Articles

Poly(1,8-naphthyridines) and 1,9,10-Anthyridines: Model Systems for "Black Orlon"

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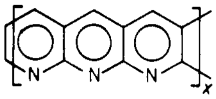
ABSTRACT: Condensation reactions of 4-aminopyrimidine-5-carboxaldehyde with aromatic diketones result in the formation of a large number of new bis(*o*-aminoaldehydes) via hydrolysis of the intermediate pyrido[2,3-*d*]pyrimidines. This facile functionalization of a pyridine moiety permits the construction of multiple 1,8-naphthyridine rings, the building unit of "black Orlon". Attempted polymerizations of these tetrafunctional monomers gave low molecular weight poly(1,8-naphthyridines) as a result of the very poor solubility of these systems in base-compatible solvents. Condensations in poly(phosphoric acid) were not successful. Phenylated poly(1,8-naphthyridines) exhibit similar solubility properties. The high reactivity of the 1,9,10-anthyridine system and its implication for the structure of "black Orlon" are also discussed.

The high thermal stability of pyrolyzed poly(acrylonitrile) has been attributed to a ladder structure composed



of condensed pyridine rings fused through their 2,3 bonds.[1] Extensive studies on the color formation in poly(acrylonitrile) treated at lower temperatures generally support this structural assignment.[2] However, even under these conditions it was found that a substantial amount of oxygen is incorporated in the final product. Thus, a random copolymer of nitrone and imine groups was proposed to accommodate the combustion data. Nevertheless, the proposed building principle constitutes an attractive structural design for incorporation into aromatic polymers. The presence of such an extended chain of linearly fused aromatic pyridine rings seemed highly unlikely since it is well-known from the analogous "acene" series of hydrocarbons that increasing linear annelation leads to aromatic systems that become progressively less stable with respect to their oxidized and reduced derivatives.[3] We decided therefore to limit our investigation to the synthesis of systems composed of two and three linearly fused pyridine rings and their incorporation into linear aromatic polymers.

We first focused our attention on the system composed of three pyridine rings joined through their 2,3 bonds, because we felt that the reactivity of an extended array of such units would first manifest itself clearly in a tricyclic unit, in analogy with the anthracene "acene" reactivity sequence. At the onset of this work, very few compounds possessing the 1,9,10-anthyridine skeleton were known, and they generally contained undesirable oxo or amino functionalities. Furthermore, synthetic pathways employed for their formation are totally unsuitable for polymerization reactions. The successful application of the Friedländer condensation of carbocyclic *o*-aminoaldehydes and ketones to polymer synthesis[4] prompted us to approach the 1,9,10-anthyridine ring system via a similar reaction sequence. This synthetic strategy required 2,6-diaminopyridine-3,5-dicarboxaldehyde (**1**). This monomer was obtained by catalytic reduction of 2,6-diamino-3,5-dicyanopyridine. Its detailed preparation and transformation into 1,9,10-anthyridines is described elsewhere.[5] Of particular interest is our finding that base-catalyzed condensations of **1** with aromatic ketones such as acetophenone, 2-acetylpyridine, and deoxybenzoin result in the formation of a dihydro derivative rather than the expected fully aromatic ring system. This unusual behavior in a Friedländer condensation was attributed to hydride transfer on the anthyridine moiety initially formed in the reaction mixture. It was possible to reoxidize the dihydro derivatives to the fully aromatic 1,9,10-anthyridines in good yield. These are readily further oxidized to the corresponding 5(10*H*)-1,9,10-anthyridones. These interconversions are illustrated in Scheme I for the reaction of **1** with acetophenone. It was also noted that the dihydro compound **2**, a white crystalline compound, rapidly turned bright yellow upon standing. Mass spectral investigations indicated its conversion into the anthyridone **4**. The high reactivity of the 1,9,10-anthyridine moiety is illustrated by the fast, quantitative conversion of **3** into **2** upon treatment with dilute base. The analogous anthrazoline unit on the other hand is stable under these conditions.[4] Replacement of the central benzene ring in the latter by a pyridine ring greatly enhances the reactivity of these comparable tricyclic systems. We believe that the accumulation of strong electron-withdrawing groups in the anthyridine moiety is responsible for the increased reactivity in oxidative as well as reducing environments. It follows then that the relative instability of the fully aromatic unit with respect to the oxidized or reduced forms will be further enhanced when new pyridine rings are linearly annelated to a 1,9,10-anthyridine unit. The facile oxidation of **2** and **3** with formation of **4** indicates that oxygen incorporation during pyrolysis of poly(acrylonitrile) would lead to anthyridone moieties rather than nitrone groups. Formation of the former would interrupt large assemblies of aromatic sextets, a critical factor in the reactivity of fused hydrocarbons,[3] whereas in the latter,

