SYNTHESIS OF SYMMETRICAL TEREPHTHALOYL DERIVATIVES OF 2-(p-AMINOPHENYL)-5-AMINOBENZIMIDAZOLES — MONOMERS FOR THE PREPARATION OF POLYAMIDES

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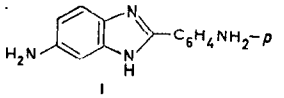
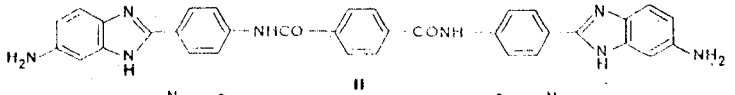
Various methods for the synthesis of symmetrical terephthaloyl derivatives of 2-(p-aminophenyl)-5-aminobenzimidazoles were studied. Acylation of the isomeric amino-nitro-2-phenylbenzimidazoles obtained in this research with subsequent reduction of the nitro groups was found to be the most preparatively convenient method.

Heterocyclic polyamides obtained by polycondensation of 2-(p-aminophenyl)-5-aminobe imidazole (I) and terephthalic acid dichloride have a valuable set of mechanical and ther physical properties [1, 2]. However, as has been previously demonstrated, because of th slight difference in the reactivities of the amino groups in diamine I, the resulting po contains both homotriads, viz., residues of symmetrical terephthalic acid amides II and and heterotriads, viz., residues of unsymmetrical amide IV, and thus has an irregular st ture [3]. At the same time the production of a completely ordered polymer is of conside interest, inasmuch as an increase in the regularity of the structure may improve the mec ical and other properties of the polymer significantly [4]. A possible method for the p tion of a completely regular polymer is polycondensation of terephthaloyl chloride with metrical terephthalic acid amide II or III. The present paper is devoted to the search the optimum method for their production from the point of view of schematic simplicity a the maximal possible purity of the final products.



I



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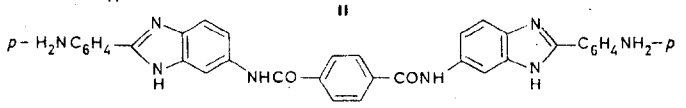

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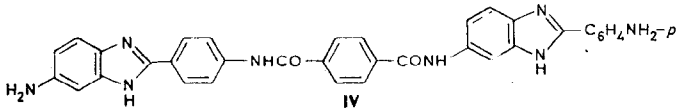

IV

To obtain diamine II (Scheme 1) we used two fundamentally different methods of synt In one of them the formation of the imidazole ring occurs in earlier stages, whereas in t other it takes place in the last step. The key compound in the preparation of monomer I the first method is 5-nitro-2-(p-aminophenyl)-benzimidazole (V), the condensation of whi with terephthalic acid dichloride and subsequent reduction led unambiguously to diamine We obtained nitro amine V by several methods, viz., by nitration of 2-(p-aminophenyl)ben imidazole (VI), by partial reduction of 2-(p-nitrophenyl)-5-nitrobenzimidazole (VII), and condensation of 4-nitro-1,2-phenylenediamine with p-aminobenzoic acid. The preparation V by nitration of amine VI was described in [5]. However, through thorough verificatior

