Selective Dimerizations of Substituted *N*-Aminopyridinium Salts and Their Benzologues

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N-Aminopyridinium salts bearing ester, aroyl, and cyano functions in position 2 as well as their differently annelated benzologues were reacted with hydroxide ion and alkoxides. In the case of ester compounds **1**, **3**, and **5**, transesterification and dimerization reactions were found. Keto salts **7**, **13**, and **15** showed dimerization reactions coupled with methanolysis. Monocyclic cyano salt **17** gave amino-*as*-triazinium double salt **20** while the benzologues (**21** and **27**) showed three different reactions depending on the conditions used: (a) removal of the cyano group (formation of **22** and **28**), (b) formation of new fused 1,2,4-triazole derivatives (**26** and **29**), and (c) formation of tetrazine-fused dimers (**24** and **30**). All *N*-amino-3-substituted-isoquinolinium salts (**32**) resulted in dimerizations retaining the 3-substituent. Comparison of these results showed that reactivity of the *N*-amino compound is mainly influenced by the nature of the substituents and by the relative position of the fused benzene ring with respect to the *N*-amino function.

In some of our recent publications[1-3] we reported on the synthesis of new bridgehead-nitrogen-containing fused heteroaromatic cations and on their reactivity toward nucleophiles. Several of these syntheses[3,4] were based on *N*-aminoazinium salts as starting materials. The chemistry of these salts is well documented in the literature, but relatively little is known about how such *N*-amino salts bearing different substituents react with negatively charged reagents.[5-9]

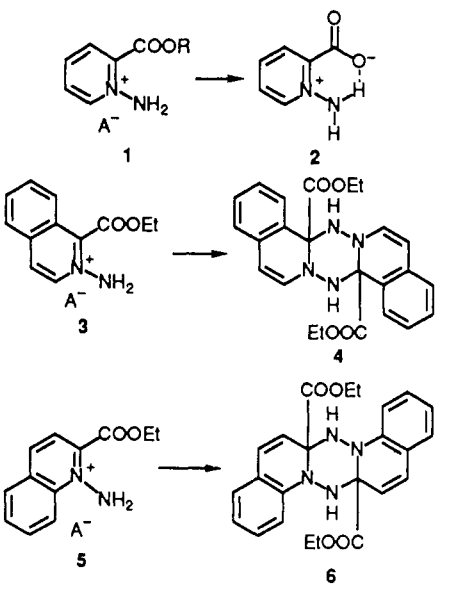
In this study, 2-substituted-*N*-aminopyridinium salts and their differently fused benzologues were investigated. Three different substituents—ester group, aroyl function, and cyano moiety—were introduced into position 2 (corresponding to numbering of the pyridine ring) and the reactivities of these and of the differently fused *N*-aminoazinium salts were also compared.

As shown in Figure 1, negatively charged reagents can react with *N*-aminoazinium salts (**a**) as nucleophiles leading to pseudobases (**b** or **c**) or, on the other hand, they can react as a base and afford an ylide represented by one of the resonance structures (**d**).

Formation of such ylides was first reported by Huisgen et al.[10,11] These authors found that the ylides formed by treatment of *N*-aminoisoquinolinium and *N*-aminoquinolinium salts with base undergo, as 1,3-dipoles, spontaneous dimerization and yield tetrahydrotetrazinodiisoquinoline or tetrazinodiquinoline, respectively. These dimers when treated with mineral acid reverted back to the starting *N*-aminoazinium salts.

In the present study sodium hydroxide and sodium methoxide (strong bases) were used as reagents. All precursors of the selected model compounds in the pyridine series (**1a**, **7**, **17**) and most of the quinoline and isoquinoline compounds have been reported in the literature.[3,12-15] The aroyl derivatives (e.g., 1-[3-(trifluoromethyl)-benzoyl]isoquinoline (**12c**), 3-(4-chlorobenzoyl)isoquinoline (**31b**), and 3-[3-(trifluoromethyl)benzoyl]isoquinoline (**31c**) were synthesized from 1- and 3-cyanoisoquinoline, respectively, by Grignard reaction using the same reaction conditions as described for synthesis of 1-acetylisoquinoline.[16] N-Amination of the ketones, esters, and cyano compounds was accomplished in good yield by using *O*-tosylhydroxylamine (TSH).[17-19]

Scheme I[a]



[a] **a**, R = C_2H_5; **b**, R = CH_3.

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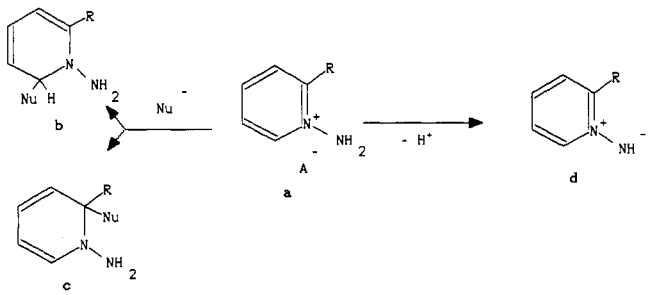


Figure 1. Reaction types of 2-substituted-*N*-aminopyridinium salts.

2-(Ethoxycarbonyl)-*N*-aminopyridinium perchlorate (**1a**) when reacted with 1 equiv of sodium hydroxide in methanol underwent, interstingly, only transesterification; the methoxycarbonyl compound **1b**[12] could be prepared in 65% yield. When **1a** was refluxed in ethanol over solid potassium carbonate, however, deprotonation and simultaneous hydrolysis took place, and zwitterion **2** strongly stabilized by the intramolecular hydrogen bond could be isolated. Although **2** was stable under the conditions of the recrystallization, it easily decarboxylated at its melting point (150 °C) as shown by the intense gas evolution observed.

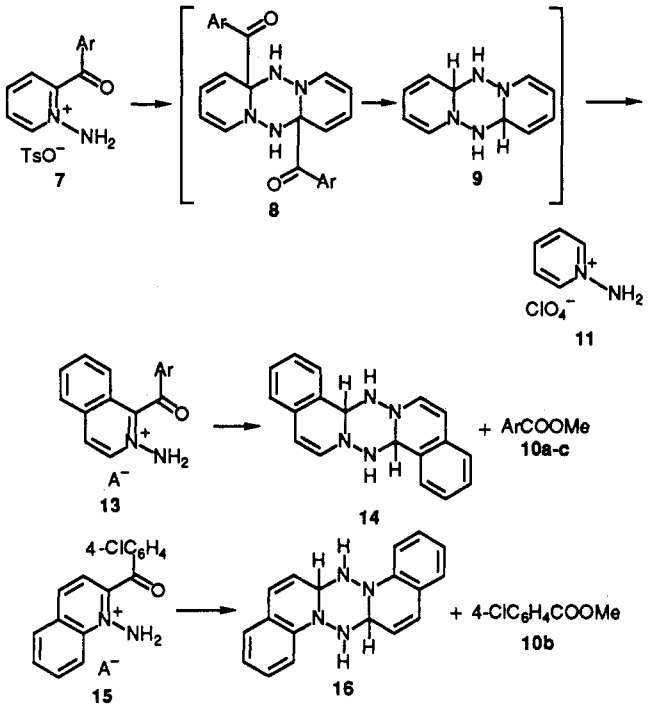
In contrast to the behavior of the pyridinium salt **1**, 1-(ethoxycarbonyl)-2-aminoisoquinolinium salt (**3**) and 2-(ethoxycarbonyl)-1-aminoquinolinium salt (**5**) gave the dimeric products **4** and **6** (Scheme I) when reacted with sodium methoxide solution at room temperature. The presence of the ester groups was unambiguously shown by NMR, whereas the dimeric nature of these products was revealed by both their mass spectra (the molecular mass at m/z 432 due to the dimeric form, while the presence of the basic peak at m/z 217 accounts for an easy retrodimerization) and by the finding that on reaction with strong acid, the starting monomeric *N*-amino salts (**3** and **5**) could be recovered.