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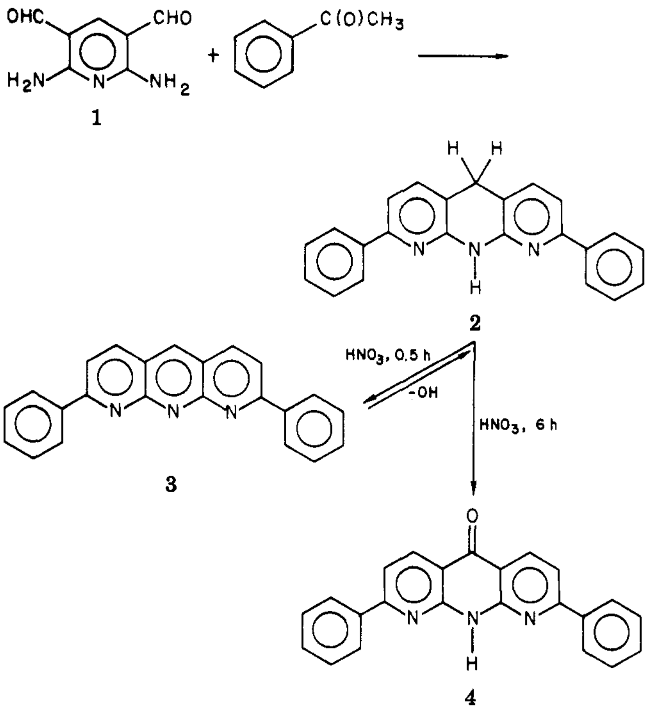
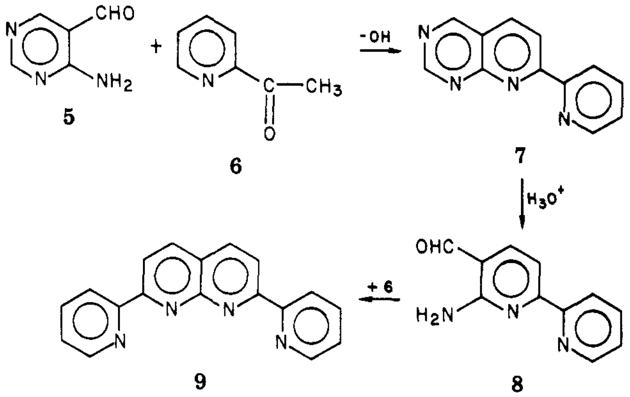
Scheme I

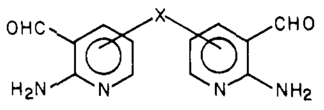


Scheme II



dilution of the sextet would remain unaffected. It is interesting to note that vacuum pyrolysis of poly(acrylonitrile) is reported to lead to a material structurally analogous to our reduced product **2**.[6] The complex reaction pattern during base-catalyzed condensation reactions of **1** made polymerization reactions with this monomer unattractive. Condensation reactions of **1** conducted in poly(phosphoric acid) were not successful.

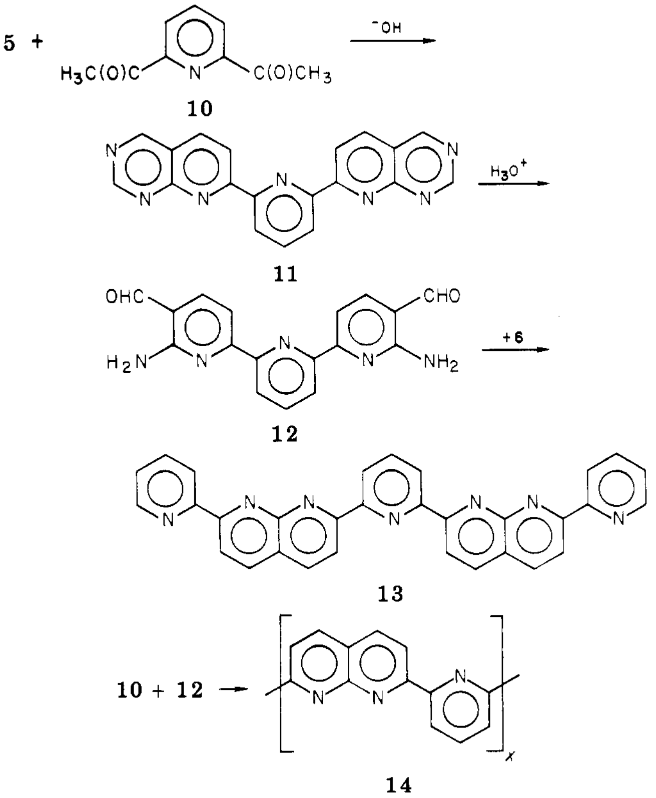
We next turned our attention to the lower homologous 1,8-naphthyridine unit. Synthetic approaches to this heterocyclic system, although more numerous than those for 1,9,10-anthyridines, are generally unsuitable for application to polymer synthesis. Once again we envisioned the Friedländer condensation as the propagation reaction for the synthesis of poly(1,8-naphthyridines). This approach required bis(*o*-aminoaldehydes) of the following general structure, where X is an interconnecting fully aromatic linkage:



