# PROPERTIES OF THE AMINO GROUP IN N-(AMINOPHENYL)PYRIDINIUM PERCHLORATES

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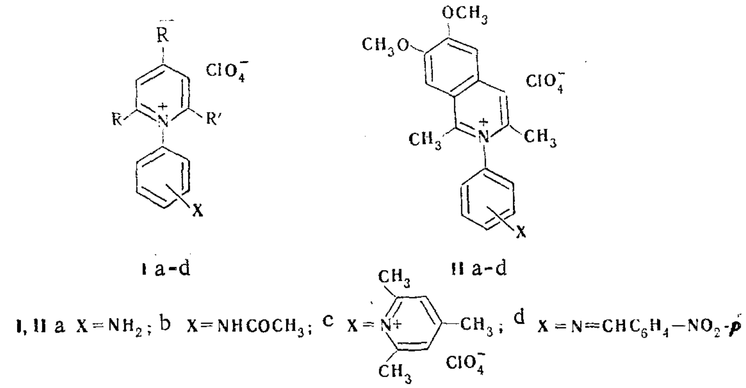
The pyridinium ring as a substituent in aniline is an electron acceptor, the effect of which is comparable to the effect of $NO_2$ and $\overset{+}{N}(CH_3)_3$ groups. Correlation of the reactivities with the basicities of the amino groups is not observed in the investigated reactions of N-(aminophenyl)pyridinium perchlorates with some electrophilic reagents, inasmuch as steric factors apparently play a greater role.

In our preceding communication [1] we showed that pyrylium salts readily react with arylenediamines to give the readily accessible N-(aminoaryl)pyridinium salts. It seemed of interest to study the effect of the pyridinium ring as a substituent on the basicity and reactivity of the amino group in salts Ia and IIa.



I a-d

II a-d

I, II a X=NH$_2$; b X=NHCOCH$_3$; c X=N+ ... —CH$_3$; d X=N=CHC$_6$H$_4$—NO$_2$-*p*

With this in mind, we measured the basicity constants of the amines and investigated their reactions with acetic anhydride, 2,4,6-trimethylpyrylium perchlorate, and p-nitrobenzaldehyde.

It is known [2, 3] that the pyridinium ring realizes transmission of electronic effects to aryl systems bonded with an "onium" center via an inductive mechanism. The magnitude of this effect can be estimated by calculating the σ constants of N-aryl-substituted pyridinium compounds. Substituting the log K values of I and II into the Hammett correlation equation for a series of substituted anilinium ions in acetonitrile [4], $\log K = -10.59 + 4.838\sigma$, we obtain the Hammett σ constants of pyridinium substituents (Table 1).

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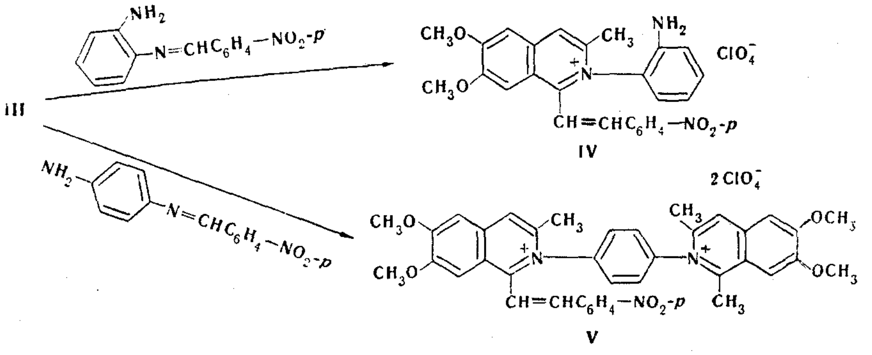
The effect of substituents in the pyridinium ring is exerted on the basicities of I and II with an amino group in the meta position. Thus the basicities of the amines increase when methyl groups in the pyridinium ring are replaced by phenyl groups or in the case of salts II condensed with veratrole. This may be explained by the fact that phenyl substituents, having labile π electrons and being in conjugation with the pyridinium ring [5], partially compensate the positive charge of the latter. The effect of pyridinium substituents is almost completely smoothed out for I with an amino group in the para position (Table 1). This effect is retained to a small degree only for p-amino compound II. The closeness of the positively charged substituent in the o-amino compounds sharply reduces the basicity of the amino group, so that it cannot be measured by potentiometric titration in acetonitrile.

A similar effect of a strong electron acceptor — the nitro group — is manifested in nitroanilines: the $pK_a$ values of the m-nitro isomer, the p-nitro isomer, and the o-nitro isomer are 7.79 [4], 6.21 [4], and 4.85 [6], respectively. N,N,N-Trimethylammonium-p-phenylenediamine has a $pK_a$ value of 7.29, which corresponds to a $\sigma$ constant of 0.68 for p-$N^+(CH_3)_3$.