A different behavior was observed with the *N*-aminoazinium salts containing a keto function on treatment with sodium methoxide. Monocyclic ketone **7** afforded a fairly complex reaction mixture, which on treatment with perchloric acid gave rise to *N*-aminopyridinium perchlorate **11** (20%) and methyl benzoate (51%) (Scheme II). Isolation of these two products suggests that the ylide formed by deprotonation of the starting salt can undergo dimerization to give presumably dimer **8**, and this intermediate undergoes methanolysis to yield methyl benzoate and tetrahydrodipyridotetrazine (**9**), which on treatment with perchloric acid gave monomeric salt **11**.

In the case of the benzologues of **7** (ketones **13a–c** and **15**), a similar dimerization reaction coupled with methanolysis was observed with the essential difference that dimers **14** and **16** were isolated in good yields. As mentioned above, these compounds have already been obtained by an independent route.[11]

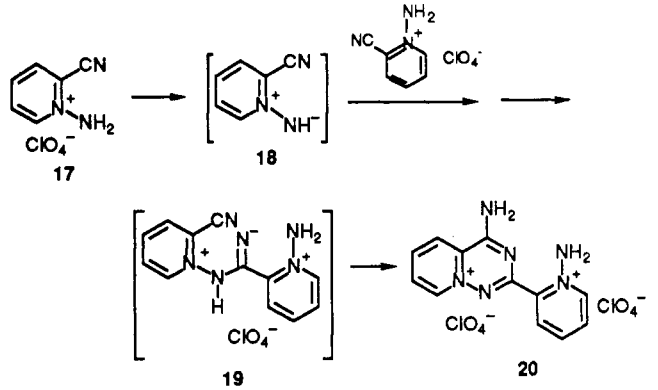
Studies on the cyano substituted *N*-aminopyridinium and related compounds led to rather unexpected results and showed that reactions of these compounds are sensitive to the conditions used. Thus, 1-amino-2-cyanopyridinium perchlorate (**17**) when treated with a catalytic amount of base (potassium hydroxide) or with weak base (e.g., formamide, formamidine acetate) undergoes a specific dimerization reaction with participation of the cyano group

Scheme II[a]



[a] **a**, Ar = C_6H_5; **b**, Ar = 4-ClC_6H_4; **c**, Ar = 3-$CF_3C_6H_4$.

Scheme III



and a new pyrido[2,1-*f*]-*as*-triazinium salt (**20**) can be isolated (Scheme III).

For formation of this product, the following mechanism is proposed: ylide **18** formed by basic treatment of one molecule of the starting *N*-amino salt first reacts at the cyano carbon atom of another starting molecule to give intermediate **19** which, after ring closure, can be stabilized by protonation to yield the isolated double salt **20**. The unexpected structure of this product was assigned by the spectral evidences that (i) in the proton spectrum, two different four-proton patterns belonging to the two pyridine rings can be clearly differentiated and (ii) in the carbon spectrum no cyano carbon shift was observed. Apart from the two five-carbon peaks of the two pyridine moieties, the two quaternary carbons (139.63 and 155.83) were assigned to the carbon atoms of the *as*-triazine ring. It is interesting to note that this ring closure reaction led rather to the six-membered *as*-triazine than to a five-membered *s*-triazole ring as found with cycloaddition of the ylide of type **d** (Figure 1) with 4-cyanopyridine.[20,21]

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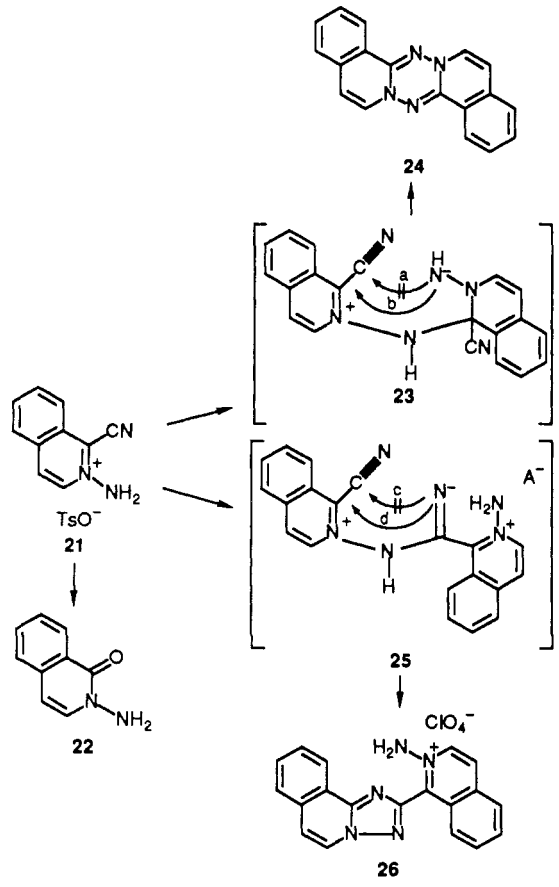
Scheme IV



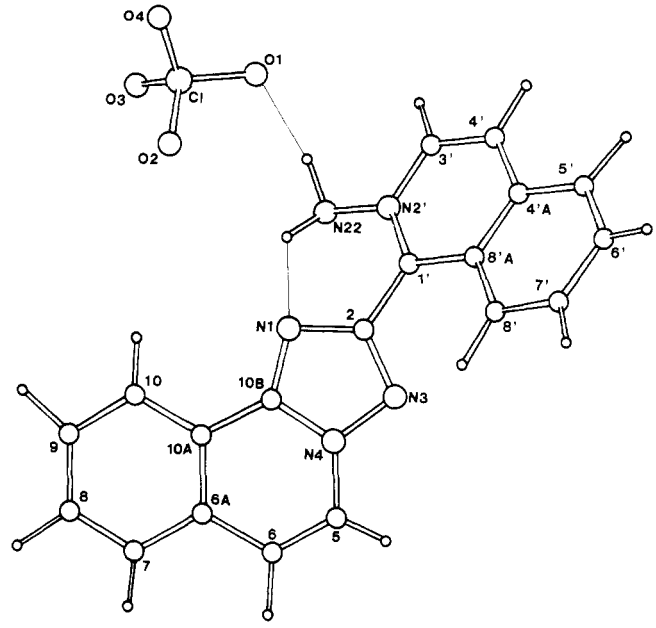
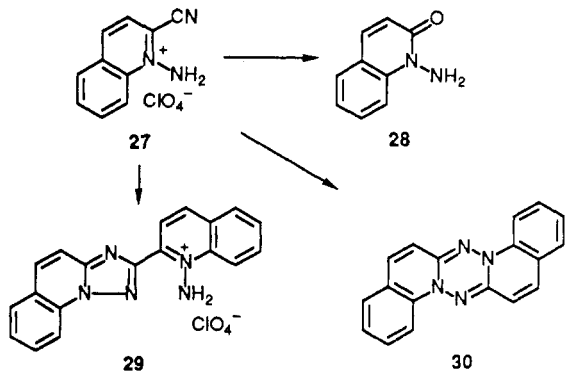


Figure 2. X-ray structure of **26**.