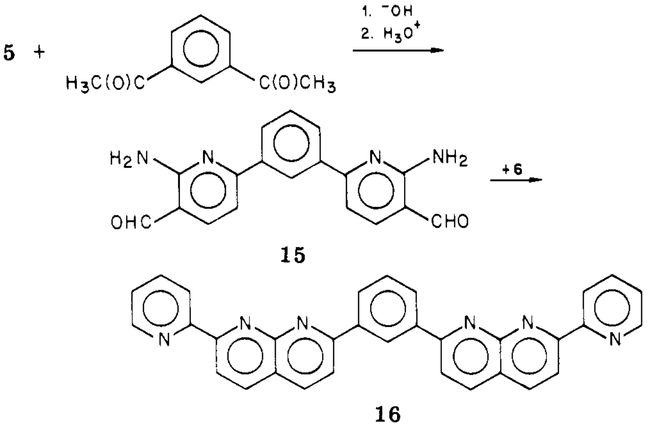
Bis(*o*-aminoaldehydes) of this type are unknown. Although such systems may be developed relatively easily in the carbocyclic series via electrophilic aromatic substitution reactions, this strategy is not possible for *N*-heterocyclic compounds. Classical elaboration of *o*-aminoaldehydes in the pyridine series generally involves reduction of *o*-aminocarboxylic acid derivatives. However, lack of suitable precursors prevented this approach to the desired monomers. An intriguing synthetic possibility seemed at hand in covalent hydration of *N*-heterocyclic compounds, especially those composed of fused pyrimidine rings.[7] This phenomenon was studied extensively in the pteridine system, where it was found that acid degradation resulted in irreversible ring opening of the pyrimidine moiety with formation of 2-aminopyrazine-3-carboxaldehyde.[8] It seemed reasonable to assume that acid hydrolysis of substituted pyrido[2,3-*d*]pyrimidines would yield the desired *o*-aminoaldehyde functionality incorporated in substituted pyridines. The general synthetic sequence developed in this laboratory has been described elsewhere[9] and is illustrated here by the quantitative formation of the interesting model compound 2,7-di(2-pyridyl)-1,8-naphthyridine (**9**) (Scheme II). We start with the readily accessible 4-aminopyrimidine-5-carboxaldehyde **5**.[10] Its base-catalyzed condensation with 2-acetylpyridine gave 7-(2-pyridyl)pyrido[2,3-*d*]pyrimidine (**7**), which was readily transformed by dilute acid into 2-amino-6-(2-pyridyl)pyridine-3-carboxaldehyde (**8**). Recondensation of the latter with 2-acetylpyridine gave **9**. All steps in this sequence take place in quantitative yield. The key element in this synthetic scheme is the conversion of **5** into **8**. The pyrimidine moiety of **5** is transformed in a pyridine unit (**8**) with the *o*-aminoaldehyde functionality preserved in the same relative position. Furthermore, this interconversion of heterocyclic rings is accompanied by the introduction of a substituent derived directly from the starting ketone. One can also consider the conversion **6** → **8**. From this point of view, it is seen that the ketone moiety of **6** is transformed into a 2-aminopyridine-3-carboxaldehyde fragment linked through the 6 position to the ketonic residue. The ready availability and wide choice of ketones, the very high yield, and the ease of operation make this sequence especially attractive for the synthesis of the desired monomers. It should be emphasized that the two individual steps (base-catalyzed **5** → **7** and acid-catalyzed **7** → **8**) remain separate so that premature condensation of **8** with the starting ketone is not possible. This feature is especially important when a different ketone is employed in the second Friedländer condensation. This option can lead to the synthesis of tailor-made polymers.

Extension of this synthetic sequence to aromatic diketones provides access to the desired bis(*o*-aminoaldehydes), wherein the interconnecting unit X is determined by the building unit of the diketone. Thus, condensation of **5** with 2,6-diacetylpyridine (**10**) followed by acid hydrolysis of the pyrido[2,3-*d*]pyrimidine moieties gave 6,6″-diamino-2,2′:6,2″-terpyridine-5,5″-dicarboxaldehyde (**12**), wherein the central pyridine ring is derived from the starting ketone (Scheme III). This simple condensation–hydrolysis sequence provides a facile entry into tetrafunctional terpyridines. Base-catalyzed condensation of **12** with 2-acetylpyridine gave the model compound **13** in quantitative yield. It should be noted that the formation of **13** is not accompanied by the side reactions encountered in the Friedländer condensation leading to the 1,9,10-anthyridine system. The 1,8-naphthyridine unit is stable under the basic reaction conditions employed for its synthesis. This confirms the analogy between linearly annelated pyriding rings and the acene series of hydrocarbons. Inspection of **13** reveals that it is constructed exclusively with pyridine rings, as is

