N-ANIONS OF HETEROAROMATIC AMINES

V.* INVESTIGATION OF THE STRUCTURE OF SODIUM SALTS OF N-HETEROAROMATIC AMINES BY MEANS OF IR SPECTROSCOPY

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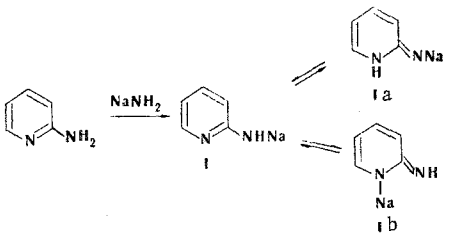
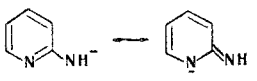
It is shown in four examples that the sodium salts of N-heteroaromatic amines exist in the amino form in the crystalline state.

Despite the large number of studies devoted to the structures of α- and γ-amino derivatives of nitrogen heterocycles [2], as far as we know, there has been no information available regarding the structure of their sodium salts up until now, whereas the sodium salts of N-heteroaromatic amines (SSHA) are widely used in laboratory practice for mono- and dialkylation of the NH_2 group, oxidation of the NH_2 group, the synthesis of heterocyclic azo compounds, etc. [3]. Theoretically, SSHA may have one of three structures (I, Ia, or Ib), two of which (Ia and Ib) are derivatives of the imino form, while one (I) is a derivative of the amino form.



I Ia Ib

Structures I and Ia differ with respect to the position of the proton (prototropy), while I and Ib differ with respect to the position of the sodium ion (metallotropy). Of course, in this case one can speak of metallotropy only with reservations, since in solution, because of ionization of the polar N—Na bond, the particles of I and Ib should form one common mesomeric ion, the distribution of charge in which is intermediate between limiting structures II and IIa.†



II IIa

In crystals, however, the structures of I and Ib may differ because of association of the Na^+ ion into an intimate ion pair with an exocyclic or endocyclic N atom.

In the present study, we have investigated the structures of the sodium salts of 2-aminopyridine (I), 2-amino-1-methyl- (V) and 2-amino-1-ethylbenzimidazoles (VII), 1-methyl-2-aminoperimidine (IX), and

* See [1] for communication IV.

† Kvartsov has described a case of metallotropy of the Ia⇌Ib type for the phenylmercury derivative of 2-phenylsulfonamidopyridine [4].

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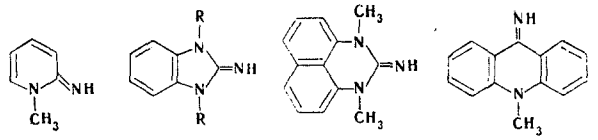
TABLE 1. Conditions for the Preparation of Sodium Salts of N-Heteroaromatic Amines (SSHA)

Compound	Solvent	$NaNH_2$, mole	Temp.* °C	Reaction time, h-min	Appearance
XIII	o-Xylene	1,5	120	2—30	Yellowish low-melting crystals
I	o-Xylene	1,7	120	2—30	Rose-colored crystals
V	Dimethylaniline	1,75	145	2—30	Colorless crystals
IX	o-Xylene	2,5	150	4—45	Colorless crystals
XI	Dimethylaniline	1,5	150—200	2—0	Yellow crystals

* Bath temperature.

9-aminoacridine (XI) by IR spectroscopy. The amines themselves and their N-methyl derivatives (Table 2) and imines (XIV-XVII) were used as model compounds to solve the problem of the structure of the SSHA.



XIV XV a,b XVI XVII XV a R = CH_3; b R = C_2H_5

To obtain the SSHA, the amine was subjected to the action of (1) sodium in liquid ammonia, (2) sodium amide in liquid ammonia, or (3) sodium amide in an aprotic solvent (xylene or dimethylaniline). In the first and second cases, the SSHA were isolated by evaporation of the liquid ammonia without access to atmospheric moisture. The crystalline residue was washed repeatedly in an inert atmosphere with benzene and ether and dried and was considered to be the sodium salt of the amino compound. In the third case, the SSHA precipitated directly from solution and was then worked up as in the other cases. It was established by IR spectroscopy that all three methods lead to identical samples of the salts. The IR spectra of the SSHA obtained primarily via the third method are subsequently compared.