Scheme V



The cyano derivatives of the isoquinoline and quinoline rings (**21** and **27**) reacted with an excess of aqueous sodium hydroxide in a rather different manner: nucleophilic displacement of the cyano group of these compounds was observed and 2-amino-1-isoquinolone (**22**) or 1-amino-2-quinolone (**28**) described earlier[22,23] was isolated.

When this reaction was performed, however, under water-free conditions using organic bases, new types of dimerization were observed. The ylide formed on the action of base can attack the other *N*-aminoisoquinolinium salt (**21**) in two different ways: (i) on the ring site (at position C-1 to yield intermediate **23**) and (ii) on the carbon atom of the cyano group (intermediate **25** is formed). These intermediates can react, in principle, in two different ways (routes **a** or **b**, and **c** or **d**) (Scheme IV).

We found that *N*-amino salt **21** when added to an excess of triethylamine yielded the fused *s*-tetrazine derivative **24** (i.e., intermediate **23** was formed and route **b** was realized). The same *N*-amino salt (**21**), on the other hand, when reacted with formamidine acetate (weak base in small concentration) resulted in a new salt as product. Its proton NMR spectrum and elementary analysis revealed that of the remaining possibilities (**a**, **c**, and **d**) route **c**, which would result in formation of an *as*-triazino[6,1-*a*]-isoquinolinium derivative substituted by an *N*-aminoisoquinolinium moiety, can unambiguously ruled out.

The assignment of the proton and the ^{13}C spectrum alone, based on homo- and heteronuclear two-dimensional chemical shift correlation experiment,[24,25] did not provide evidence to decide between the still remaining two alternatives **a** and **d** (i.e., formation of a diisoquinolinotetrazepinium salt and **26**, respectively). In a homonuclear NOE difference experiment, however, a marked intensity enhancement (17%) could be measured on the proton (at 8.82 ppm) next to the charged N atom when irradiating the singlet of the NH_2 group at 8.68 ppm. This observation makes structure **26** very likely. Final evidence of formation of structure **26** was provided by the X-ray analysis (Figure 2).

The analogous *N*-amino-2-cyanoquinolinium compound **27** afforded three similar products **28**, **29**, and **30** (Scheme V) with these reagents. The structure of compound **29** is based on homo- and heteronuclear 2D chemical shift correlation NMR spectra and homonuclear NOE experiments (see Experimental Section).

Recently, Balli et al.[26] reported on the formation of fused tetrazines (**24** and **30**) from 2-amino-1-chloroisoquinolinium and 1-amino-2-chloroquinolinium salts. Because of the considerably higher yield found as well as the relatively easy access to the starting cyano compounds, our approach seems to be superior for preparation of these recently

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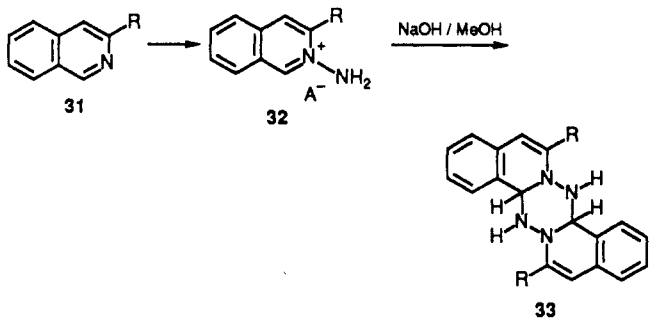
Scheme VI[a]



[a] **a**, R = COOMe; **b**, R = 4′-ClC$_6$H$_4$CO; **c**, R = 3′-CF$_3$C$_6$H$_4$CO; **d**, R = CN.

recognized and interesting structures.

Besides the above-mentioned cases, there is a third possible benzologue of the 2-substituted-*N*-aminopyridinium salts: the 3-substituted-*N*-aminoisoquinolinium salts **32**. Reactions of these derivatives (ester **32a**, ketones **32b,c**, and cyano compound **32d**) showed that dimeric products **33a–d** of the same type were formed in every case, and no elimination of the substituents occurred (Scheme VI).

This finding shows that primarily formed ylides undergo cycloaddition as 1,3-dipoles in such a fashion that carbon 1 rather than 3 is involved as the positively polarized reactive center. The proton NMR spectra of **32c** gave unambiguous proof for these structures: H-1 could easily be assigned and the H1–NH coupling (13 Hz) evidently showed the vicinal positions of these protons. As in the above cases, the dimeric nature could be supported by detection of the large molecule peaks in the mass spectra as well as by the finding that the starting *N*-amino salts were recovered when they were treated with acid (e.g., **33** gave **32**).

Comparison of reactions of the differently substituted monocyclic and bicyclic *N*-aminoazinium salts with hydroxide ion and alkoxides reveals that in the first step of these reactions, a proton has been removed from the amino group resulting in the ylide intermediate. Reactivity of this ylide was found, furthermore, to depend on three main factors: (i) whether the ylide is monocyclic or a fused bicyclic compound, (ii) the relative position of the annelated benzene ring with respect to the *N*-amino function, and (iii) the nature of the substituent.

The difference betwen reactivities of the monocyclic pyridinium derivatives (**1**, **7**, **17**) and their benzologues (**3**, **5**, **13**, **15**, **21**, **27**, **32**) can be satisfactorily interpreted by consideration of the aromatic π-sextet of the fused benzene ring. Nucleophilic attack at the position adjacent to the positively charged bridgehead nitrogen (α-position)—as found in reactions resulting from structures **b** and **c** in Figure 1—as well as formation of "Huisgen-type" dimers (e.g., **4**, **6**, **8**) implies destruction of the π-sextet of the pyridine ring; the aromatic structure of the fused benzene moiety in quinolines and isoquinolines, however, is still retained in these reactions. This may be accounted for by formation of ylide **2** instead of the corresponding dimer like **8**, for the poor yield (20%) of formation of the debenzoylated derivative **11** (i.e., for the relative instability of **8**), as well as for formation of the pyrido-*as*-triazinium double salt **20** (i.e., for the attack at the cyano carbon atom instead of the α-carbon of the pyridine ring).

The influence of the relative position of the annelated benzene ring in the bicyclic *N*-amino salts can be studied by comparison of the isoquinoline derivatives **3**, **13**, and **21** vs **32a–d**. It is generally known that C-1 in the isoquinoline ring is preferred for nucleophilic attack compared to the other adjacent carbon atom C-3.[27] The formation of dimers **33a–d** from the 3-substituted derivatives **32a–d** reveals that even in those cases where an activating electron-withdrawing group is attached to position 3, C-1 still remains as the most active center for such reactions.

Finally, in our model systems, the role of substituents was found to be important particularly in subsequent reactions of the primarily formed ylides. In this respect the cyano derivatives—besides being appropriate leaving groups—represent a peculiarity compared to the other cases because the carbon atom of the cyano group is also a possible target of the nucleophile. The dimerization of these compounds in an excess of base is supposed to proceed as an ylide–ylide interaction, whereas the reaction of an ylide and a cation can become predominant when a reduced amount of base is used. In the former case, the 1,3-dipoles of the ylides result obviously in formation of dimers containing a six-membered ring (**24**, **30**, and **33d**). In the latter type of reaction, however, the attack at the cyano carbon atom is favored as shown by formation of intermediates **19** and **25**. This can be the explanation of the selective formation of the new *as*-triazinium (**20**) and triazole (**26**, **29**) derivatives.

Investigations of reactivities of *N*-aminoazinium salts containing novel substituents as well as studies relating to the chemistry of the new heterocyclic rings are in progress.