Scheme III



Scheme IV

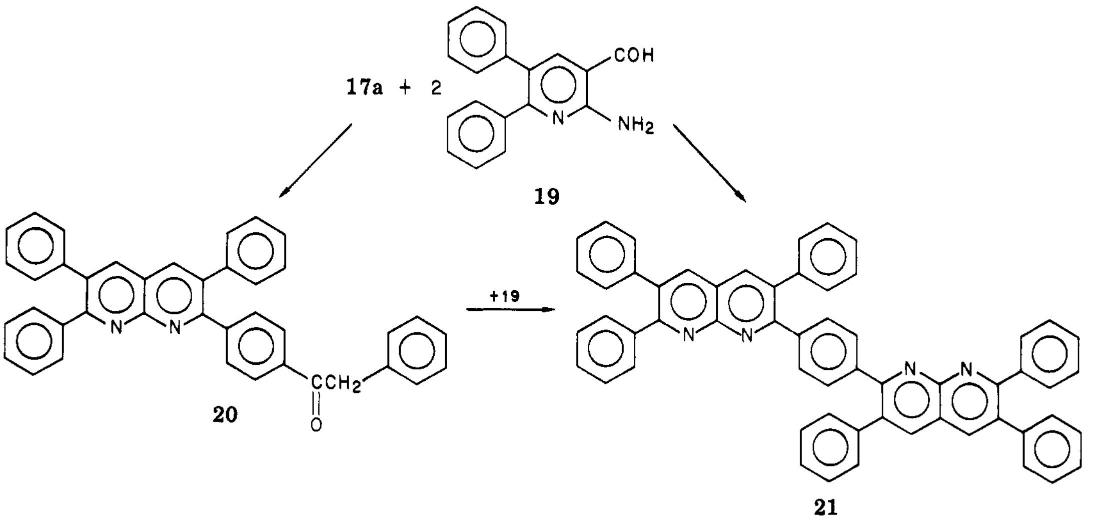


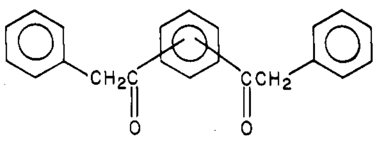
pyrolyzed poly(acrylonitrile), and it may be regarded therefore as a single-strand model for the ladder structure of the pyrolytic material. We were particularly interested therefore in polycondensation reactions of bis(*o*-aminoaldehyde) **12** and 2,6-diacetylpyridine. These polymerization reactions were carried out in a variety of base-compatible solvent systems (*N*,*N*-dimethylformamide, dimethyl sulfoxide, hexamethylphosphoramide in the presence of lithium chloride). However, the polymer precipitated out early in the reaction, and this prevented attainment of high molecular weight as evidenced by residual carbonyl absorption in the infrared spectrum of the reaction product. Extensive solubility tests on its model compound **13** revealed the poor solubility of this type of compound. It may be recrystallized from boiling *N*,*N*-dimethylacetamide, but it is insoluble in pyridine, chloroform, dimethyl sulfoxide, xylene, etc. As expected, **13** is soluble in trifluoroacetic acid. Attempts to conduct the condensation of **12** and acetylpyridine in polyphosphoric acid were not very successful, resulting in a poor yield of impure material. It was found that **12** and similar *o*-aminoaldehydes in the pyridine series are not very stable in concentrated solutions in acid medium. In fact, the synthesis of **12** by acid hydrolysis of **11** is best conducted in dilute solutions.

It was felt that interruption of this extended sequence of pyridine units could lead to more soluble systems. To this end we selected to replace the central pyridine ring in **13** with the sterically analogous *m*-phenylene unit as the interconnecting linkage. Condensation of **5** with *m*-diacetylbenzene followed by hydrolysis of the pyrido[2,3-*d*]pyrimidine moieties gave 6,6′-*m*-phenylenebis(2-aminonicotinaldehyde) (**15**) in nearly quantitative yield. Condensation of this bis(*o*-aminoaldehyde) with 2-acetylpyridine gave the *m*-phenylene analogue of **13** 2,2′-*m*-phenylenebis[7-(2-pyridyl)-1,8-naphthyridine] (**16**) (Scheme IV). It is noteworthy that replacement of the central pyridine ring in **13** by a similarly connected *m*-phenylene unit (**16**) leads to a decrease in melting point of nearly 130 °C. It was found that the solubility of **16** in base-compatible solvents, although higher than that of **13**, was too low to warrant the formation of high molecular weight polymer from the condensation of **15** and 2,6-diacetylpyridine. Similar results were obtained when other bis acetyl compounds were used as starting ketones in our condensation–hydrolysis sequence. This solubility-imposed limit to high molecular weight poly(1,8-naphthyridines) prompted us to investigate the synthesis and solubility characteristics of polyphenylated derivatives. The effect of such side phenyl groups on the properties of fully aromatic polymers such as polyphenylenes and polyquinoxalines is well documented.[11]

Our synthetic sequence permits the introduction of up to four phenyl groups per 1,8-naphthyridine unit, as illustrated by the formation of 2,3,6,7-tetraphenyl-1,8-naphthyridine from deoxybenzoin and 5,6-diphenyl-2-aminopyridine-3-carboxaldehyde (**19**).[5] Two deoxybenzoin moieties may be assembled in two distinct ways leading to the isomeric diketones **17** and **18**, wherein the central aromatic ring is either a meta or para phenylene unit. Base-catalyzed condensation of **17a** and **19** in a 1:2 molar ratio in ethanol gave a precipitate (90%) which was identified as the monocondensation product **20** (Scheme V). Unreacted **19** was quantitatively recovered from the reaction mixture. Spectroscopic data and analysis confirm this structural assignment. The very poor solubility of **20** in the condensation medium clearly prevented its further reaction with **19**. If the condensation is conducted in a 1:1 mixture of ethanol and benzene, the bis condensation product **21** is the sole product, isolated in quantitative yield. Recrystallization from benzene gave a white product, mp 365 °C, soluble in chloroform (3%) and benzene (1%) and fairly soluble in pyridine. Recondensation of **19** and **20** in ethanol–benzene gave **21**, confirming the structure of **20** as a monocondensed product. The same product could be obtained by an alternative sequence starting from **5** and **17a** (Scheme VI). The availability of ketone **20** gave us the opportunity to further extend the naphthyridine chain in **21**. Condensation of **20** and **5** in ethanol/benzene gave *o*-aminoaldehyde **23** after hydrolysis of the pyrido[2,3-*d*]pyrimidine moiety (Scheme VII). Condensations of **17a** and excess **23** were carried out in an attempt to synthesize the extended model compound **24** (Scheme VIII). Infrared monitoring of the progress of this condensation indicated an initially fast reaction with formation of a monocondensed product of very limited solubility. Further reaction with **23** proceeded very slowly and incompletely. After prolonged reaction times, the final product was a mixture of **24** and the monocondensation product which could not be separated. It is clear that