In working with aprotic solvents, it is convenient to observe the course of the ionization of the NH_2 group from the amount of ammonia evolved. For all of the amines, the reaction proceeds initially rapidly, and the yield of SSHA reaches 58-85% after 30-60 min. After this, the process slows down abruptly and gradually ceases. In the long run, when the reaction is carried out in dimethylaniline (DMA), the amount of evolved ammonia is close to the theoretical amount, while it does not exceed 74-89% of the theoretical amount in o-xylene. The incompleteness of the conversion in xylene is surely explained by the heterogeneous character of the reaction conditions and the inertness of xylene itself, owing to which the SSHA formed gradually coats the surface of the sodium amide and removes it from the reaction. Evidence for this is, for example, the fact that the percent of conversion of the amine to the salt in o-xylene decreases as the area of the SSHA molecule increases (I < V < IX) and amounts to 89, 75, and 74%, respectively, after heating for 2 h. On the other hand, DMA, which is to some degree capable of solvating metal cations (through the N atom) and is capable of at least partially purifying the sodium amide surface by removal of the precipitated salt, fosters the completion of the ionization process. Nevertheless, the incompleteness of the reaction in xylene did not interfere with the measurements, since the unchanged amine was usually readily (except for salt IX) washed out of the SSHA with benzene. The conditions for the preparation of SSHA in xylene and DMA are presented in Table 1.

Two types of sodium amide—obtained by low- and high-temperature methods [5] — were used in the synthesis of the SSHA. Judging from their IR spectra, both $NaNH_2$ samples are absolutely identical. The samples contain 80-85% pure material. The chief impurity is sodium hydroxide, which has several peaks at 3600 cm^{-1}, of which the most intense peak is at 3640 cm^{-1}. Sodium amide itself has three intense characteristic bands at 3264, 3218, and 1540 cm^{-1}, which are related to vibrations of the amino group of the ν_{as}, ν_s, and δ type, respectively.

Because of the use of excess sodium amide and the presence in it of impurities, the SSHA were not obtained in analytically pure form. It also does not seem possible to purify them by recrystallization. The criterion for the formation of SSHA was the liberation of ammonia during the reaction (ammonia is not evolved when $NaNH_2$ is heated in DMA or xylene in the absence of the amine), and the major factor was the IR spectrum itself of the salt: the absence in it of ν_{as} and ν_s bands of a primary amino group at

TABLE 2. Absorption-Band Frequencies in the IR Spectra of Sodium Salts of N-Heteroaromatic Amines and N-Methylated Amines in Mineral Oil (cm^{-1})*