Experimental Section

Melting points were determined by a Büchi apparatus and are uncorrected. IR spectra were recorded on Specord IR-75 and UV spectra on Unicam SP-800 equipment. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-100 and XL 400 instruments at ambient temperature. ^{1}H{^{1}H} NOE spectra were recorded in the difference mode.[28] Mass spectra were obtained with an AEI MS-902 spectrometer.

X-ray analysis for 26, crystal data: $C_{19}H_{14}N_5O_4Cl$, M_r 411.8, a = 10.041 (1), b = 12.055 (1), and c = 15.178 (1) Å, β = 99.63 (1)°, V = 1811.1 (5) Å^3; D_x = 1.51 g·cm^{-3}; μ(Cu K$_\alpha$, λ = 1.5418 Å) = 22.2 cm^{-1}; z = 4; space group $P2_1/n$.

A total of 3300 unique reflections were collected on an Enraf-Nonius CAD4 computer-controlled four-circle diffractometer with a θ–2θ scan in the $3 < 2\theta < 150°$ range (approximate crystal size was 0.10 × 0.25 × 0.30 mm). The structure was solved by direct methods and was refined by full-matrix least squares. Hydrogen atoms belonging to the NH_2 groups were located in difference maps, while other hydrogen atoms were generated from assumed geometries. They were included in structure factor calculation but were not refined. The final R values were 0.052 for 2763 [$I > 3\sigma(I)$] reflections. Atomic coordinates are given in the supplementary material.[31] One of the NH_2 hydrogen atoms participates in an intramolecular hydrogen bond [N(22)–H(22a)···N1]. The ClO_4^- anion is linked to the cation by the N(22)–H(22)···O hydrogen bond. No unusual bond distances and angles were observed.

Preparation of Starting Ketones. 1-[3-(Trifluoromethyl)benzoyl]isoquinoline (12c). A solution of a Grignard reagent prepared from magnesium (0.735 g, 30 mmol) and 3-(trifluoromethyl)bromobenzene (6.76 g, 30 mmol) in ether (100 mL) was added dropwise and with stirring to a solution of 1-cyanoisoquinoline (3.1 g, 20 mmol) in dry ether (50 mL). The

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(28) Kinns, M.; Sanders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518–520.
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(30) Available from Aldrich.
(31) See paragraph at the end of paper regarding supplementary material.

stirring was continued for an additional 3 h and the mixture was left to stand at 0 °C overnight. It was then poured onto crushed ice containing ammonium chloride (2 g), the mixture was then acidified with sulfuric acid to pH 1, and it was shaken thoroughly for few minutes and was then basified with aqueous sodium hydroxide to pH 8. The organic layer was separated, the aqueous layer was extracted three times with ether, and the residue was recrystallized from ethanol to give 4.6 g (77%) of colorless crystals, mp 95–97 °C.

Anal. Calcd for $C_{17}H_{10}F_3NO$ (301.28): C, 67.77; H, 3.35; N, 4.65. Found: C, 67.75; H, 3.88; N, 4.45. IR (KBr): 3060, 1670 cm^{-1}. ^1H NMR ($CDCl_3$): 8.83 (d, 1 H, H-3), 8.6–8.2 (m, 3 H, H-5,7,8), 8.1–7.5 (m, 6 H, H-4,6 and *m*-$CF_3C_6H_4$) ppm.

3-(4-Chlorobenzoyl)isoquinoline (31b). This compound was prepared from 3-cyanoisoquinoline[30] (1.54 g, 10 mmol) and the appropriate Grignard reagent according to the previous procedure. Yield: 1.7 g, (64%); mp 125–127 °C.

Anal. Calcd for $C_{16}H_{10}ClNO$ (267.72): C, 71.78; H, 3.77; N, 5.23. Found: 71.76, H, 3.91; N, 5.25. IR (KBr): 3000, 1670, 1620, 1590 cm^{-1}. NMR (TFA): 9.9 (s, 1 H, H-1), 9.0 (s, 1 H, H-4), 8.9–7.6 (m, 8 H) ppm.

3-[3-(Trifluoromethyl)benzoyl]isoquinoline (31c). This compound was prepared from 3-cyanoisoquinoline[30] (1.54 g, 10 mmol) and the appropriate Grignard reagent according to the previous procedure. Yield: 1.7 g (64%); mp 109–111 °C.

Anal. Calcd for $C_{17}H_{10}NOF_3$ (301.28): C, 67.77; H, 3.35; N, 4.65. Found: C, 67.58; H, 3.27; N, 4.50. IR (KBr): 3050, 1650, 1500, 1480, 1420 cm^{-1}.

Preparation of *N*-Amino Salts. 1-Amino-2-(methoxycarbonyl)pyridinium Perchlorate (1b). A solution of 1-amino-2-(ethoxycarbonyl)pyridinium perchlorate (**1a**, 1 g, 38 mmol) in methanol (10 mL) was stirred with a solution of sodium hydroxide (0.15 g, 38 mmol) in water (1 mL) at room temperature for 3 h. The solution was then mixed with water (10 mL) and allowed to stand overnight. The precipitated crystals were filtered off to give white needles (0.62 g, 65%), mp 114–116 °C.

Anal. Calcd for $C_7H_9ClN_2O_6$ (252.62): C, 33.28; H, 3.59; N, 11.09. Found: C, 33.45; H, 3.65; N, 10.91. IR (KBr): 3160, 3040, 2820, 1710, 1580, 1490, 1420, 1270, 1060 cm^{-1}. ^1H NMR (TFA): 8.92 (d, 1 H, H-6); 8.8–8.0 (m, 3 H, H-3,4,5), 4.25 (s, 3 H, CH_3) ppm.

2-Amino-1-(ethoxycarbonyl)isoquinolinium Tosylate (3). A solution of TSH (1.87 g, 10 mmol) in dichloromethane (40 mL) was added to a stirred solution of ethyl isoquinoline-1-carboxylate (2.01 g 10 mmol) in dichloromethane (15 mL) at room temperature. Stirring was continued for 5 h; then the product was precipitated by addition of ether (50 mL). The crude product was recrystallized from ethanol to give 3.45 g (89%) of cream-colored crystals, mp 144–146 °C.

Anal. Calcd for: $C_{19}H_{20}N_2O_5S$ (388.45): C, 58.75; H, 5.17; N, 7.21. Found: C, 59.04; H, 5.19: N, 7.06. IR (KBr): 3220, 3110, 3080, 2990, 2940, 2910, 1740, 1200 cm^{-1}. ^1H NMR (TFA): 8.77 (d, 1 H, H-3), 8.47 (d, 1 H, H-4), 8.30 (m, 4 H, *H*-5,6,7,8), 7.92 (m, 2 H, H-2′,6′-tosyl), 7.34 (m, 2 H, H-3′,5′-tosyl), 4.92 (q, 2 H, CH_2), 2.42 (s, CH_3-tosyl), 1.60 (t, 3 H, CH_3) ppm.

1-Amino-2-(ethoxycarbonyl)quinolinium Perchlorate (5). This compound was prepared starting from ethyl quinoline-2-carboxylate (2.01 g, 10 mmol) using the above procedure with the following modification: the reaction mixture was evaporated to dryness, and to the aqueous solution of the residue (in 15 mL of water) was added 70% perchloric acid (3 mL). Recrystallization from ethanol gave 2.4 g (76%) of pale yellow crystals, mp 144–146 °C.