Scheme V





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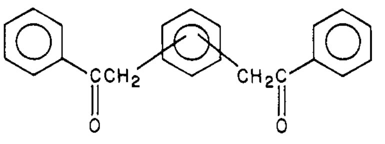

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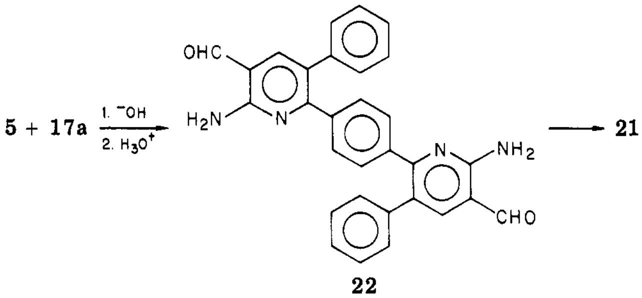
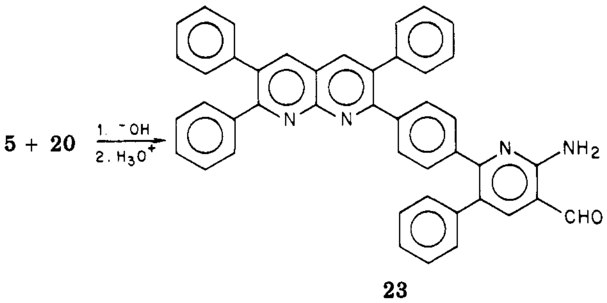
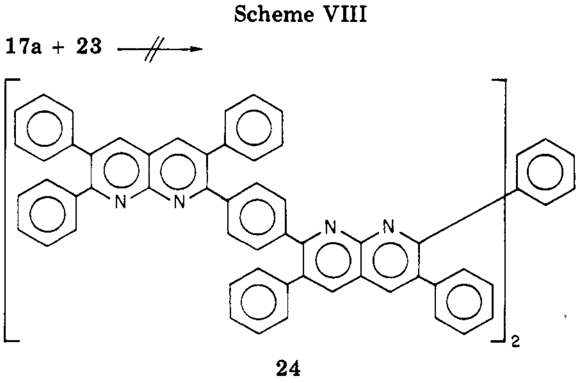
Scheme VI



Scheme VII



Scheme VIII

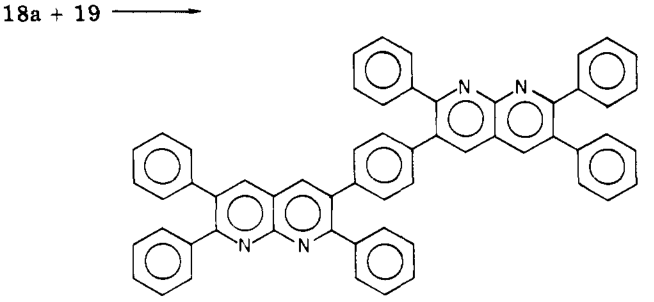


introduction of phenyl groups in a 1,8-naphthyridine backbone is not a sufficient condition to lead to soluble polymeric materials.

It was of interest also to examine the effect of the position of the interconnecting phenylene unit on the overall physical properties of phenylated 1,8-naphthyridines. Where ketones **17** lead to 1,8-naphthyridine units linked through their 2 positions to the phenylene moiety, employment of the isomeric ketones **18** on the other hand establishes the connecting unit at the 3 position of the heterocyclic system. This is illustrated by the formation of **25** (80%) from **18a** and excess **19** (Scheme IX). It was found that the melting point of **25** is twenty degrees higher than that of the isomeric **21** and is characterized by an even lower solubility in common organic solvents (insoluble in boiling benzene, monochlorobenzene, pyridine, and alcohols; fairly soluble in boiling *o*-dichlorobenzene, hexamethylphosphoramide, and *N*,*N*-dimethylacetamide). It was also noted that Friedländer condensations with **18a** were less satisfactory than reactions with **17a**. These findings make **18a** an undesirable monomer for use in Friedländer polycondensations with N-heterocyclic *o*-aminoaldehydes.