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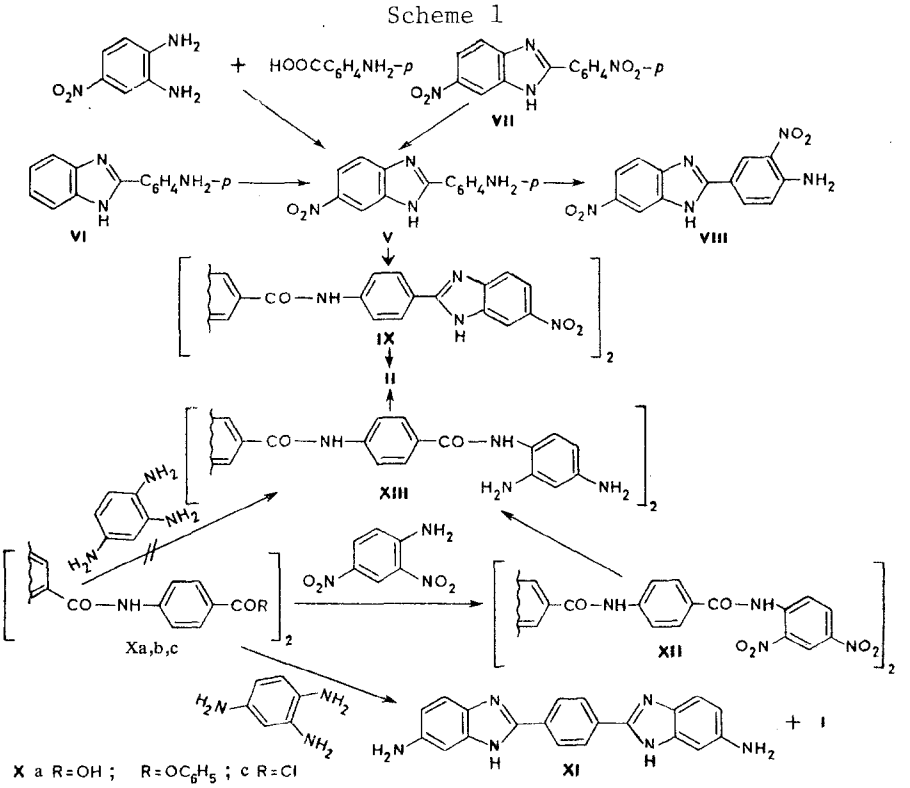
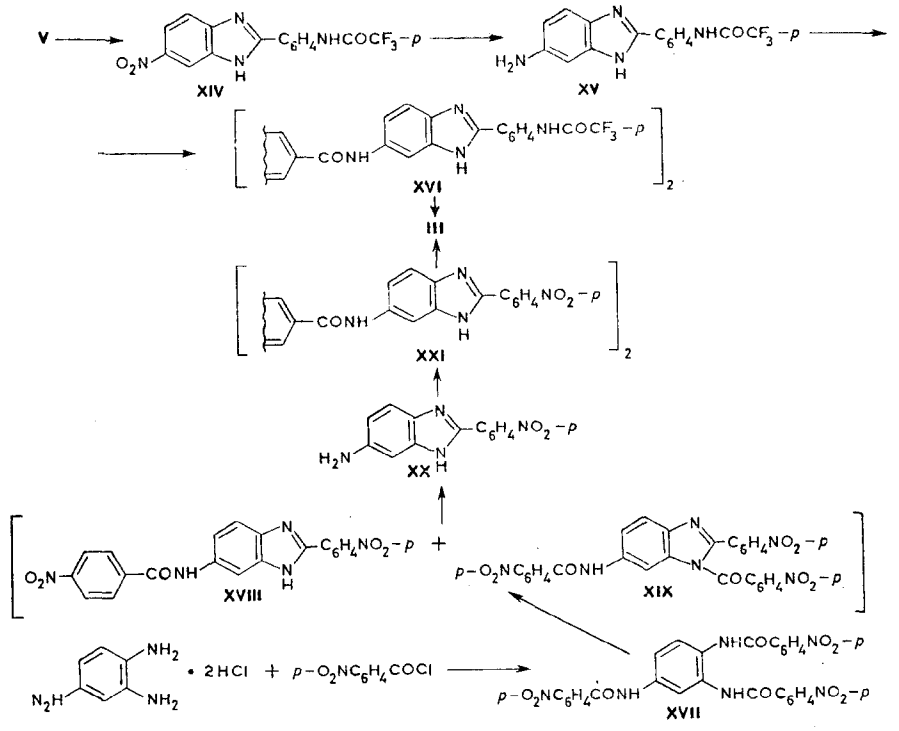
Scheme 1