In an investigation of the reactions of amines I and II with electrophilic reagents we found that they are readily acetylated at the amino group. It was also demonstrated that all meta and para derivatives condense with 2,4,6-trimethylpyrylium perchlorate. Only o-amino compounds do not undergo this reaction because of the steric effect of the substituents of the pyridinium and pyrylium rings. A decrease in the yield of azomethines of o-amino compounds I in the reaction with p-nitrobenzaldehyde is probably observed for this same reason. However, no explanation has been found for the depressed yield of m- and p-azomethines when the methyl groups in the pyridinium ring are replaced by aryl groups nor for the complete deactivation of the amino groups in salts II during reaction with p-nitrobenzaldehyde. Despite the fact that the conditions of the latter reaction were varied over broad limits, the starting perchlorates were isolated unchanged in all cases. We made attempts to obtain the desired azomethines by reaction of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (III) with phenylenediamine monoazomethines. However, IV and V were obtained unexpectedly in this case.



It is known [7] that the azomethines of anilines and aromatic aldehydes react with pyrylium salts via a scheme involving dipolar 1,2-cycloaddition to give N-arylpyridinium salts and an aldehyde molecule, which may then further condense at the active methyl group. The transformation with perchlorate III apparently proceeds preferably at the —N=CH— group rather than at the amino group. In the reaction of III with N-(p-nitrobenzal)-p-phenylenediamine the first product formed is the p-aminoaryl derivative, which may then react with the pyrylium salt to give V. Perchlorate IV does not undergo this reaction. Thus we were unable to obtain the expected azomethines.

It follows from the present investigation that a correlation between the basicities of amino groups that differ only slightly (0.2-0.4 $pK_a$ units) and their reactivities is not observed, inasmuch as steric factors apparently play a more substantial role in this case.

TABLE 1. Ionization Constants ($pK_a$), σ Values of Pyridinium Rings, and Yields of N-Substituted Amines I and II

| Compound | R | R′ | Position of the $NH_2$ group | $pK_a$ | σ value of the onium substituent | Yield, % | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Ib | Id | Ic |
| I | $CH_3$ | $CH_3$ | o— | — | — | Quantitative | 75 | 0 |
| | $CH_3$ | $CH_3$ | m— | 7,27±0,03 | 0,69 | Quantitative | 96 | Quantitative |
| | $CH_3$ | $CH_3$ | p— | 7,18±0,03 | 0,71 | 80 | 96 | Quantitative |
| | $C_6H_5$ | $CH_3$ | o— | — | — | 75 | 0 | 0 |
| | $C_6H_5$ | $CH_3$ | m— | 7,43±0,03 | 0,65 | 82 | 50 | 74 |
| | $C_6H_5$ | $CH_3$ | p— | 7,21±0,03 | 0,70 | 79 | 47 | 70 |
| | $C_6H_5$ | $C_6H_5$ | o— | — | — | Quantitative | 26 | 0 |
| | $C_6H_5$ | $C_6H_5$ | m— | 7,56±0,03 | 0,63 | Quantitative | 67 | Quantitative |
| | $C_6H_5$ | $C_6H_5$ | p— | 7,17±0,03 | 0,71 | 80 | 41 | Quantitative |
| | | | | | | IIb | IId | IIc |
| II | — | | o— | — | — | 82 | 0 | 0 |
| | — | | m— | 7,46±0,06 | 0,65 | 96 | 0 | Quantitative |
| | — | | p— | 7,40±0,03 | 0,66 | Quantitative | 0 | 62* |

*A second compound with an unestablished structure was isolated.

## EXPERIMENTAL

The $pK_a$ values were measured by potentiometric titration in absolute acetonitrile by the method in [8] at 25 ± 0.1°. The IR spectra of mineral-oil suspensions of the compounds were recorded with a UR-20 spectrometer.

N-(Aminophenyl)isoquinolinium Perchlorates (II). These compounds were obtained in quantitative yields by refluxing equimolecular amounts of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate [9] and o-, m-, or p-phenylenediamines in ethanol for 1 h. They were light-yellow crystalline substances, data on which are presented in Table 2. IR spectrum, $\text{cm}^{-1}$: 1640, 1570 (pyridinium ring), 3450, 3300 ($NH_2$).

N-(Acetylaminophenyl)pyridium Perchlorates (Ib, IIb). These compounds were obtained by refluxing the original amines in acetic anhydride for 1 h (Table 2).

N-(1-Collidiniumphenyl)pyridinium Diperchlorates (Ic, IIc). These compounds were obtained by refluxing equimolecular amounts of I and II ($X = NH_2$) and 2,4,6-trimethylpyrylium perchlorate in ethanol for 1 h. Data on these compounds are presented in Table 2.