Condensations of **19** and *m*-phenylene-linked **18b** gave **26** in approximately 60% yield (Scheme X). This bis condensation product is very soluble in common solvents and constitutes therefore a very attractive repeating unit for poly(1,8-naphthyridines). However, the moderate yield of the above Friedländer reaction prevented its direct application to the synthesis of high molecular weight polymers. We envisioned incorporation of such units into tailor-made polymers via the use of two different diketones in our synthetic scheme. This required bis(*o*-aminoaldehyde) **28**, which then would be condensed with a large variety of more reactive diketones. This monomer not only ensures the presence of **26** in the polymeric backbone but can also lead to alternating 1,8-naphthyridine units linked through their 2 and 3 positions. Condensations of **5** and **18b** proved to be unexpectedly troublesome (Scheme XI). A very low, unreproducible yield of impure **27** was generally obtained, and the reaction failed completely several times for no apparent reason. Extensive variations in reaction conditions (solvent, temperature, base, and its

Scheme IX



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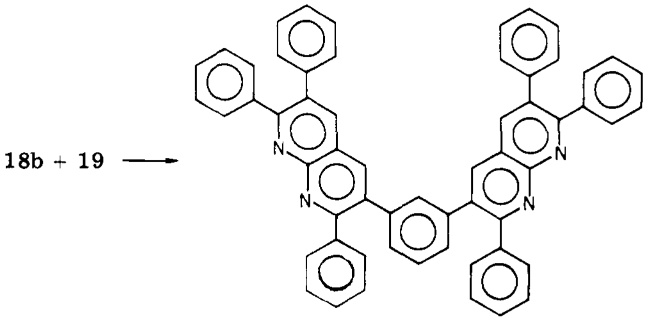
Scheme X



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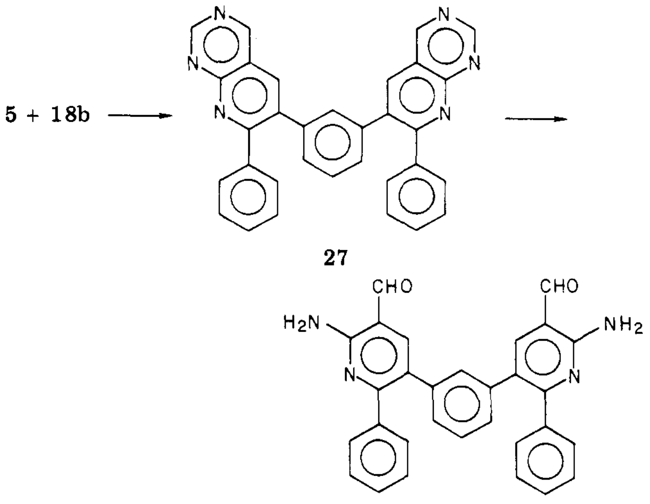
Scheme XI



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concentration) did not lead to a significant improvement.

Experimental Section

General. All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU6E instrument. Analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Instranal Laboratory, Inc., Rensselaer, N.Y.

2,7-Di(2-pyridyl)-1,8-naphthyridine (9). To a refluxing solution of 1.62 g (8.1 mmol) of 2-amino-6-(2-pyridyl)pyridine-3-carboxaldehyde[9] (8) and 1.09 g (9 mmol) of 2-acetylpyridine in 25 mL of ethanol was added 5 drops of a 20% KOH solution in methanol. Reflux was continued for 24 h to yield 2.1 g of product. Recrystallization and decoloration with carbon in ethanol gave colorless 9: mp 223–223.5 °C; IR (Nujol) 1585, 1560, 1515, 1490, 1420, 1300, 1235, 1055, 985, 860, 780, 745, and 735 cm^{-1}; mass spectrum M$^+$ at m/e 284. Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.04; H, 4.25; N, 19.71. Found: C, 76.18; H, 4.26; N, 19.73.

7,7′-Pyridine-2,6-diylbis(pyrido[2,3-*d*]pyrimidine) (11). To a refluxing solution of 3 g (0.024 mol) of 4-aminopyrimidine-5-carboxaldehyde (5) and 1.7 g (0.01 mol) of 2,6-diacetylpyridine in 50 mL of ethanol was added 5 drops of 20% KOH solution in methanol. The mixture was refluxed for 24 h and filtered, and the precipitate was washed with boiling ethanol to give 3.5 g (100%) of 11: mp >360 °C (from acetic acid); IR (Nujol) 1600, 1540, 1420, 1280, 1230, 1180, 1140, 1080, 990, 940, 930, 810, and 795 cm^{-1}. Anal. Calcd for $C_{19}H_{11}N_7$: C, 67.64; H, 3.28; N, 29.06. Found: C, 67.52; H, 3.27; N, 29.11.

6,6″-Diamino-2,2′:6′,2″-terpyridine-5,5″-dicarboxaldehyde (12). A mixture of 0.9 g of 11 and 500 mL of 2 N HCl was refluxed for 4 h, cooled, and neutralized (NH_4OH). The precipitate was filtered and recrystallized from acetic acid-water (0.7 g, 90%): mp >360 °C dec; IR (Nujol) 3530, 3350, 1667, 1590, 1560, 1530, 1290, 1200, 830, 765, 730, and 700 cm^{-1}. Anal. Calcd for $C_{17}H_{13}N_5O_2$: C, 63.94; H, 4.10; N, 21.93. Found: C, 64.02; H, 4.19; N, 21.82.

2,2′-Pyridine-2,6-diylbis[7-(2-pyridyl)-1,8-naphthyridine] (13). To a solution of 0.32 g (1 mmol) of 12 and 0.5 g (4 mmol) of 2-acetylpyridine in 10 mL of dimethyl sulfoxide was added 2 drops of a 20% KOH solution in methanol. The mixture was heated to 60 °C and kept at that temperature for 12 h. The precipitate was filtered and washed with boiling ethanol to give 0.47 g (95%) of 13, mp 422–424 °C, recrystallized from a large volume of *N,N*-dimethylacetamide: IR (Nujol) 1600, 1560, 1525, 1490, 1300, 1235, 1120, 1085, 1065, 990, 870, 845, 820, 805, 775, and 740 cm^{-1}. Anal. Calcd for $C_{31}H_{19}N_7$: C, 76.06; H, 3.91; N, 20.03. Found: C, 76.15; H, 3.95; N, 20.06.