Compound	Name	ν_{N-H}	δ_{N-H}	ν_{ring}	ν_{ring-N}	$\delta_{C-H(ring)}$	$\nu_{C-H(ring)}$	Ring breathing vibrations
III†	2-Methylaminopyridine	3440(3) 3275(5) 3153(1,5)	1526	1608(10) 1577(6,5) 1500(9)	1334(5) 1290(6,5)	1160(7) 1083(5)	778(8,5) 740(7,0) 704(3)	985(3)
I	2-Sodioaminopyridine	3465(2) 3380(2) 3280(1)	1545(7)	1605(10) 1570(6) 1500(10)	1340(10) 1280(8)	1155(8) 1093(3)	850(5) 780(9) 740(9) 718(5)	983(9)
IV	1-Methyl-2-methyliminobenzimidazole	3180(4, broad)	1535(7)	1625(9) 1610(9,5) 1585(10)	1320(4) 1288(8) 1245(8,5) 1225(2)	1152(3) 1130(4,5) 1098(1,5)	760(4) 740(9)	1015(4)
V	1-Methyl-2-sodioaminobenzimidazole	3280(3)	1525(8)	1615(4) 1595(5) 1557(10)	— 1296 1250 1226	1152(4) 1125(3) 1095(1,5)	767(5) 732(6) 720(7)	1020
VI	1-Ethyl-2-methylaminobenzimidazole	3195(4,broad)	—	1625(9,5) 1612(9,5) 1580(10)	1280(8) 1245(7)	1195 1150(3) 1135(6) 1100(2,5) 1088(3)	767(3) 745(9)	1020(3)
VII	1-Ethyl-2-sodioaminobenzimidazole	3329(3) 3180(3, broad)	—	1627(2) 1650(4) 1616(3) 1600(3) 1555(10)	1355(4) 1330(1) 1292(8) 1245(4)	1195(3) 1130(7) 1100(3) 1087(2)	767(7) 753(8) 740(9)	1020(2)
VIII	1-Methyl-2-methylaminoperimidine	3457(3)	—	1628(6) 1588(10) 1547(7)	1352(4) 1336(5) 1315(4) 1228(2)	1200(4) 1180(1) 1152(2) 1120(1) 1080(1) 1048(2) 1020(2)	824(4) 770(6) 720(2)	—
IX	1-Methyl-2-sodioaminoperimidine	3378(3)	—	1626(7) 1600(8) 1555(9) 1510(10)	1352(8) 1343(3) 1320(7) 1300(6) 1227(6)	1200(6) 1180(2) 1152(2) 1120(1) 1080(1) 1057(5) 1032(2)	820(8) 770(9) 750(8) 728(3)	—
X	9-Methylaminoacridine	3250(5, broad)	—	1620(5) 1570(10) 1530(9)	1360(7) 1260(7)	1160(4) 1142(6)	850(2) 765(10) 730(2)	980(2) 955(2) 938(2)
XI	9-Sodioaminoacridine	3480(6)	1560 (shoulder)	1620(7,5) 1570(8,5) 1520(7)	1345(8) 1308(4) 1265(8)	1170(5) 1160(6) 1125(2) 1030(1)	860(3) 762(6) 750(10) 730(4)	980(3) 960(3) 940(2) 920(2)
XII†	N-Methylaniline	3420(7)	1482(4)	1610(10) 1520(9)	1326(8)	1185(7) 1158(6) 1133(2) 1080(5) 1030(2)	758(10) 700(9)	998(4)
XIII	N-Sodioaniline	3390(4)	—	1590(10)	1345(8) 1300(10)	1175(9) 1150(8) (плечо) 1125(5) 1068(6) 1025(5)	755(9) 700(9)	987(9)

* The relative intensity on an arbitrary 10-point scale is indicated in parentheses.

† This is the spectrum of a liquid film.

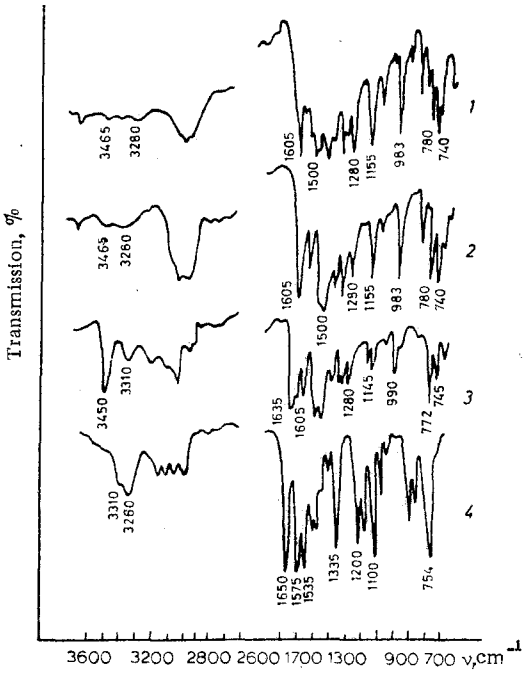
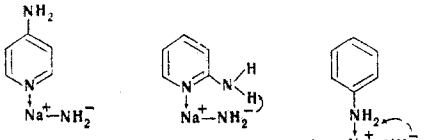


Fig. 1. IR spectra of 2-aminopyridine derivatives: 1) sodium salt obtained from the amine via method A; 2) sodium salt from the Chichibabin reaction; 3) 2-aminopyridine; 4) 1-methyl-2-pyridonimine.

3200-3500 cm^{-1} and of a δ band at 1640 ± 30 cm^{-1} attested to conversion of the amine to an SSHA. Decomposition of the SSHA with water gave an extremely pure starting amine; this proved the absence in the salt of a considerable amount of organic impurities. When there was an appreciable amount of $NaNH_2$ present in an SSHA sample, the bands of the former were very readily distinguished from the IR spectral bands belonging to the sodium salt molecule.