found that, in addition to the principal product, 4'-amino-5,3'-dinitro-2-phenylbenzimidazole (VIII), the structure of which was confirmed by alternative synthesis, is invariably formed as an impurity (up to 6%). This is evidently associated with incomplete protonation of the amino group in the starting compound, as a result of which nitration takes place in the ortho position under the influence of its activating effect. We therefore attempted to decrease the amount of dinitro derivative VIII by increasing the acidity of the medium. Unfortunately, we found that the amount of this impurity can be reduced to only 2% by changing the nitration conditions (reaction temperature 0-25°C and sulfuric acid concentration 70-100%). Its complete elimination is achieved by repeated fractional precipitation of the nitration product from dilute HCl or in a subsequent step, viz., by reaction with terephthaloyl chloride. One can "crosslink" only the needed V by using the difference in the rates of acylation of the dinitro and mononitro derivatives (a factor of ~10) and by using insufficient acid chloride. Amide IX is readily purified to remove amine VIII by crystallization from dimethylacetamide. Partial reduction of the readily accessible 5-nitro-2-(p-nitrophenyl)benzimidazole (VII) [6] also leads to the desired amine V; in view of the greater deficiency of the electron density in the 4' position as compared with the 5 position, the reaction proceeds selectively, and amine V is obtained only slightly contaminated with isomeric XX, which is readily separated by crystallization. The third method for the preparation of amino nitro compound V, which consists in the condensation of 4-nitro-1,2-phenylenediamine with p-aminobenzoic acid in polyphosphoric acid (PPA), is somewhat inferior to the first two methods because of the formation of unidentified colored impurities that are difficult to separate.

Another method for the preparation of diamine II is reduction of the nitro group in the initial stages and the formation of an imidazole ring in the last step. Terephthalic acid N,N'-bis(p-carboxyphenyl)diamide (Xa) and its derivatives at the carboxy group were used as the starting compounds. An attempt to obtain monomer II by the direct reaction of acid Xa or its diphenyl ester Xb with 1,2,4-triaminobenzene in PPA led unexpectedly to the formation of diamines I and XI. The condensation of acid chloride Xc with 2,4-dinitroaniline led to tetranitro derivative XII, the successive reduction and cyclization of which gave diamine II in satisfactory yield. Thus diamine II can be obtained by any of the methods presented above.

Scheme 2



We studied methods for the synthesis of diamine III (Scheme 2). One of them was based on nitro amine V. In contrast to Scheme 1, we used a method with temporary protection of the amino group by conversion of V to trifluoroacetyl derivative XIV, which was reduced to monoacylated diamine XV with subsequent condensation with terephthalic acid dichloride and removal of the protective group. However, the many steps involved in this method and the considerable difficulties involved in the purification of trifluoroacetyl derivative XVI do not make it advantageous.

Another scheme for the preparation of diamine III proved to be most successful. According to the literature data, the key compound, viz., 5-amino-2-(p-nitrophenyl)benzimidazole (XX), is obtained by cyclization of 1,2,4-triaminobenzene with p-nitrobenzaldehyde in alcohol in the presence of an oxidizing agent [7]. However, the extremely low yield of the cyclization product and the formaton of difficult-to-separate impurities compelled us to reject this method. We acylated 1,2,4-triaminobenzene dihydrochloride with p-nitrobenzoyl chloride and thereby obtained XVII, all of the amino groups of which are acylated, after which we subjected it to cyclization. The reaction was carried out both with and without isolation of XVII. In the first case the synthesis was carried out in dimethylacetamide (DMA), and we obtained a mixture of benzimidazole derivatives XVIII and XIX; an increase in the refluxing time in DMA led to an increase in the fraction of XVIII, which constitutes evidence for the ease of hydrolysis of the product of acylation at the imide nitrogen atom. In order to increase the yield of cyclization products XVII was isolated and cyclized thermally in the fused state. The cyclization takes place most vigorously at temperatures above 300°C; just as in the case of the reaction in DMA, XVIII and XIX, the ratio of which depends on the temperature and reaction time, are formed. Hydrolysis of the cyclization products in H_2SO_4 leads to the formation of nitro amine XX, the melting point of which is 30°C higher than that obtained in [7]. It is readily acylated by terephthaloyl chloride to give dinitro derivative XXI, the catalytic hydrogenation of which leads to monomer III.

It should be noted that in the preparation of diamines II and III we used an amide–salt system (dimethylacetamide with 3% LiCl) as the solvent in the hydrogenation of the slightly soluble nitro compounds IX, XIII, and XXI; due to the strong complexing the solubilities of these compounds increased by a factor of approximately five as compared with their solubilities in pure DMA, which made it possible for us to carry out the reaction homogeneously with small volumes of the solvent.