N-(p-Nitrobenzalaminophenyl)pyridinium Perchlorates (Id). These compounds were obtained by refluxing an equimolecular mixture of amine and p-nitrobenzaldehyde in ethanol for 1 h. The products were yellow crystalline substances (Table 2). IR spectrum: 1570, 1640 $\text{cm}^{-1}$ (pyrylium ring) the absorption band of an $-N{=}CH-$ group is found as an inflection on the absorption band of the pyridinium ring.

1-(p-Nitrostyryl)-3-methyl-6,7-dimethoxy-2-(o-aminophenyl)isoquinolinium Perchlorate (IV). This compound was obtained by refluxing equimolecular amounts of o-phenylenediamine monoazomethine with III in ethanol for 1 h, after which the mixture was cooled to precipitate an orange substance with mp 209-210° (from alcohol) in 71% yield. Found: C 57.2; H 4.9; Cl 5.9; N 7.4%. $C_{26}H_{24}ClN_3O_8$. Calculated: C 57.6; H 4.5; Cl 6.5; N 7.7%. IR spectrum, $\text{cm}^{-1}$: 3470, 3385 ($NH_2$), 1640, 1570 (pyridinium ring). The product decolorized bromine water.

N-(1,3-Dimethyl-6,7-dimethoxyisoquinolinium-2-phenyl)-1-(p-nitrostyryl)-3-methyl-6,7-dimethoxyisoquinolinium Diperchlorate (V). This compound was similarly obtained, and the orange product with mp 245-246° (from ethanol–nitromethane) was obtained in quantitative yield. IR spectrum: 1640, 1570 $\text{cm}^{-1}$ (pyridinium ring). The absorption