Polycondensation of 12 and 2,6-Diacetylpyridine. To a solution of 0.319 g (1 mmol) of 12 and 0.163 g (1 mmol) of 10 in 5 mL of hexamethylphosphoramide was added 3 drops of a 20% KOH solution in methanol. Soon after the addition, a precipitate was formed. The reaction mixture was heated at 120 °C and kept at this temperature for 3 h. The mixture was cooled, diluted with water, and filtered. Infrared analysis of this material showed an absorption around 1690 cm^{-1} which is absent in the model compound 13.

6,6′-*m*-Phenylenebis(2-aminonicotinaldehyde) (15). To a refluxing solution of 0.52 g (4 mmol) of 5 and 0.324 g (2 mmol) of *m*-diacetylbenzene in 30 mL of ethanol was added 10 drops of a 10% KOH solution in methanol. A precipitate appeared within minutes after the addition of the base. *N,N*-Dimethylacetamide (20 mL) was then added, and heating was continued for 12 h. The product was filtered to give 0.63 g of the bis(pyrido[2,3-*d*]pyrimidine), mp 385 °C (*N,N*-dimethylacetamide). Hydrolysis of this product as above gave 15 in 95% yield: mp >360 °C dec; IR (Nujol) 3425, 3300, 3175, 1667, 1600, 1585, 1540, 1280, 1215, 1175, 1140, 800, 780, and 770 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_2N_4$: C, 67.92; H, 4.43; N, 17.60. Found: C, 67.01; H, 4.47; N, 17.51.

2,2′-*m*-Phenylenebis[7-(2-pyridyl)-1,8-naphthyridine] (16). To a refluxing solution of 0.32 g (1 mmol) of 15 and 0.3 g (2.5 mmol) of 2-acetylpyridine in 10 mL of dimethyl sulfoxide was added 3 drops of a 20% KOH solution in methanol. The mixture was heated to 60 °C and kept at this temperature for 12 h. The precipitate was filtered and washed with hot ethanol to give 0.45 g of 16: mp 294 °C (dimethyl sulfoxide); IR (Nujol) 1600, 1565, 1530, 1505, 1300, 1040, 865, 860, 795, 785, 780, 735, 725, and 690 cm^{-1}. Anal. Calcd for $C_{32}H_{20}N_6$: C, 78.67; H, 4.12; N, 17.20. Found: C, 78.74; H, 4.17; N, 17.24.

2,3,6-Triphenyl-7-[4-(phenylacetyl)phenyl]-1,8-naphthyridine (20). To a refluxing solution of 0.548 g (2 mmol) of 2-amino-5,6-diphenylpyridine-3-carboxaldehyde (19) and 0.628 g (2 mmol) of 17a in 40 mL of ethanol was added 5 drops of a 20% KOH solution in methanol. Reflux was continued for 12 h. The precipitate was collected and washed with hot ethyl acetate to give 0.99 g (90%) of 20: mp 259–261 °C (benzene–ethanol); IR (Nujol) 1670, 1600, 1560, 1515, 1490, 1390, 1250, 1175, 1150, 1010, 950, 865, 810, 785, 770, 755, 745, and 700 cm^{-1}. Anal. Calcd for $C_{40}H_{28}N_2O$: C, 86.93; H, 5.11; N, 5.07. Found: C, 87.05; H, 5.20; N, 5.12.

2,2′-*p*-Phenylenebis(3,6,7-triphenyl-1,8-naphthyridine) (21). To a refluxing solution of 0.6 g (2.2 mmol) of 19 and 0.314 g (1 mmol) of 17a in 25 mL of ethanol was added 2 drops of a 20% KOH solution in methanol. After 2 h a yellow precipitate was formed. At this point 10 mL of benzene and 1 mL of a 20% KOH solution in methanol were introduced, and reflux was continued for 48 h. The precipitate was collected and recrystallized from benzene to give **21** as a white crystalline material (0.79 g, 100%): mp 365 °C; IR (Nujol) 1590, 1515, 1410, 1330, 1245, 1175, 1065, 1045, 1020, 1010, 945, 930, 910, 855, 805, 780, 765, 730, 695, and 675 cm^{-1}. Anal. Calcd for $C_{58}H_{38}N_4$: C, 88.52; H, 4.35; N, 7.12. Found: C, 88.61; H, 4.39; N, 7.15.

6,6′-*p*-Phenylenebis(2-amino-5-phenylpyridine-3-carboxaldehyde) (22). To a refluxing solution of 1 g (8 mmol) of **5** and 1 g (3 mmol) of **17a** in 20 mL of ethanol was added four drops of a 20% KOH solution in methanol. Reflux was continued for 12 h, and the precipitate was collected and recrystallized from chloroform to give 1.3 g (90%) of the corresponding bis(pyrido[2,3-*d*]pyrimidine). Hydrolysis of this material in 700 mL of 2 N HCl gave 1.1 g of **22**, recrystallized from *N*,*N*-dimethylformamide–acetone (mp >360 °C): IR (Nujol) 3510, 3360, 1665, 1605, 1515, 1280, 1175, 960, 845, 780, 740, and 700 cm^{-1}. Anal. Calcd for $C_{30}H_{22}N_4O_2$: C, 76.58; H, 4.71; N, 11.91. Found: C, 76.74; H, 4.62; N, 11.80.