As a result of low-temperature polycondensation of diamines II and III with terephthaloyl chloride we obtained linear polymers with a degree of polymerization of ~50 that form stable solutions in DMA.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in dimethylacetamide (DMA) containing 3% LiCl were recorded with a Tesla BS-487C spectrometer (80 MHz).

2-(p-Aminophenyl)-5-nitrobenzimidazole (V). A) A 62.7-g (0.3 mole) sample of 2-(p-aminophenyl)benzimidazole (VI) in 300 ml of H_2SO_4 (70-100%) was nitrated at 0°C using 13 ml of HNO_3 (sp. gr. 1.5) in 50 ml of H_2SO_4. After 1 h, the mixture was poured into 2.5 liters of 20% ammonium hydroxide, and the orange precipitate was separated, washed with water, and dried at 120°C to give 74 g (96%) of a product with mp 272-274°C. The reaction product was purified to remove dinitro compound VIII by five to seven fractional precipitations from solution in dilute HCl by the addition of ammonia. The overall yield of product with mp 283-285°C and R_f 0.46 [Silufol-254, chloroform–propanol (10:1)] and 0.35 (methyl acetate) was 31%. PMR spectrum: 8.42 (1H, d, J_{46} = 2 Hz, 4-H), 8.02 (1H, dd, J_{67} = 9 Hz, J_{46} = 2 Hz, 6-H), 7.66 (1H, d, 7-H), 8.28 (2H, d, $j_{2'3'} = J_{5'6'}$ = 8 Hz, 2'-H, 6'-H), 6.73 (2H, d, 3'-H, 5'-H), and 6.28 ppm (2H, m, 4'-NH_2). Found: C 61.4, H 3.7; N 22.1%. $C_{13}H_{10}N_4O_2$. Calculated: C 61.4, H 3.9; N 22.0%.

B) A mixture of 7.6 g (50 mmole) of 2-amino-4-nitroaniline and 6.9 g (50.5 mmole) of p-aminobenzoic acid was heated in 100 ml of 50% PPA at 120°C, and the mixture was stirred until all of the solid material dissolved, after which the solution was heated at 130°C for another 2 h. It was then poured into water, and the aqueous mixture was neutralized with ammonium hydroxide. The precipitate was treated with boiling water and purified by fractional precipitation from dilute HCl by means of ammonium hydroxide to give 8 g (63%) of yellow crystals with mp 280-284°C.

C) Water (5 ml) and 2.84 g (0.01 mole) of dinitro derivative VII (mp 357-358°C) were added to 30 g of $Na_2S \cdot 9H_2O$, and the mixture was refluxed for 5 h. It was then diluted with water, and the aqueous mixture was neutralized with acetic acid to give 1.2 g (45%) of orange-yellow V with mp 278-282°C (from DMA).

2-(4'-Amino-3'-nitrophenyl)-5-nitrobenzimidazole (VIII). A 5.2-g (20 mmole) sample of 2-(p-acetamidophenyl)benzimidazole (mp 330-332°C) was nitrated in 20 ml of H_2SO_4 (sp. gr. 1.84) at 5-10°C using 1.9 ml of HNO_3 (sp. gr. 1.5) in 5 ml of H_2SO_4. The solution was allowed to stand overnight, after which it was poured into 300 ml of water. The yellow precipitate was separated and washed with sodium acetate solution and water to give 6 g (85%) of 2-(4'-acetamido-3'-nitrophenyl)-5-nitrobenzimidazole (XXII) with mp 254-258°C (from DMA). A 3.5-g (10 mmole) sample of XXII was added to a solution of 0.6 g (11 mmole) of KOH in 50 ml of methanol, and the mixture was refluxed for 15 min. It was then cooled and filtered to give 2.9 g (97%) of dark-red crystals of amine VIII with mp >360°C (from DMA–methanol). Found: N 23.2%. $C_{13}H_9N_5O_4$. Calculated: N 23.4%.