Anal. Calcd for $C_{12}H_{13}ClN_2O_6$ (316.71): C, 45.51; H, 4.14; N, 8.85. Found: C, 45.73; H, 4.09; N, 8.63. IR (KBr): 3250, 3180, 3090, 3050, 3010, 2970, 2930, 1720, 1100 cm^{-1}. ^1H NMR (TFA): 9.04 (d, 1 H, H-4), 8.91 (d, 1 H, H-8), 8.63 (d, 1 H, H-3), 8.5–8.0 (m, 3 H, H-5,6,7), 4.78 (q, 2 H, CH_2), 1.58 (t, 3 H, CH_3) ppm.

2-Amino-1-cyanoisoquinolinium Tosylate (21). This compound was prepared from 1-cyanoisoquinoline (1.54 g, 10 mmol) according to the previous procedure. Yield: 2.7 g (79%) of beige crystals; mp 198–199 °C.

Anal. Calcd for $C_{17}H_{15}N_3O_3S$ (341.40): C, 59.81; H, 4.43; N, 12.31. Found: 59.58; H, 4.13; N, 12.01. IR (KBr): 3200, 3080, 2950, 1200 cm^{-1}. ^1H NMR (TFA): 9.0 (d, 1 H, H-3), 8.66 (d, 1 H, H-4), 8.6–8.2 (m, 4 H, H-5,6,7,8), 7.84 (m, 2 H, H-2′,6′-tosyl), 7.32 (m, 2 H, H-3′,5′-tosyl), 2.41 (s, 3 H, CH_3-tosyl) ppm.

1-Amino-2-cyanoquinolinium Perchlorate (27). This compound was prepared from 2-cyanoquinoline (1.54 g, 10 mmol) by using the procedure described for compound **3**; 1.7 g (63%) of beige crystals were obtained, mp 187–190 °C.

Anal. Calcd for $C_{10}H_8ClN_3O_4$ (269.66): C, 44.54; H, 2.99; N, 15.58. Found: C, 44.52; H, 3.05; N, 15.53. IR (KBr): 3320, 3250, 3100, 3070, 2240, 1100 cm^{-1}. ^1H NMR (TFA): 9.36 (d, 1 H, H-4), 8.94 (d, 1 H, H-8), 8.7–8.1 (m, 4 H, H-3,5,6,7), 7.5 (broad, 2 H, NH_2) ppm.

2-Amino-3-(methoxycarbonyl)isoquinolinium Perchlorate (32a). This compound was prepared from methyl isoquinoline-3-carboxylate[30] (1.87 g, 10 mmol) according to the previous procedure. The crude perchlorate salt was recrystallized from 50% aqueous methanol to yield 2.5 g, 75%; mp 159–160 °C.

Anal. Calcd for $C_{11}H_{11}N_2O_6Cl$ (302.68): C, 63.92; H, 5.36; N, 13.55. Found: C, 63.66; H, 5.19; N, 13.20. IR (KBr): 3500–2800, 1710, 1610, 1410, 1110 cm^{-1}. ^1H NMR (TFA): 9.55 (s, 1 H, H-1), 9.10 (s, 1 H, H-4), 8.70–8.05 (m, 4 H, H-Ar), 4.20 (s, 3 H, CH_3) ppm.

2-Amino-3-(4-chlorobenzoyl)isoquinolinium Tosylate (32b). This compound was prepared from 3-(4-chlorobenzoyl)-isoquinoline (**31b**; 2.0 g, 7.5 mmol) by the previous procedure. Yield: 2.5 g (79%); mp 200–202 °C.

Anal. Calcd for $C_{23}H_{19}ClN_2O_4$ (422.88): C, 65.33; H, 4.53; N, 6.63. Found: C, 65.26; H, 4.37; N, 6.49. IR (KBr): 3300–2800, 1680 cm^{-1}. NMR (TFA): 9.8 (s, 1 H, H-1), 8.5–7.1 (m, 13 H), 2.4 (s, 3 H, CH_3).

2-Amino-3-[3-(trifluoromethyl)benzoyl]isoquinolinium Tosylate (32c). This compound was prepared from 3-[3-(trifluoromethyl)benzoyl]isoquinoline (**31c**; 2.0 g, 6.6 mmol) by the previous procedure. Yield: 2.3 g (71%); mp 158–160 °C.

Anal. Calcd for $C_{24}H_{19}F_3N_2O_4S$ (488.43) C, 59.01; H, 3.92; N, 5.74. Found: C, 58.85; H, 3.76; N, 5.61. IR (KBr): 3300–3200, 3030, 1670, 1620, 1600, 1560 cm^{-1}.

2-Amino-3-cyanoisoquinolinium Tosylate (32d). This compound was obtained from 3-cyanoisoquinoline (1.54 g, 10 mmol)[30] by the previous procedure. Yield: 2.55 g (75%) of colorless crystals; mp 163–165 °C.

Anal. Calcd for: $C_{17}H_{15}N_3O_3S$ (341.40): C, 59.81; H, 4.42; N, 12.31. Found: C, 59.51; H, 4.18; N, 12.10. IR (KBr): 3300–3000, 2100, 1600, 1470, 1150 cm^{-1}. ^1H NMR (DMSO-d_6 + TFA): 10.3 (s, 1 H, H-1), 9.40 (s, 1 H, H-4), 8.70–8.05 (m, 4 H, H-Ar), 7.65 and 7.15 (AA′BB′, 4 H, H-tosyl) ppm.

Reactions of *N*-Amino Salts. 1-Amino-2-carboxypyridinium Hydroxide Inner Salt (2). A solution of 1-amino-2-(ethoxycarbonyl)pyridinium perchlorate (**1a**; 2.67 g, 10 mmol) in ethanol (54 mL) was refluxed with potassium carbonate (6.9 g, 50 mmol) for 20 min. The reaction mixture was filtered while hot and then cooled, and the separated crystals were filtered off. The crude product (0.95 g, 69%, mp 145–148 °C) was recrystallized from ethanol (40 mL) to give 0.6 g (43%) of colorless, small needles, mp 151–153 °C.

Anal. Calcd for $C_6H_6N_2O_2$ (138.13): C, 52.17; H, 4.38; N, 20.28. Found: C, 51.69; H, 4.63; N, 19.74. IR (KBr): 3180, 3090, 3070, 3000, 2900, 1660, 1590, 1490, 1310 cm^{-1}. ^1H NMR (DMSO-d_6): 8.64 (m, 1 H, H-6), 8.41 (m, 1 H, H-3), 8.16 (m, 1 H, H-4), 7.90 (m, 1 H, H-5) ppm.

8a,16a-Bis(ethoxycarbonyl)-7,8,15,16-tetrahydro-*s*-tetrazino[6,1-*a*:3,4-*a*′]diisoquinoline (4). A solution of sodium methoxide (114 mg, 2.1 mmol) in methanol (0.47 mL) was added to a stirred solution of 2-amino-1-(ethoxycarbonyl)isoquinolinium tosylate (**3**; 0.78 g, 2 mmol) at room temperature. After being stirred for 15 min, the crystals were filtered and recrystallized from dimethylformamide to give 0.22 g (51%) of pale yellow prisms, mp 197–199 °C.

Anal. Calcd for $C_{24}H_{24}N_4O_4$ (432.49): C, 66.65; H, 5.59; N, 12.96. Found: C, 66.51; H, 5.76; N, 12.83. IR (KBr): 3220, 3090, 3060, 2990, 2970, 2945, 2900, 1720 cm^{-1}. ^1H NMR (DMSO-d_6): 7.76 (dd, 2 H, H-1,9), 7.4–6.8 (m, 6 H, H-2,3,4,10,11,12), 6.52 (d, 2 H, H-6,14), 5.32 (s, 2 H, N-H), 5.26 (d, 2 H, H-5,13), 4.17 (m, 4 H, CH_2), 1.18 (t, 6 H, CH_3) ppm.