An attempt was also made to obtain the sodium salts of aniline and 4-aminopyridine. Aniline readily forms a sodium salt on brief heating with sodium amide in o-xylene. Despite the fact that the sodium salt of 4-aminopyridine has been repeatedly used to carry out various reactions in solution [6], we did not find information regarding its isolation in the crystalline form in the literature. Chichibabin and Osetrova were unable to obtain this salt on heating 4-aminopyridine in ether [7]. According to our observations, ionization occurs very slowly in xylene and dimethylaniline at 140-170° (the temperature was not raised to a higher level in order to avoid amination of the pyridine ring). Although ammonia was also evolved under these conditions, primarily the amine is present in a sample that might have been taken for the sodium salt, judging from the IR spectrum. A similar pattern is observed in the action of sodium or sodium amide in liquid ammonia, although there is no doubt that an N-anion is formed in solution in this case [6]. Thus we were unable to obtain the sodium salt of 4-aminopyridine in the crystalline state. It is interesting that the sodium salt of 9-aminoacridine is formed with just as much difficulty. We obtained it by heating 9-aminoacridine with $NaNH_2$ in DMA at 150-200°.

The difficulty in the ionization of the γ-amino group in aprotic solvents may be due to sorption of the amine molecule on the $NaNH_2$ surface through coordination of the pyridine N atom with the Na^+ ion (XVIII). It is clear that the remoteness of the amino group from the NH_2^- ion in complex XVIII will markedly hinder salt formation. On the other hand, sorption of the XIX type for α-amino derivatives of nitrogen heterocycles should be conducive to ionization of the NH_2 group.



The amine nitrogen itself (XX) can coordinate with the Na^+ ion. This sort of coordination will result in an increase in the acidity of the N–H bonds and will considerably facilitate the formation of the sodium salt.

IR Spectra of the Sodium Salts

Suspensions in mineral oil or liquid films were used to measure the spectra of the SSHA and model compounds (Figs. 1-3). The assignment of some of the absorption bands is presented in Table 2.

In the 3200-3500-cm^{-1} Region. The majority of the SSHA have one sharp peak of average intensity in this range; this peak undoubtedly corresponds to the stretching vibrations of the N–H bond in unassociated –NH–Na^+ groups. However, there is no sharply isolated ν_{NH} peak in the spectrum of the sodium salt of 2-aminopyridine (Fig. 1, curve 1), but there are a number of low-intensity diffuse bands, the most clearly expressed one of which at 3465 cm^{-1} we adopted as the stretching vibrations of a free NH^- group. Similar broad low-intensity bands and a distinct ν_{N-H} peak are present in the IR spectra of the sodium

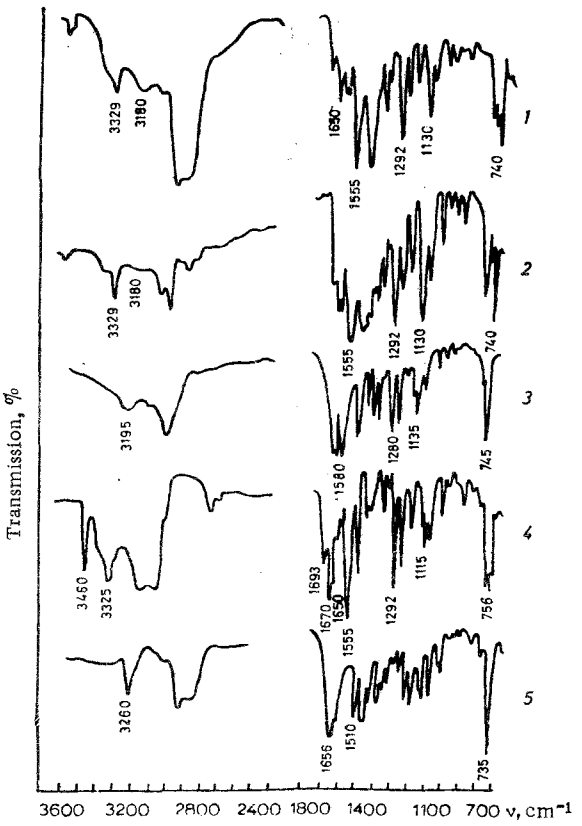


Fig. 2. IR spectra of 1-ethyl-2-aminobenzimidazole derivatives: 1) sodium salt obtained via method B; 2) sodium salt from the Chichibabin reaction; 3) 1-ethyl-2-methylaminobenzimidazole; 4) 1-ethyl-2-aminobenzimidazole; 5) 1,3-diethyl-2-benzimidazolonimine.