N,N'-Bis[4'-(5-nitrobenzimidazole-2-phenyl)]terephthaloyl Diamide (IX). An 18.3-g (0.09 mole) sample of terephthaloyl chloride was added with stirring and cooling to a solution of 50.8 g (0.2 mole) of V in 250 ml of DMA containing 3% LiCl, after which the mixture was poured into ammonium hydroxide, and the brown-yellow precipitate was removed by filtration and washed with water and ethanol to give 46 g (80%) of a product with mp >360°C (from DMA containing 3% LiCl). Found: C 64.3; H 3.6; N 17.2%. $C_{34}H_{22}N_8O_6$. Calculated: C 64.0; H 3.5; N 17.6%.

Reaction of N,N'-Terephthaloylbis(p-aminobenzoic Acid) (Xa) and Its Diphenyl Ester (Xb) with 1,2,4-Triaminobenzene. A 7.8-g (40 mmole) sample of 1,2,4-triaminobenzene dihydrochloride and 11.1 g (20 mmole) of Xb were heated with stirring in 110 ml of 50% PPA in a nitrogen atmosphere at 180°C for 2 h, after which the dark-green mass was poured into water, and the resulting precipitate was separated and suspended in water. The suspension was made alkaline to pH 8 with sodium carbonate, and the precipitate was removed by filtration and washed with water. Fractional precipitation from dilute HCl gave 5.2 g of p-phenylene-2,2-bis(5-aminobenzimidazole) (XI), the structure of which was proved by comparison of the IR and PMR spectra with the spectra of the genuine compound [6]. Workup of the acidic mother liquor gave 3.6 g of a reaction product that was identical (with respect to the IR and PMR spectra) to 2-(p-aminophenyl)-5-aminobenzimidazole (I) [6] and did not depress its melting point. The same substances were formed when dicarboxylic acid Xa was used (the reaction temperature was 230-250°C in this case).

N,N'-Terephthaloylbis(p-aminobenzoyl Chloride) (Xc). A mixture of 100 ml of $SOCl_2$, 40.4 g (0.1 mole) of Xa, and 2 ml of DMA was refluxed for 8 h, after which it was cooled and treated with 100 ml of chloroform. The crystalline precipitate was separated, washed with $SOCl_2$, and dried in vacuo at 100°C to give 22 g (50%) of a white powder with mp >360°C. Found: Cl 16.3%. $C_{22}H_{14}Cl_2N_2O_4$. Calculated: Cl 16.1%.

N,N'-Bis[4-(2,4-dinitrophenylamino)phenyl]terephthaloyl Diamide (XII). A 22-g (50-mmole) sample of Xc was added with stirring to 19 g (104 mmole) of 2,4-dinitroaniline in 40 ml of DMA, and the mixture was heated to 150°C. After 1 h, it was cooled and treated with 100 ml of ethanol. The yellow precipitate was separated and crystallized from DMA–ethanol (1:3) to give 28 g (76%) of a product with mp 325-330°C and R_f 0.52 [Silufol-254, chloroform–propanol (15:1)]. Found: N 15.1%. $C_{34}H_{22}N_8O_{12}$. Calculated: N 15.3%.

N,N'-Bis[4-(5-aminobenzimidazol-2-yl)phenyl]terephthaloyl Diamide (II). A) A 5-g (6.8 mmole) sample of tetranitro derivative XII was dissolved in a mixture of 100 ml of DMA containing 3% LiCl and 5 ml of ethanol, 2 g of Pd/C (1.7%) was added, and hydrogenation was carried out at atmospheric pressure. The light-green solution was filtered to remove the catalyst, part of the solvent was removed by distillation until the vapor temperature rose to 166.5°C, and dry HCl, obtained from 5 ml of hydrochloric acid, was passed through the mixture. The solution was refluxed for 5 h with slow removal of the DMA by distillation. The mixture was cooled, 8 ml of triethylamine was added, and the mixture was filtered and mixed with 300 ml of ethanol. The precipitate was separated and washed with ethanol to give 2.9 g (69%) of greenish-yellow crystals with mp >400°C. PMR spectrum: 7.10 (2H, d, J_{46} = 2 Hz, 4-H), 6.90 (2H, dd, J_{67} = 8.5 Hz, 6-H), 7.38 (2H, d, 7-H), 8.56 (8H, m, 2'-, 3'-, 5'-, and 6'-H), 8.52 (4H, s, 2"-, 3"-, 5"-, and 6"-H), and 11.80 ppm (2H, s, NHCO). Found: C 70.8; H 4.5; N 19.3%. $C_{34}H_{26}N_8O_2$. Calculated: C 70.6; H 4.5; N 19.4%.

