask equipped with a stirrer and an argon inlet tube, after which 30 ml of dry freshly distilled N,N-dimethylacetamide and 1.63 g (0.02 mole) of sodium carbonate were added. A 2.93-g (0.01 mole) sample of I was then added with stirring to the reaction mixture in a stream of argon, and the resulting dark-red solution was stirred at room temperature for 2 h. It was then poured into 200 ml of water, and the resulting orange precipitate was removed by filtration, washed with water, and recrystallized from dimethylformamide (DMF)-water (1:1) until it had mp 338-340°C. The yield of II was 3.82 g (78%).

[1,3-Bis(5-phenyl-1,2,4-triazol-3-yl)-4,6-dinitro]benzene (III). This compound was obtained by heating 4.9 g (0.01 mole) of II at 250-270°C (1 mm) for 3 h. The color of the reaction product changed from orange to light-beige. The product was recrystallized from isopropyl alcohol until it had mp 345-346°C. The yield of III was 2.86 g (63%).

[1,3-Bis(5-phenyl-1,2,4-triazol-3-yl)-4,6-diamino]benzene (IV). A 4.54-g (0.01 mole) sample of III, 300 ml of isopropyl alcohol, 0.5 cm<sup>3</sup> of Raney nickel, and 25 ml of hydrazine hydrate were placed in a 500-ml three-necked flask equipped with a stirrer and a reflux condenser, and the mixture was refluxed with stirring for 3 h. The hot solution was filtered to remove the Raney nickel, and 200 ml of isopropyl alcohol was removed from the filtrate by distillation. The concentrate was cooled, and the resulting precipitate was purified by recrystal-lization from ethanol until it had mp  $335-336^{\circ}$ C. The yield was 3.03 g (77%).

<u>4,6-Dinitroisophthalic Acid Bis(o-nitroanilide) (V).</u> A 2.93-g (0.01 mole) sample of I was added to 2.76 g (0.02 mole) of o-nitroaniline in 20 ml of N-methylpyrrolidone, and the mixture was stirred at 5-10°C for 18 h. It was then poured into 200 ml of water containing ice, and the resulting precipitate was removed by filtration and recrystallized from DMF-water (3:1). The yield of V, with mp 256-257°C, was 3.12 g (63%).

<u>4,6-Diaminoisophthalic Acid Bis (o-aminoanilide) (VI)</u>. A 4.96-g (0.01 mole) sample of V was hydrogenated over Raney nickel in 100 ml of DMF at room temperature and an initial hydrogen pressure of 150 atm. The Raney nickel was separated, and the solution was poured into water. The gray-beige product was subjected, without additional purification, to cyclization by refluxing in 4 N HCl for 24 h. The [1,3-di (2-benzimidazolyl)-4,6-diamino]benzene dihydrochloride was treated with ammonium hydroxide and dried to give 1.87 g [55% based on 4,6-dinitroisophthalic acid bis (o-nitroanilide)] of VII. Compound VII was purified by sublimation at 340-360°C ( $10^{-4}$  mm) to give a product with mp 412-413°C.

[1,3-Bis(5-phenyl-1,2,4-triazol-3-yl)-4,6-dibenzamido]benzene (VIII). A 2.81-g (0.02 mole) sample of benzoyl chloride was added at room temperature to a solution of 3.94 g (0.01 mole) of IV in 60 ml of hexamethylphosphoric triamide, and the solution was stirred for 2 h. It was then poured into water, and the resulting white powder was removed by filtration, washed with water, and recrystallized from DMF-water (1:1) until it had mp 367° (in a previously heated block). The yield of VIII was 4.42 g (73%).

 $\frac{3,5,9,11-\text{Tetraphenyl[benzo[1,2-a;4,5-a']bis(1,2,4-triazolo[4,3-c]pyrimidine)]}(IX)}{\text{asample of VIII in a condensation test tube was subjected to heat treatment at 370°C (10<sup>-3</sup> mm). Cyclization was accompanied by sublimation of the product. Resublimation gave IX, which melted at 400-402°C. The yield was 4.9 g (86%).$ 

[1,3-Di(2-benzimidazolyl)-4,6-dibenzamido] benzene (X). A 2.81-g (0.02 mole) sample of benzoyl chloride was added to a solution of 3.40 g (0.01 mole) of VII in 60 ml of hexamethylphosphoric triamide, and the resulting solution was stirred for 2 h and poured into water. The precipitated yellow powder (VIII) was removed by filtration, washed with water, and recrystallized from DMF until it had mp 365-366°C (in a previously heated block). The yield of X was quantitative.

 $\frac{2,16-\text{Diphenyl[benzo[1,2-a;4,5-a']bis(pyrimido[1,6-a]benzimidazole)]}}{\text{XI}}$  A 5.48-g (0.01 mole) sample of X was placed in a condensation test tube and heated at 300-350°C (10<sup>-4</sup> mm). Cyclization was accompanied by sublimation of the product; the sublimate was collected and resublimed to give XI with mp 436-440°C. The yield of XI was 4.60 g (90%).

The UV spectra of solutions of the synthesized compounds in 98% H<sub>2</sub>SO<sub>4</sub> were recorded with a Hitachi spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer.

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