salts of 1-alkyl-2-aminobenzimidazoles (V and VII, Fig. 2, curve 1). This is evidence for appreciable association of salts of I, V, and VII in the crystalline state. Outside of the ν_{N-H} peak (free), there are no other bands in this region in the IR spectra of sodium salts of 1-methyl-2-aminoperimidine and 9-aminoacridine; this indicates the absence of hydrogen bonds in their crystal lattices, as is also observed for sodium amide [8] and potassium methylamide [9].

Data on the position of the vibrational bands of free NH groups in SSHA can apparently be used for the qualitative evaluation of the state of hybridization of the nitrogen atom in the N-anions as compared with the parent amines. The ν_{N-H} band in the spectra of the sodium salts of I, V, VII, and XI lies in the higher-frequency region as compared with the analogous band in the spectra of corresponding methylamino derivatives. The same phenomenon is observed for potassium methylamide when it is compared with dimethylamine [9]. This probably may be due to an increase in the s character of the hybrid orbitals of the amine nitrogen and consequently in the force constant of the N–H bond [10] on passing from the amine or its N-methyl derivative (in which the N atom is approximately sp^2-hybridized) to the corresponding metal salt.

The salt of 1-methyl-2-aminoperimidine, for which the ν_{N-H} band (3378 cm^{-1}) lies in the low-frequency region and coincides with the low-intensity ν_{N-H} band of 1,3-dimethylperimidonimine (Fig. 3), is an exception in this respect. At first glance, this may be explained by the imine structure of the salt of IX, but the absorption of the salt of IX at 1600 cm^{-1} coincides more with the absorption of an amine than an imine. It is more probable that this anomaly is associated with a decrease in the s character of the hybrid orbital of the N atom in IX as compared with the nonionized amine. It may be due to repulsion of the π-surplus electron system of the perimidine ring [11] and the electron pair of the negatively charged nitrogen. It is apparent that this sort of repulsion will be lower if the amine nitrogen takes on a more pyramidal configuration, i.e., if the contribution of the sp^3 orbitals increases. This effect is apparently manifested to a certain degree also in the sodium salt of aniline (ν_{N-H} 3390 cm^{-1}) if it is compared with N-methylaniline (ν_{N-H} 3420 cm^{-1}). Of course, the quantitative evaluation of the change in the state of hybridization of the amine nitrogen on passing to the N-anionic form is possible only on the basis of measurements in solution.

In the 1500-1700-cm^{-1} Region. The bands of the stretching vibrations of the aromatic C=C and C=N bonds lie in this region. With only slight deviations, they closely coincide with the similar bands of the parent amine (the δ_{HN_2} band at 1630 ± 30 cm^{-1}, of course, vanishes) and its N-methyl derivative for all of the SSHA. In a number of cases, the spectrum of the salt in this region is not entirely in agreement with the spectrum of the methylamino derivative, but then there is always complete agreement with the spectrum of the amine. Thus, for example, in the IR spectrum of the salt of VII or in the spectrum of the amine itself there is a band of medium intensity at 1697 cm^{-1}, while no such band is present in the spectrum of 1-ethyl-2-methylaminobenzimidazole. The same applies to the band at 1510 cm^{-1} in the spectrum of the salt of IX and the band at 1662 cm^{-1} in the spectrum of XI (Table 2). In addition, the absorption of all of the SSHA at 1500-1700 cm^{-1} differs considerably from the absorption of the corresponding imines (Figs. 1-3).