6a,14a-Bis(ethoxycarbonyl)-7,8,15,16-tetrahydro-*s*-tetrazino[1,6-*a*:4,3-*a*′]diquinoline (6). A suspension of 1-amino-2-(ethoxycarbonyl)quinolinium perchlorate (**5**; 0.64 g, 2 mmol) in water (10 mL) was stirred at room temperature with sodium

hydroxide (0.4 g, 5.0 mmol) in water (2 mL) for 5 min. Crystals separated that were then filtered, washed with water, and recrystallized from acetonitrile (3 mL) to give 0.18 g (42%) of yellow needles, mp 85–87 °C.

Anal. Calcd for $C_{24}H_{24}N_4O_4$ (432.49): C, 66.65; H, 5.59; N, 12.96. Found: C, 66.63; H, 5.69; N, 12.86. IR (KBr): 3210, 3100, 3050, 2980, 2920, 1650 cm^{-1}. ^1H NMR (DMSO-d_6): 8.80 (m, 2 H, H-1,9), 7.8–7.4 (m, 8 H, H-2,3,4,5,10,11,12,13), 6.80 (d, 4 H, H-6,14 and N-H), 4.38 (q, 4 H, CH_2), 1.39 (t, 6 H, CH_3) ppm.

Reaction of 1-Amino-2-benzoylpyridinium Tosylate (7) with Sodium Methoxide; Formation of 1-Aminopyridinium Perchlorate (11). A sodium methoxide solution prepared from sodium (108 mg, 2 mmol) in dry methanol (0.6 mL) was added at room temperature to a stirred solution of 1-amino-2-benzoylpyridinium tosylate (7; 0.37 g, 1 mmol) in dry methanol (10 mL). After being stirred for 10 min, the reaction mixture was treated with 70% perchloric acid (2 mL) and was evaporated to dryness. The residue was triturated with petroleum ether (3 × 10 mL) and the combined organic extracts were evaporated to dryness to give methyl benzoate (**10a**) as a colorless oil (70 mg, 51%; identified by comparison with an authentic sample).

The residue obtained from the petroleum ether treatment was then dissolved in water (20 mL), the solution was treated with charcoal, and the filtered clear solution was extracted with nitromethane (5 × 5 mL). The combined extracts were evaporated to dryness, the residue was dissolved in ethyl acetate (5 mL), and the precipitated crysals were filtered off. Recrystallization from acetonitrile–ether gave 40 mg (20%) of white needles, mp 198–201 °C (lit.[29] mp 203–204 °C).

Anal. Calcd for: $C_5H_7ClN_2O_4$ (194.58): C, 30.86; H, 3.63; N, 14.40. Found: C, 31.13; H, 3.84; N, 14.21. IR (KBr): 3170, 3100, 3040, 1610, 1500, 1480, 1100 cm^{-1}.

Reactions of 2-Amino-1-aroylisoquinolinium Salts 13a–c with Sodium Methoxide. General Procedure. A solution of sodium methoxide (120 mg, 2.2 mmol) in methanol (0.55 mL) was dropped into a stirred suspension of the appropriate 2-amino-1-aroylisoquinolinium salt (**13a–c**; 2 mmol) in methanol (10 mL) at room temperature. Stirring was continued for 10 min and then water (10 mL) was added and the separated crystals were filtered off and washed with methanol. In each case, the same product (**14**) was obtained (from **13a**, 0.24g, 86%, mp 165–167 °C; from **13b**, 0.21 g, 75%, mp 168–170 °C; from **13c**, 0.23 g, 82%, mp 162–165 °C). This compound was found to be identical with the product prepared according to the literature from 2-aminoisoquinolinium perchlorate and base (lit.[11] mp 164–166 °C).

Treatment of the mother liquor obtained above with water (50 mL) and extraction with chloroform (3 × 10 mL) afforded an oily residue, which was then dissolved in petroleum ether (20 mL), treated with charcoal, filtered, and evaporated to yield benzoic ester derivative depending on which starting compound was used (from **13a**, methyl benzoate, 0.15 g, 56%, oil: from **13b**, methyl 4-chlorobenzoate, 0.22 g, 65%, mp 40–42 °C; from **13c**, methyl 3-(trifluoromethyl)benzoate, 0.21 g, 60%, oil).

Reaction of 1-Amino-2-(4-chlorobenzoyl)quinolinium Tosylate (15) with Sodium Methylate. A solution of 1-amino-2-(4-chlorobenzoyl)quinolinium tosylate (**15**, 0.91 g, 2 mmol) in methanol (15 mL) and water (2 mL) was stirred at room temperature with a solution of sodium hydroxide (80 mg, 2 mmol) in water (0.5 mL) for 30 min. The precipitated crystals were filtered off and were recrystallized from benzene to give 0.16 g (55%) of pale yellow needles of **16**; mp 152–154 °C (lit.[11] mp 151–152 °C). The mother liquor of the reaction was worked up as in the previous case to give 0.15 g (44%) of methyl 4-chlorobenzoate; mp 40–42 °C.

1-Amino-3-(1-aminopyridin-1-ium-2-yl)pyrido[2,1-*f*]-*as*-triazinium Diperchlorate (20). A. Synthesis with Formamidinium Acetate. 1-Amino-2-cyanopyridinium perchlorate (**17**, 0.22 g, 1 mmol) was stirred with formamidinium acetate (0.1 g, 1 mmol) in dry acetonitrile (5 mL) at room temperature for 5 h. Then 70% perchloric acid (0.5 mL) and water (15 mL) were added to the reaction mixture, which was then extracted with nitromethane (3 × 5 mL). The extracts were evaporated and recrystallized from a mixture of acetonitrile and ether to give 70 mg (32%) of colorless crystals, mp 287–289 °C.

Anal. Calcd for $C_{12}H_{12}Cl_2N_6O_8$ (439.19): C, 32.82; H, 2.75; N, 19.14. Found: C, 33.14; H, 2.70; N, 18.99. IR (KBr): 3320, 3250, 3180, 3110, 3080, 3000, 2930, 2800, 2700, 1655, 1570, 1540, 1525, 1460, 1100 cm^{-1}. ^1H NMR (DMSO-d_6 + D_2O): 9.53 (dd, 1 H, H-6′), 9.11 (dd, 1 H, H-3′), 9.01 (dd, 1 H, H-6), 8.87 (t, 1 H, H-4′), 8.71 (dd, 1 H, H-9), 8.56 (m, 1 H, H-5′), 8.53 (m, 1 H, H-8), 8.22 (m, 1 H, H-7) ppm. ^{13}C NMR (DMSO-d_6): 158.46 (C-2′), 155.84 (C-3), 144.04 (C-4′), 141.86 (C-6′), 140.38 (C-6), 140.34 (C-8), 139.63 (C-1), 130.94 (C-9), 130.02 (C-7), 129.95 (C-5′), 129.44 (C-9a), 124.415 (C-3′) ppm.

B. Synthesis with Potassium Hydroxide. To a stirred solution of 1-amino-2-cyanopyridinium perchlorate (**17**) (0.22 g, 1 mmol) in 3 mL of acetonitrile was added dropwise a solution of potassium hydroxide (20 mg, 0.36 mmol) in ethanol (1 mL) in such a rate that every drop was added only after disappearance of the yellow color formed from the previous drop. Then 70% perchloric acid (0.1 mL) was added to the reaction mixture, and the resulting crystals were filtered off, and recrystallized from acetonitrile–ether to give 0.13 g (59%) of colorless crystals, mp 287–289 °C. This compound was found to be identical with the product obtained from **17** by the formamidinium acetate reaction described above.