B) A 25.6-g (40 mmole) sample of dinitro derivative IX was dissolved in 250 ml of DMA containing 10 ml of ethanol and 3% LiCl, and hydrogenation was carried out at atmospheric pressure in the presence of 8 g of Pd/C (1.7%). The solution was filtered to remove the catalyst, 1.5 liters of ethanol was added to the filtrate, and the mixture was allowed to stand for 1 h. The precipitate was separated and washed with ethanol to give 17.6 g (75%) of diamine II with mp >400°C.

5-Nitro-4'-trifluoroacetamido-2-phenylbenzimidazole (XIV). A 25.4-g (0.1 mole) sample of amino nitro compound V was dissolved in 100 ml of distilled DMA, the solution was cooled to 0-5°C, and 14.5 ml (0.103 mole) of trifluoroacetic anhydride was added dropwise. The mixture was allowed to stand for 30 min, after which it was poured into a solution of 15 g of $NaHCO_3$ in 400 ml of water. The precipitate was separated, treated with water, and air dried. The acylation product was washed with chloroform and crystallized from methanol–chloroform (1:3) to give 22.5 g (65%) of a product with mp 215-218°C. PMR spectrum: 8.43 (1H, s, 4H), 8.04 (1H, d, J_{67} = 9 Hz, 6-H), 7.71 (1H, d, 7-H), 8.52 (2H, d, $J_{2',3'}$ = 8 Hz, 2'- and 6'-H), 8.30 (2H, d, 3'- and 5'-H), and 13.30 ppm (1H, s, NHCO). Found: N 16.1%. $C_{15}H_9F_3N_4O_3$. Calculated: N 16.0%.

N,N'-Bis[2-(4-trifluoroacetamidophenyl)benzimidazol-5-yl]terephthaloyl Diamide (XVI). A 7.0-g (20.3 mmole) sample of nitro compound XIV was hydrogenated in a mixture of 40 ml of DMA with 3% LiCl and 10 ml of ethanol under atmospheric pressure in the presence of 2 g of Pd/C, during which 1.4 liters of hydrogen was consumed. The light-green solution was filtered, the solvent was removed by distillation until the vapor temperature rose to 166.5°C, and the residue was cooled to 0°C and treated with stirring with 2.03 g (10 mmole) of terephthaloyl chloride. The resulting precipitate was separated, washed with DMA and alcohol, and treated with 50 ml of DMA containing 5 ml of triethylamine, and the mixture was stirred for 30 min. The solution was filtered, 200 ml of ether was added, and the precipitate was separated, washed with ethanol, and air dried to give 14 g (85%) of amine XVI with mp >350°C. Found: N 14.5%. $C_{38}H_{24}F_6N_8O_4$. Calculated: N 14.5%.

1,2,4-Tris(p-nitrobenzamido)benzene (XVII). A 5.85-g (30 mmole) sample of p-nitrobenzoyl chloride was added with cooling to a solution of 1.96 g (10 mmole) of 1,2,4-triaminobenzene hydrochloride in 30 ml of distilled DMA containing 2.8 ml of triethylamine, and the mixture was stirred for 1 h. It was then poured into 200 ml of water, as a result of which a yellow precipitate of amide XVII, with mp 337-340°C [from DMA–alcohol (1:1)], separated. Found: N 14.7%. $C_{27}H_{18}N_6O_9$. Calculated: N 14.7%.

5-(p-Nitrobenzamido)-2-(p-nitrophenyl)benzimidazole (XVIII). A) A 57-g (0.1 mole) sample of triamide XVII was melted with stirring in a stream of nitrogen, and the melt was maintained at 300-330°C for 10 min. The cooled friable mass was then ground into a powder to give 36 g (90%) of amide XVIII with mp 302-303°C. Found: N 17.4%. $C_{20}H_{13}N_5O_5$. Calculated: N 17.4%. Treatment of the mother liquor with water gave 1.1 g (2%) of a yellow precipitate of 1,5-bis(p-nitrobenzamido)-2-(p-nitrophenyl)benzimidazole (XIX) with mp 252-256°C (from methanol). Found: N 15.1%. $C_{27}H_{16}N_6O_8$. Calculated: N 15.2%.