Bands of in-plane deformation vibrations of the N–H bonds should also lie between 1500 and 1600 cm^{-1}. In fact, a band of moderate intensity, which we will ascribe to δ_{N-H}, is present in the spectra of the SSHA and several methylamino derivatives at ~1540 ± 20 cm^{-1} (it is not present in the spectra of the amines).

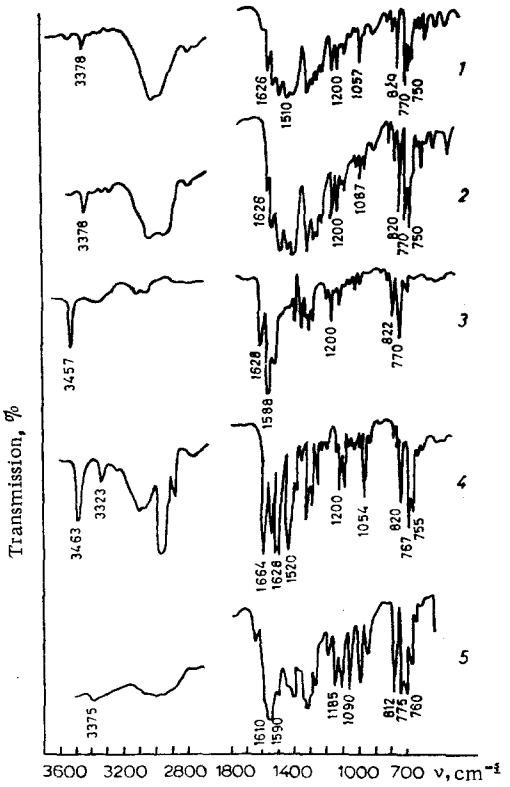


Fig. 3. IR spectra of 1-methyl-2-aminoperimidine derivatives: 1) sodium salt obtained via method B; 2) sodium salt from the Chichibabin reaction; 3) 1-methyl-2-methylaminoperimidine; 4) 1-methyl-2-aminoperimidine; 5) 1,3-dimethyl-2-perimidonimine.

In the 1200-1400-cm^{-1} Region. All of the compounds have a complex system of bands with intensities from 10 to 2 (with respect to an arbitrary 10-point scale) in this region. The majority of the bands apparently are affiliated with the $\nu_{\text{ring-N}}$ and $\nu_{CH_3\text{-N}}$ stretching vibrations. In those cases where it is possible (I and III, for example), the bands of the latter type were isolated and are not included in Table 2. Unfortunately, they could not be separated in other cases. Nevertheless, it can be definitely stated that while there is a certain (expected) shift of the $\nu_{\text{ring-N}}$ band to the high-frequency region in the spectra of the SSHA, it is extremely insignificant as compared with the spectra of the amines and their N-methyl derivatives. This indicates that the negative charge in the crystalline state of the SSHA remains primarily localized on the exocyclic N atom (structure II), in connection with which the $C_{\text{ring}}-N$ bond order undergoes practically no increase. The localization of the charge on the amine nitrogen also means intimate bonding of the Na^+ ion and N-anion in the crystal lattice of the SSHA with realization of a structure of the I type.

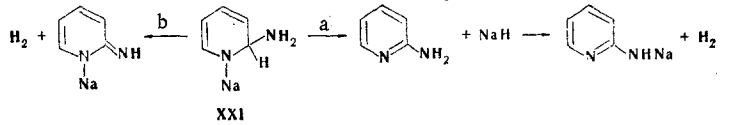
In the 1000-1200-cm^{-1} Region. The bands of the in-plane deformation vibrations of the C–H bonds of the aromatic rings, which lie in this region, closely coincide in both number and position for all of the SSHA with the analogous bands of model amino compounds and differ considerably (except for the salt of IX) from the absorption of imines.

In the 700-1000-cm^{-1} Region. The few bands at the upper boundary of this region can be affiliated with the breathing vibrations of the aromatic rings. The γ_{N-H} band, which should lie at about 900 cm^{-1}, as is well known [11], is of low intensity and is very difficult to distinguish. The extremely characteristic bands of the out-of-plane deformation vibrations of the C–H bonds of aromatic rings (γ_{C-H}) lie at 700-850 cm^{-1}. The γ_{C-H} bands for all of the SSHA and the corresponding amines or N-methyl derivatives of amines coincide closely. The difference between the absorption of the SSHA and the imines is apparent here. An exception to this is the salt of IX, the absorption of which at 700-850 cm^{-1} coincides both with that of the amine and imine. Thus it can be concluded that the salt of 1-methyl-2-aminoperimidine has an amine structure only on the basis of an analysis of its absorption at 1600 cm^{-1}.