2-Amino-1,2-dihydroisoquinolin-1(2*H*)-one (22). A solution of 2-amino-1-cyanoisoquinolinium tosylate (**21**; 1.7 g, 5 mmol) in water (50 mL) was added to an aqueous 20% sodium hydroxide solution (10 mmol) dropwise at room temperature. The resulting solution was filtered and extracted with dichloromethane (3 × 30 mL). The combined extracts were dried on magnesium sulfate and evaporated and the residue was recrystallized from *n*-hexane to give 0.48 g (58%) of white needles, mp 100–102 °C (lit.[22] mp 102 °C).

Anal. Calcd for $C_9H_8N_2O$ (160.18): C, 67.49; H, 5.03; N, 17.49. Found: C, 67.73; H, 5.15; N, 17.69.

1-Amino-1,2-dihydroquinolin-2(1*H*)-one (28). A solution of 1-amino-2-cyanoquinolinium perchlorate (**27**; 0.54 g, 2 mmol) in water (20 mL) was added dropwise to a stirred solution of sodium hydroxide (0.8 g, 20 mmol) in water (4 mL) at room temperature. The solution was filtered and extracted with dichloromethane (3 × 15 mL). The residue obtained from the combined extracts was recrystallized from benzene–petroleum ether to give 0.11 g (34%) of colorless needles; mp 126–128 °C (lit.[22] mp 128 °C).

Anal. Calcd for $C_9H_8N_2O$ (160.18): C, 67.49; H, 5.03; N, 17.49. Found: C, 67.65; H, 5.21; N, 17.35.

2-(2-Aminoisoquinolinium-1-yl)[1,2,4]triazolo[5,1-*a*]isoquinoline Perchlorate (26). A. Synthesis with Formamidinium Acetate. 2-Amino-1-cyanoisoquinolinium tosylate (**21**; 10.2 g, 30 mmol) was stirred with formamidinium acetate (3.1 g, 30 mmol) in dry acetonitrile (150 mL) at room temperature for 6 h. The solvent was evaporated, and the residue was dissolved in a mixture of water (40 mL) and ethanol (60 mL). Sodium perchlorate (20.0 g) and 70% perchloric acid (5 mL) were added to the solution, and the crystals were filtered and recrystallized from a mixture of acetonitrile (110 mL) and ether (50 mL) to give 4.6 g (74%) of beige needles, mp 213–215 °C.

Anal. Calcd for $C_{19}H_{14}ClN_5O_4$ (411.82): C, 55.42; H, 3.43; N, 17.01. Found: C, 55.88; H, 3.75; N, 17.15. IR (KBr): 3330, 3250, 3190, 3080, 1630, 1600, 1570, 1510, 1450, 1100 cm^{-1}. ^1H NMR (DMSO-d_6): 8.95 (d, $J_{5,6}$ = 7.3 Hz, 1 H, H-5), 8.82 (d, $J_{3',4'}$ = 7 Hz, 1 H, H-3′), 8.72 (d, 1 H, H-4′), 8.68 (s, 2 H, NH_2), 8.66 (dd, $J_{9,10}$ = 7.8 Hz, $J_{8,10}$ = 1.4 Hz, 1 H, H-10), 8.40 (d, $J_{5',6'}$ = 8.2 Hz, 1 H, H-5′), 8.33 (dd, $J_{7',8'}$ = 8.6 Hz, $J_{6',8'}$ = 1 Hz, 1 H, H-8′), 8.22 (dd, $J_{7,8}$ = 8 Hz, $J_{7,9}$ = 1.1 Hz, 1 H, H-7), 8.17 (t, $J_{6',7'}$ = 7 Hz, 1 H, H-6′), 7.98 (t, 1 H, H-7′), 7.97 (t, 1 H, H-8), 7.92 (t, $J_{8,9}$ = 7.5 Hz, 1 H, H-9), 7.85 (d, 1 H, H-6) ppm. ^{13}C NMR (DMSO-d_6): 151.48 (C-2), 149.75 (C-10b), 138.88 (C-1′), 134.43 (C-6′), 134.35 (C-4′a), 132.21 (C-3′), 131.81 (C-7′), 131.41 (C-6a), 131.09 (C-8), 129.17 (C-9), 128.37 (C-8′), 127.86 (C-7), 127.63 (C-5′), 127.56 (C-4′ and C-8′a), 125.43 (C-5), 123.91 (C-10), 121.18 (C-10a), 116.26 (C-6) ppm.

B. Synthesis with Sodium Methoxide. A solution of sodium methoxide (60 mg, 1.1 mmol) in methanol (0.3 mL) was added dropwise and very slowly (approximately within 20 min) to a solution of 2-amino-1-cyanoisoquinolinium tosylate (**21**; 0.34 g, 1 mmol) in methanol (10 mL). Stirring was continued for 3 h, then 70% perchloric acid (0.2 mL) and water (15 mL) were added, and the formed crystals were filtered off and were recrystallized from ethanol–ether to give 0.1 g (48%) of beige crystals found

to be identical with the sample obtained as described in the previous procedure.

***s*-Tetrazino[6,1-*a*:3,4-*a*']diisoquinoline (24).** 2-Amino-1-cyanoisoquinolinium tosylate (21; 0.68 g, 2 mmol) was added to a stirred solution of triethylamine (2 g, 2.75 mL, 20 mmol) in acetonitrile (7 mL) at room temperature. The reaction mixture was stirred for 1 h, and the crystals were filtered and recrystallized from dimethylformamide to give 0.16 g (58%) of green crystals, mp 261–262 °C (lit.[26] mp 263–265 °C).

Anal. Calcd for $C_{18}H_{12}N_4$ (284.33): C, 76.04; H, 4.25; N, 19.71. Found: C, 76.13; H, 4.12; N, 19.44. IR (KBr): 3090, 3050, 1610, 1580, 1530, 1480, 1440, 1420, 1310 cm^{-1}.

2-(1-Aminoquinolinium-2-yl)[1,2,4]triazolo[1,5-*a*]quinoline Perchlorate (29). 1-Amino-2-cyanoquinolinium perchlorate (27; 1.08 g, 4 mmol) was stirred in dry acetonitrile (20 mL) with formamidinium acetate (0.4 g, 4 mmol) at room temperature for 12 h. The reaction mixture was treated with 70% perchloric acid (0.4 mL), it was warmed up to boiling, mixed then with ether (10 mL), and cooled, and the precipitated crystals were recrystallized from a mixture of acetonitrile (15 mL) and water (1 mL) to give 0.31 g (38%) of beige crystals, mp 290–292 °C.