B) A 55.8-g (0.3 mole) sample of p-nitrobenzoyl chloride was added with stirring to a solution of 19.6 g (0.1 mole) of 1,2,4-triaminobenzene dihydrochloride in 300 ml of DMA, and the mixture was refluxed for 15 h. It was then filtered and poured into 1 liter of hot water, and the precipitate was separated and dried to give a mixture of XVIII and XIX. According to the PMR spectrum, the mixture contained 15% diamide XIX; after refluxing for 30 h, the mixture contained 6% diamide XIX. The mixture was crystallized from DMA to give 20.1 g (30%) of amide XVIII with mp 301-303°C.

2-(p-Nitrophenyl)-5-aminobenzimidazole (XX). A 210-g sample of a mixture of XVIII and XIX was refluxed for 12 h in 3 liters of 55% H_2SO_4, after which it was made alkaline to pH 8 with ammonium hydroxide. The red-brown precipitate was separated, washed with water, and purified by fractional precipitation from dilute HCl to give 85 g of red crystals that were converted at 100°C to violet crystals with mp 300-305°C. PMR spectrum: 7.29 (1H, d, J_{46} = 1.5 Hz, 4-H), 7.04 (1H, dd, J_{67} = 8.8 Hz, 6-H), 7.40 (1H, d, 7-H), 8.85 (2H, d, $J_{2'3'}$ = 8.8 Hz, 2'- and 6'-H), and 8.22 ppm (2H, d, 3'- and 5'-H). Found: N 22.2%. $C_{13}H_{10}N_4O_2$. Calculated: N 22.0%.

N,N'-Bis[2-(4-nitrophenyl)benzimidazol-5-yl]terephthaloyl Diamide (XXI). A 32.5-g (0.16 mole) sample of terephthaloyl chloride was added with stirring in the course of 1 h to a cooled solution of 89 g (0.35 mole) of amino nitro compound XX in 1.4 liters of DMA. After 2 h, 30 ml of ammonia and 1.5 liters of ethanol were added, and the orange precipitate was separated and dried to give 88 g of a substance. An additional 14 g of a brown precipitate was precipitated from the mother liquor by means of water. Recrystallization from DMA gave 82.5 g (75%) of amide XXI with mp 407-410°C. The orange substance was converted to a yellow substance at 180-200°C. PMR spectrum: 8.62 (1H, s, 4-H), 8.14 (1H, d, J_{67} = 9 Hz, 6-H), 7.55 (1H, d, 7-H), 8.96 (2H, d, $J_{2'3'}$ = 8 Hz, 2'- and 6'-H), 8.25 (2H, d, 3'- and 5'-H), and 8.54 ppm (4H, s, 2"-, 3"-, and 6"-H). Found: C 64.2; H 3.5; N 17.3%. $C_{34}H_{22}N_8O_6$. Calculated: C 64.0; H 3.5; N 17.6%.

N,N'-Bis[2-(4-aminophenyl)benzimidazol-5-yl]terephthaloyl Diamide (III). A) A solution of 0.25 g (4.5 mmole) of potassium hydroxide in 3 ml of methanol was added to a solution of 1.6 g (2 mmole) of amide XVI in 25 ml of distilled DMA, and the mixture was stirred at room temperature for 1 h. It was then filtered and mixed with 50 ml of ether, and the precipitate was separated, washed with ethanol, and dried to give 0.75 g (60%) of oligomer III with mp 370-375°C (from DMA). PMR spectrum: 8.54 (2H, d, J_{46} = 2 Hz, 4-H), 8.02 (2H, dd, J_{67} = 8.5 Hz, 6-H), 7.55 (2H, d, 7-H), 8.31 (4H, d, J = 8 Hz, 2'- and 6'-H), 7.02 (4H, d, 3'- and 5'-H), 8.60 (4H, s, 2"-, 3"-, 5"-, and 6"-H), 10.92 (2H, s, CONH), and 5.92 ppm (4H, m, NH_2). Found: C 70.9; H 4.7; N 19.6%. $C_{34}H_{26}N_8O_2$. Calculated: C 70.6; H 4.5; N 19.4%.