On the whole, the investigation has unambiguously demonstrated that the sodium salts of the investigated N-heteroaromatic amines exist in the amino form in the crystalline state with considerable localization of the negative charge on the amine nitrogen. This conclusion is also in complete agreement with data on the reactivities of SSHA, which, despite their formal ambident character (II ↔ IIa), always react with electrophilic reagents exclusively at the exocyclic N atom [3, 6].

Structure of the SSHA Formed in the Chichibabin Reaction

It is known that the final product of the amination of N-heteroaromatic compounds by means of sodium amide (the Chichibabin reaction) is the sodium salt of the corresponding α- (sometimes γ-) amino compound [5]. The generally accepted mechanism of the reaction consists in the addition of sodium amide to the C=N bond of the heteroring (first step) with subsequent aromatization of adduct XXI to the amine by splitting out of sodium hydride (second step). The sodium hydride immediately reacts with the NH_2 group of the amine, as a result of which the SSHA is formed and hydrogen is evolved.



XXI

In general outline, the first step apparently does not raise any doubts. However, the second step could theoretically occur differently – by direct elimination of a hydrogen molecule from adduct XXI (path b in the scheme presented above). The SSHA formed in this case should already have the imino structure and should differ in properties (for example, with respect to the IR spectrum) from the salt obtained by the ionization method.

In terms of energy, path b is less favorable, since the formation of the sodium salt is associated with a loss of aromatic character (the ΔH factor). However, the difference between the π-electron energies of the amino and imino forms becomes less significant for heterosystems with reduced aromaticity, such as acridine and perimidine [13]. In these cases, the entropy factor (ΔS), which apparently favors (because of the closeness of the two H atoms that are split out in XXI) loss of hydrogen via mechanism b, may prove to be important in the stabilization of the adduct. However, our comparison of the IR spectra of the SSHA of I, VII, and IX,* which were isolated from the Chichibabin reaction (Fig. 1, curve 2; Fig. 3, curve 2) and obtained from amines, demonstrated that they are completely identical and have the amino structure (Figs. 1-3, curves 1 and 2). Although this is also a weighty proof in favor of the mechanism of stabilization of the adduct with splitting out of NaH, alternative mechanism b cannot be considered to be completely repudiated, since the sodium salt of the imino form that is formed when it is realized could isomerize to the more stable salt of the amino form under the conditions of the Chichibabin reaction (120-150°).

EXPERIMENTAL

Commercial-grade 2-aminopyridine was purified by vacuum distillation (160° at 7 mm). 1-Alkyl-2-aminobenzimidazoles and 1-methyl-2-aminoperimidine were obtained via the method in [5], while 9-aminoacridine was obtained via the method in [15]. All of the amines were dried at 100° and 2 mm for 1 h prior to the reactions.

Compounds IV, VI, and VIII were obtained by methylation of the appropriate SSHA in absolute toluene via the method in [6]. The previously undescribed 1-ethyl-2-methylaminobenzimidazole (VI) was obtained in 58% yield as colorless needles with mp 158° (from benzene). Found: N 23.9%. $C_{10}H_{13}N_3$. Calculated: N 24.0%.

9-Methylaminoacridine (X). This compound was synthesized by heating 9-chloroacridine [15] with methylamine [16].