2-Amino-5-phenyl-6-(2′-*p*-phenyl-3′,6′,7′-triphenyl-1,8-naphthyridinyl)pyridine-3-carboxaldehyde (23). To a refluxing mixture of 0.63 g (1.1 mmol) of **20** and 0.16 g (1.3 mmol) of **5** in 20 mL of ethanol and 5 mL of benzene was added five drops of a 20% KOH solution in methanol. Reflux was continued for 12 h to yield the corresponding pyrido[2,3-*d*]pyrimidine in quantitative yield. Hydrolysis of this material gave **23** in nearly quantitative yield: mp >400 °C dec; IR (Nujol) 3450, 3330, 1665, 1610, 1515, 1410, 1275, 1175, 1010, 960, 950, 855, 810, 790-785, 770, 740, and 700 cm^{-1}. Anal. Calcd for $C_{44}H_{30}N_4O$: C, 83.78; H, 4.79; N, 8.88. Found: C, 83.97; H, 4.69; N, 8.76.

3,3′-*p*-Phenylenebis(2,6,7-triphenyl-1,8-naphthyridine) (25). To a refluxing solution of 0.4 g (1.5 mmol) of **19** and 0.22 g (0.7 mmol) of **18a** in 25 mL of ethanol and 15 mL of benzene was added 15 drops of a 20% KOH solution in methanol. Reflux was continued for 48 h, and the precipitate was collected and washed with boiling benzene to give a 95% yield of **25**: mp 384–385 °C (chloroform); IR (Nujol) 1595, 1515, 1390, 1335, 1250, 1205, 1175, 1065, 1060, 1050, 1010, 970, 945, 920, 910, 845, 790, 775, 765, 735, and 695 cm^{-1}. Anal. Calcd for $C_{58}H_{38}N_4$: C, 88.52; H, 4.35; N, 7.12. Found: C, 88.64; H, 4.38; N, 7.18.

3,3′-*m*-Phenylenebis(2,6,7-triphenyl-1,8-naphthyridine) (26). To a refluxing solution of 0.56 g (2 mmol) of **19** and 0.314 g (1 mmol) of **18b** in 30 mL of ethanol was added 10 drops of a 10% KOH solution in methanol. The mixture was refluxed for 24 h, filtered, and recrystallized from benzene to give 0.45 g (60%) of **26**: mp 265 °C; IR (Nujol) 1590, 1515, 1335, 1245, 1175, 1065, 1020, 1000, 955, 945, 925, 810, 790, 770, and 695 cm^{-1}. Anal. Calcd for $C_{58}H_{38}N_4$: C, 88.52; H, 4.35; N, 7.12. Found: C, 88.56; H, 4.35; N, 7.14.

Acknowledgment. This work was supported in part by the U.S. Army Research Office, Durham, N.C.

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Synthesis of Graft Copolymer by Coupling Condensation through Acetalization

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Received March 13, 1979

ABSTRACT: A condensation coupling through acetalization is performed between hydroxyl groups on poly(vinyl alcohol) (PVA) and an aldehyde group attached to the chain end of poly(vinyl acetate) (PVAc) to produce PVA–VAc graft copolymers. The aldehyde-terminated PVAc is prepared by polymerization of VAc with monochloroacetaldehyde or monochloroacetaldehyde diethyl acetal as the chain transfer agent. The coupling reaction of PVAc with cross-linked porous beads of PVA, followed by extraction of ungrafted PVAc, permits us to estimate the fraction of PVAc carrying the terminal aldehyde group. The observed fractions range from 0.1 to 0.5. In addition to the heterogeneous grafting onto the cross-linked beads and a membrane, PVAc is grafted onto a linear PVA in dimethyl sulfoxide, which is a common solvent for both polymers. Based on the weights of the isolated graft copolymer and the two homopolymers, the number of branches in the graft copolymer is evaluated; for instance, 18 branches of PVAc with $\bar{P}_n$ of 53 are found to be coupled to the PVA backbone with $\bar{P}_n$ of 1340.

Graft copolymers have been generally synthesized either by polymerizing a monomer from initiating sites on a backbone polymer or by linking two different polymers through polymer reactions. The latter includes deactivation of an anionic living polymer with a different polymer having polar side groups such as ester and benzyl halide and condensation reactions between functional groups attached to an end of a polymer chain and to side groups of a backbone polymer. As examples of the syntheses of graft copolymers by the condensation coupling, we can mention the condensation of hydroxyl groups in a partially acetylated poly(vinyl alcohol) (PVA) with a terminal acyl chloride group of poly(vinyl acetate) (PVAc),[1] the condensation of chlorine groups in poly(2-chlorocyanurate) ester of bisphenol A with a terminal amino group of poly(methyl methacrylate),[2] and the condensation of amino groups in partially aminoacetalized PVAc with a terminal acyl chloride group on polystyrene.[3]

The present study will describe grafting through acetalization of hydroxyl groups in PVA with an aldehyde group attached to an end of PVAc chain produced by chain

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