TABLE 2. N-Arylpyridinium Perchlorate Derivatives I and II

| Compound | R | R′ | Position of the group | mp, °C | Crystallization solvent | Empirical Formula | Found, % |  |  | Calc., % |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | C | H | Cl | C | H | Cl |
| Ib | $CH_3$ | $CH_3$ | o- | 172 | ethanol | $C_{16}H_{19}ClN_2O_5$ | 54,4 | 5,6 | 10,0 | 54,1 | 5,4 | 9,9 |
|  | $CH_3$ | $CH_3$ | m- | 181—182 | " | $C_{16}H_{19}ClN_2O_5$ | 54,1 | 5,5 | 9,6 | 54,1 | 5,4 | 9,9 |
|  | $CH_3$ | $CH_3$ | p- | 162—163 | " | $C_{16}H_{19}ClN_2O_5$ | 53,9 | 5,4 | 10,1 | 54,1 | 5,4 | 9,9 |
|  | $C_6H_5$ | $C_6H_5$ | o- | 153—154 | propanol | $C_{31}H_{25}ClN_2O_5$ | 68,3 | 5,0 | 6,2 | 68,8 | 4,6 | 6,6 |
|  | $C_6H_5$ | $C_6H_5$ | m- | 236—237 | methanol | $C_{31}H_{25}ClN_2O_5$ | 68,3 | 4,8 | 6,3 | 68,8 | 4,6 | 6,6 |
|  | $C_6H_5$ | $C_6H_5$ | p- | 252—253 | ethanol | $C_{31}H_{25}ClN_2O_5$ | 68,7 | 4,5 | 6,9 | 68,8 | 4,6 | 6,6 |
|  | $C_6H_5$ | $CH_3$ | o- | 132—133 | water | $C_{26}H_{23}ClN_2O_5$ | 64,9 | 5,3 | 7,7 | 65,2 | 4,8 | 7,4 |
|  | $C_6H_5$ | $CH_3$ | m- | 147—148 | " | $C_{26}H_{23}ClN_2O_5$ | 64,8 | 5,3 | 7,0 | 65,2 | 4,8 | 7,4 |
|  | $C_6H_5$ | $CH_3$ | p· | 252—253 | " | $C_{26}H_{23}ClN_2O_5$ | 64,9 | 5,1 | 7,1 | 65,2 | 4,8 | 7,4 |
| Id | $CH_3$ | $CH_3$ | o- | 213—214 | ethanol | $C_{21}H_{20}ClN_3O_6$ | 57,0 | 4,9 | 7,8 | 56,5 | 4,5 | 8,0 |
|  | $CH_3$ | $CH_3$ | m- | 202—203 | methanol | $C_{21}H_{20}ClN_3O_6$ | 56,7 | 4,5 | 8,4 | 56,5 | 4,5 | 8,0 |
|  | $CH_3$ | $CH_3$ | p- | 230—231 | methanol | $C_{21}H_{20}ClN_3O_6$ | 56,8 | 4,6 | 8,2 | 56,5 | 4,5 | 8,0 |
|  | $C_6H_5$ | $C_6H_5$ | o- | 161—162 | ethanol | $C_{36}H_{26}ClN_3O_6$ | 68,6 | 4,4 | 6,0 | 68,4 | 4,1 | 5,6 |
|  | $C_6H_5$ | $C_6H_5$ | m· | 168—169 | " | $C_{36}H_{26}ClN_3O_6$ | 68,0 | 4,4 | 6,0 | 68,4 | 4,1 | 5,6 |
|  | $C_6H_5$ | $C_6H_5$ | p | 177—178 | " | $C_{36}H_{26}ClN_3O_6$ | 68,1 | 3,6 | 5,4 | 68,4 | 4,1 | 5,6 |
|  | $C_6H_5$ | $CH_3$ | m- | 153—154 | isobutanol | $C_{31}H_{24}ClN_3O_6$ | 65,1 | 4,7 | 6,6 | 65,3 | 4,2 | 6,2 |
|  | $C_6H_5$ | $CH_3$ | p | 162—163 | " | $C_{31}H_{24}ClN_3O_6$ | 65,2 | 4,8 | 6,8 | 65,3 | 4,2 | 6,2 |
| Ib | $CH_3$ | $CH_3$ | m- | >350 (dec.) | Water | $C_{22}H_{26}Cl_2N_2O_4$ | 57,7 | 5,3 | 15,1 | 58,2 | 5,7 | 15,6 |
|  | $CH_3$ | $CH_3$ | p- | >350 (dec.) | " | $C_{22}H_{26}Cl_2N_2O_4$ | 58,0 | 5,3 | 15,5 | 58,2 | 5,7 | 15,6 |
|  | $C_6H_5$ | $CH_3$ | m- | >350 (dec.) | nitromethane | $C_{32}H_{30}Cl_2N_2O_4$ | 66,0 | 4,9 | 11,8 | 66,5 | 5,2 | 12,2 |
|  | $C_6H_5$ | $CH_3$ | p | >350 (dec.) | " | $C_{32}H_{30}Cl_2N_2O_4$ | 66,2 | 4.9 | 12,0 | 66,5 | 5,2 | 12,2 |
|  | $C_6H_5$ | $C_6H_5$ | m- | >350 (dec.) | glacial acet. acid | $C_{37}H_{32}Cl_2N_2O_4$ | 68,9 | 5,1 | 11,3 | 69,4 | 5,4 | 11,8 |
|  | $C_6H_5$ | $C_6H_5$ | p· | >350 (dec.) | glacial acet. acid | $C_{37}H_{32}Cl_2N_2O_4$ | 69,0 | 4,9 | 11,5 | 69,4 | 5,4 | 11,8 |
| IIa |  |  | o- | 292—293 | nitromethane | $C_{19}H_{21}ClN_2O_6$ | 55,6 | 5,3 | 8,8 | 55,8 | 5,2 | 8,7 |
|  |  |  | m- | 254—255 | " | $C_{19}H_{21}ClN_2O_6$ | 55,4 | 5,1 | 8,7 | 55,8 | 5,2 | 8,7 |
|  |  |  | p- | 277—278 | " | $C_{19}H_{21}ClN_2O_6$ | 55,6 | 5,4 | 8,3 | 55,8 | 5,2 | 8,7 |
| IIb |  |  | o- | 226—227 | glacial acet. acid | $C_{21}H_{23}ClN_2O_7$ | 55,9 | 5,3 | 7,9 | 55,9 | 5,1 | 7,9 |
|  |  |  | m- | 202—203 | glacial acet. acid | $C_{21}H_{23}ClN_2O_7$ | 55,5 | 5,4 | 7,6 | 55,9 | 5,1 | 7,9 |
|  |  |  | p· | 200—201 | glacial acet. acid | $C_{21}H_{23}ClN_2O_7 \cdot H_2O$ | 53,8 | 5,5 | 7,0 | 53,8 | 5,4 | 7,9 |
| IIc |  |  | m· | 203—204 | glacial acet. acid | $C_{27}H_{31}Cl_2N_2O_{10}$ | 52,3 | 5,5 | 11,4 | 52,8 | 5,1 | 11,5 |
|  |  |  | p· | >350 (dec.) | glacial acet. acid | $C_{27}H_{31}Cl_2N_2O_{10}$ | 52,7 | 5,3 | 11,1 | 52,8 | 5,1 | 11,5 |

band of the —HC=CH— bond is found as an inflection on the absorption band of the pyridinium ring. Found: C 55.1; H 4.5; Cl 7.9; N 5.0%. $C_{39}H_{37}Cl_2N_3O_{14}$. Calculated: C 55.6; H 4.4; Cl 8.4; N 5.0%. The product decolorized bromine water.

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