Anal. Calcd for $C_{19}H_{14}ClN_5O_4$ (411.82): C, 55.42; H, 3.43; N, 17.01. Found: C, 55.92; H, 3.71; N, 16.94. IR (KBr): 3260, 3090, 3040, 1640, 1610, 1540, 1445, 1080 cm^{-1}. ^1H NMR (DMSO-d_6): 9.60 (s, 2 H, NH_2), 9.07 (d, $J_{3',4'}$ = 8.8 Hz, 1 H, H-4'), 8.98 (d, 1 H, H-3'), 8.78 (d, $J_{7',8'}$ = 9 Hz, 1 H, H-8'), 8.68 (d, $J_{8,9}$ = 8.4 Hz, 1 H, H-9), 8.44 (dd, $J_{5',6'}$ = 8.3 Hz, $J_{5',7'}$ = 1.4 Hz, 1 H, H-5'), 8.38 (d, $J_{4,5}$ = 9.5 Hz, 1 H, H-5), 8.30 (t, $J_{6',7'}$ = 7.1 Hz, 1 H, H-7'), 8.23 (dd, $J_{6,7}$ = 8 Hz, $J_{6,8}$ = 1.2 Hz, 1 H, H-6), 8.07 (t, 1 H, H-6'), 8.04 (d, 1 H, H-4), 7.99 (t, $J_{7,8}$ = 7.2 Hz, 1 H, H-8), 7.79 (t, 1 H, H-7) ppm. ^{13}C NMR (DMSO-d_6): 154.11 (C-2), 148.70 (C-3a), 140.63 (C-4'), 138.30 (C-2'), 136.86 (C-8'a), 134.99 (C-7'), 133.93 (C-5), 132.08 (C-9a), 131.27 (C-8), 130.65 (C-6'), 129.69 (C-5'), 129.40 (C-6), 129.24 (C-4'a), 127.54 (C-7), 123.64 (C-5a), 121.97 (C-3'), 118.79 (C-8'), 115.79 (C-9), 114.19 (C-4) ppm. Result of the homonuclear NOE difference experiment: irradiation at the NH_2 singlet at 9.60 ppm resulted in a 16% intensity enhancement at H-8' at 8.78 ppm.

***s*-Tetrazino[1,6-*a*:4,3-*a*']diquinoline (30).** Triethylamine (1.0 g, 1.36 mL, 10 mmol) was added to a solution of 1-amino-2-cyanoquinolinium perchlorate (27; 0.27 g, 1 mmol) in acetonitrile (6 mL) at room temperature. After stirring for 3 h, water (15 mL) was added to the reaction mixture and the precipitated crystals were filtered off, washed with water, and recrystallized from a mixture of acetonitrile (5 mL) and dimethylformamide (1 mL) to give 50 mg (35%) of beige needles of 30; mp 278–281 °C (lit.[26] mp 271–272 °C).

Anal. Calcd for $C_{18}H_{12}N_4$ (284.33): C, 76.04; H, 4.25; N, 19.71. Found: C, 75.71; H, 4.02; N, 20.18.

General Procedure for Preparation of Dimers 33a–d. To a solution or suspension of the appropriate *N*-amino salt 32 (3.0 mmol) was added a 0.4 N sodium hydroxide solution in methanol (9 mL, 3.6 mmol) with stirring. The product precipitated immediately and was filtered off in 5 min. Recrystallization from dimethylformamide afforded crystalline needles.

6,14-Bis(methoxycarbonyl)-8,8a,16,16a-tetrahydro-[1,2,4,5]tetrazino[6,1-*a*:3,4-*a*']diisoquinoline (33a). Yield: 0.44 g (72%), mp 255–257 °C, colorless needles.

Anal. Calcd for $C_{22}H_{20}N_4O_4$ (404.43): C, 65.34; H, 4.98; N, 13.85. Found: C, 65.09; H, 4.75; N, 13.79. MS: *m/z* 404 (M^+). IR: 3280, 3060, 3000, 2930, 1700, 1600, 1470, 1430, 1410 cm^{-1}.

6,14-Bis(4'-chlorobenzoyl)-8,8a,16,16a-tetrahydro-[1,2,4,5]tetrazino[6,1-*a*:3,4-*a*']diisoquinoline (33b). Yield: 0.56 g (66%), mp >300 °C, yellow needles.

Anal. Calcd for $C_{32}H_{22}N_4O_2Cl_2$ (565.47): C, 67.97; H, 3.92; N, 9.91. Found: C, 67.81; H, 3.78; N, 9.80. MS: *m/z* 565 (M^+). IR (KBr): 3280, 3080, 1640, 1580, 1460, 1430 cm^{-1}.

6,14-Bis[3'-(trifluoromethyl)benzoyl]-8,8a,16,16a-tetrahydro[1,2,4,5]tetrazino[6,1-*a*:3,4-*a*']diisoquinoline (33c). Yield: 0.55 g (58%), mp 214–216 °C, yellow needles.

Anal. Calcd for $C_{34}H_{22}F_6N_4O_2$ (632.58): C, 64.56; H, 3.51; N, 8.86. Found: C, 64.38; H, 3.30; N, 8.81. MS: *m/z* 632 (M^+). IR (KBr): 3280, 3080, 1640, 1560, 1460, 1430 cm^{-1}. ^1H NMR (DMSO-d_6): 8.29 (d, 1 H, H-4'), 8.19 (s, 1 H, H-2'), 8.00 (d, 1 H, H-6'), 7.79 (t, 1 H, H-5'), 7.20 (t, 1 H, H-3), 7.06 (d, 1 H, H-4), 7.00 (t, 1 H, H-2), 6.45 (d, 1 H, H-1), 5.99 (d, 1 H, H-9a), 5.72 (d, 1 H, H-8), 5.66 (s, 1 H, H-5) ppm.

6,14-Dicyano-8,8a,16,16a-tetrahydro[1,2,4,5]tetrazino[6,1-*a*:3,4-*a*']diisoquinoline (33d). Yield: 0.35 g (69%), mp 246–248 °C, colorless crystals.

Anal. Calcd for $C_{20}H_{14}N_6$ (338.38): C, 70.99; H, 4.17; N, 24.84. Found: 70.85; H, 3.98; N, 24.61. MS: *m/z* 338 (M^+). IR (KBr): 3280, 3070, 2210, 1600, 1470, 1430 cm^{-1}. ^1H NMR (DMSO-d_6): 7.40–7.18 (m, 4 H, H-1,2,3,4), 6.44 (s, 1 H, H-5), 6.35 (d, 1 H, H-9a), 5.93 (d, 1 H, H-8) ppm.

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Registry No. **1a**, 82319-27-5; **1b**, 120332-65-2; **2**, 120332-59-4; **3**, 120332-60-7; **3** (free base), 50458-78-1; **4**, 120332-61-8; **5**, 120332-63-0; **5** (free base), 4491-33-2; **6**, 120332-64-1; **7**, 82319-60-6; **10a**, 93-58-3; **10b**, 1126-46-1; **10c**, 2557-13-3; **11**, 28460-20-0; **12c**, 120332-66-3; **13a**, 97110-14-0; **13b**, 82319-68-4; **13c**, 120332-85-6; **14**, 31436-50-7; **15**, 82319-82-2; **16**, 7184-52-3; **17**, 120332-67-4; **20**, 120332-69-6; **21**, 120332-71-0; **21** (free base), 1198-30-7; **22**, 66193-87-1; **24**, 226-65-3; **26**, 120332-73-2; **27**, 120332-75-4; **27** (free base), 1436-43-7; **28**, 26539-38-8; **29**, 120332-77-6; **30**, 13090-26-1; **31a**, 27104-73-0; **31b**, 82319-66-2; **31c**, 120332-79-8; **31d**, 26947-41-1; **32a**, 120360-47-6; **32b**, 82319-29-7; **32c**, 120332-81-2; **32d**, 120332-83-4; **33a**, 120332-78-7; **33b**, 120332-86-7; **33c**, 120332-87-8; **33d**, 120332-88-9; 3-$CF_3C_6H_4Br$, 401-78-5; 4-ClC_6H_4Br, 106-39-8.

Supplementary Material Available: Atomic coordinate table for **26** (1 page). Ordering information is given on any current masthead page.