2-Methylaminopyridine. A 9.25-g (0.05 mole) sample of 2-benzylaminopyridine was added to a solution of sodium amide, obtained from 1.15 g (0.05 g-atom) of sodium and 100 ml of liquid ammonia [5], and the mixture was stirred for 1 h. A 3.2-ml (0.05 mole) sample of methyl iodide was then added in the course of 20 min to the green solution, and the mixture was stirred until the ammonia had completely evaporated. The residue was treated with chloroform (50 ml), and the mixture was filtered. The extract was washed with water and dried with potassium carbonate. The chloroform was removed by distillation, and the residue was dissolved in hot petroleum ether. The solution was cooled to give 2.4 g (26%) of 2-benzylaminopyridine. The petroleum ether was removed from the filtrate by distillation, and the residue was vacuum-distilled to give 4.2 g (57%, based on the converted material) of 2-(N-methyl-N-benzyl)aminopyridine as a light-yellow oil with bp 170-172° (12 mm). Found: C 78.2; H 6.9; N 14.9%. $C_{13}H_{14}N_2$. Calculated: C 78.7; H 7.1; N 14.2%. Small pieces [1.86 g (0.08 g-atom)] of sodium were added with stirring to a suspension of 8 g (0.04 mole) of 2-(N-methyl-N-benzyl)aminopyridine in 100 ml of liquid ammonia, and the mixture was stirred for 1 h until all of the solid had dissolved, after which 4 ml of water was added dropwise, and the ammonia was evaporated. The residue was treated with chloroform (75 ml), and the extract was dried with potassium carbonate. The chloroform was then removed, and the residue was vacuum-distilled to give 2.5 g (58%) of 2-methylaminopyridine as a light-yellow oil with bp 98-100° (2 mm). The compound was identical to the product obtained by heating 2-chloropyridine with methylamine.

Imines XIV-XVII. These imines were obtained via the methods in [16-19], respectively.

Sodium Salts of N-Heteroaromatic Amines (SSHA). A. A 0.01 g-atom sample of sodium was added in small portions with stirring to a suspension (or solution in the case of 2-aminopyridine) of 0.01 mole of amine in 50 ml of liquid ammonia. The sodium reacted rapidly with the amine, and the latter dissolved as

* The salt of XI cannot be isolated in sufficiently pure form from the Chichibabin reaction because of the difficulty involved in the amination of acridine [14].

the sodium salt. The liquid ammonia was evaporated in a stream of dry ammonia. The flask containing the residue was immediately transferred to a box, in which the residue was washed under nitrogen with absolute benzene and ether until the ether was colorless. After this, the salt was dried by bubbling dry nitrogen through the filter on which it was situated.

B. A 0.01-mole sample of amine was added to 0.01 mole of freshly prepared sodium amide [4] in 50 ml of liquid ammonia, and the mixture was cooled and stirred for 1 h. The ammonia was then evaporated in a stream of dry ammonia. The remaining operations were the same as in method A.

C. A 0.015-mole sample (based on a 100% pure preparation) of finely ground sodium amide was added to a solution of 0.01 mole of amine in absolute xylene or DMA (the amount of solvent was such that the amine dissolved completely in it), and the mixture was stirred under nitrogen at a temperature that insured uniform evolution of ammonia. The ammonia was absorbed in a trap filled with 0.01 N hydrochloric acid. The amount of evolved ammonia was determined by titration of samples selected periodically from the absorption trap with 0.05 N sodium tetraborate in the presence of methyl orange. Upon completion of the reaction, the flask was cooled and transferred to a box, in which the residue was removed by filtration and worked up as in method A. The data on the preparation of the SSHA and sodium anilide in o-xylene and DMA are presented in Table 1.

D. The SSHA were obtained via the Chichibabin reaction by heating 0.01 mole of the heterocyclic compound with 0.02 mole of sodium amide in absolute toluene (I) at the boiling point for 3 h, in absolute o-xylene (VII) at 120-125° (3 h), or in dimethylaniline (IX) at 130-140° (2 h). The mixture was cooled, and the flask was transferred to a box, in which the sodium salt was removed by filtration and worked up as in method A. The entire reaction and the isolation of the salt were carried out under a stream of dry nitrogen.

Measurement of the IR Spectra. The spectra were measured with a UR-20 double-beam spectrometer at 600-3800 cm^{-1} with KBr, NaCl, and LiF prisms. Suspensions of the SSHA in absolute mineral oil were prepared in a box in an atmosphere of dry nitrogen by grinding 10-20 mg of the salt with two to three drops of mineral oil for 25-30 min in an agate mortar. The resulting pastes were placed in a demountable liquid cuvette with a layer thickness of 0.04 mm and KBr windows. The spectra were measured with slit program 4 at a rate of 64 cm^{-1} per min.

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