B) The reduction of dinitro compound XXI was carried out in the same way as method B for the preparation of amide II. The yield of diamine III, with mp 372-375°C, was 72%.

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SYNTHESIS OF 2- AND 6-ARYLAMINOPYRIMIDINEDIONES

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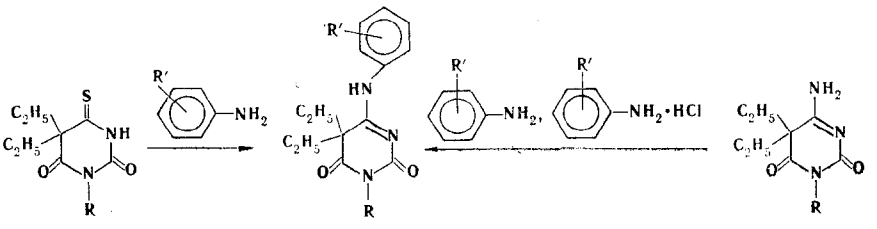
Methods for the synthesis of 6-arylamino-5,5-diethyl-3H,5H-pyrimidine-2,4-diones from the corresponding 6-thioxo and 6-amino derivatives were developed. The isomeric 2-arylamino-5,5-diethyl-1H,5H-pyrimidine-4,6-diones were obtained by the reaction of 2-mercapto- and 2-methylthio-1H,5H-pyrimidine-4,6-diones with substituted anilines. The ionization constants of the compounds obtained were determined.

In contrast to the substituted (at the amino group) 5,5-dialkyl-2-amino-1H,5H-pyrimidine-4,6-diones, for the preparation of which several rather general methods are known [1-4], little study has been devoted to the synthesis of the isomeric 6-amino derivatives. Only the preparation of 3-methyl-6-methylamino-5,5-diethyl-3H,5H-pyrimidine-2,4-dione by methylation of the corresponding 6-amino derivative has been described [5]. However, this method cannot be regarded as convenient from a preparative point of view, since methylation proceeds ambiguously to give a mixture of isomeric 6-imino-1,3-dimethyl-1H,3H,5H- and 3-methyl-6-methylamino-1H,5H-pyrimidine-2,4-diones [6]. The aim of the present research was to develop methods for the synthesis of 6-arylamino derivatives of 3H,5H-pyrimidine-2,4-dione (III). For this, we investigated the reaction of 6-thioxo-5,5-diethyl-1H,3H,5H-pyrimidine-2,4-diones (I) with aromatic amines. We found that heating thioxo derivatives I with excess aromatic amine at 160-180°C for 6-20 h without a solvent leads to 6-arylamino-1H,3H-pyrimidine-2,4-diones (III) in good yields (Table 1).

Thioxo derivatives I are relatively difficult to obtain. We therefore attempted to obtain III by transamination under the conditions described for 2-amino derivatives of 5,5-dialkyl-1H,5H-pyrimidine-4,6-diones [7]. We established that heating equimolar amounts of the arylamine, the arylamine hydrochloride, and II at 170-180°C leads to the corresponding 6-arylamino-substituted derivatives III. However, the yields and reaction times depend substantially on the presence of a substituent attached to the N_3 atom. Thus in the case of IIb the reaction with various arylamines under the selected conditions takes place in 1-2 h, and the yields amount to 80-90%. However, in the absence of a substituent (IIa) the reaction time increases considerably, and the yields are reduced to 30%.



I, IIa, R=H; b R=CH_3; IIIa-e, R=H; a R′=H; b R′=*p*-Cl; c R′=*p*-CH_3; d R′=*m*-CH_3; e R′=*p*-CH_3O; IIIf-h R=CH_3; f R′=H; g R′=*m*-Cl; h R′=*p*-Cl

Compounds III are white, high-melting, crystalline substances. Absorption bands corresponding to the vibrations of NH and C=O groups at 3200 and 1700 cm^{-1} are present in their IR spectra. The PMR spectra contain signals of protons of aryl and alkyl substituents. The mass

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