STUDY OF THE EFFECT OF ANNELATION ON THE REARRANGEMENT OF 1,2-DIALKYLPYRIDINIUM SALTS BY THE MO LCAO SELF-CONSISTENT FIELD (SCF) METHOD

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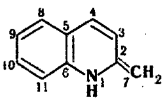
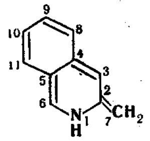
The anhydro bases formed from 1,2-dialkylquinolinium (I), 1,2-dialkylisoquinolinium (II), and 2,3-dialkylisoquinolinium (III) salts were calculated within the framework of the π-electron approximation of the MO LCAO self-consistent field (SCF) method. It is shown that, in contrast to II and III, I does not undergo recyclization; annelation of the pyridine ring facilitates recyclization. The recyclization indexes are linked with the aromatic character of the pyridine ring and increase as the aromatic character decreases.

We have previously shown [1] that the long-range positive π-electron bond orders are reactivity indexes of recyclization reactions of 1,2-dialkylpyridinium salts to anilines. In the present research we studied the effect of annelation of the pyridine ring on these reactions and the relationship between the aromatic character of the investigated systems and this rearrangement.

As in [1], we assume that the recyclization of 1,2-dialkylquinolinium, 1,2-dialkylisoquinolinium, and 2,3-dialkylisoquinolinium salts proceeds through the formation of the corresponding anhydro bases I-III,* the electrondensity distribution of which was calculated with the parametrization and the method presented in [2] and is presented in Table 1.



I



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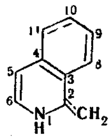

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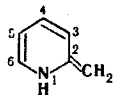

IV

It follows from Table 1 that annelation of 1H-2-methylene-1,2-dihydropyridine (IV) leads to the development of charge on the pyridine ring; this charge decreases in the order I > III > II (+0.05801, +0.00684, and −0.00373, respectively); this constitutes evidence for the greater susceptibility of the pyridine ring in I to attack by a nucleophile than in II.

Let us note that the charges on the methylene groups in I and III are approximately equal (−0.18254 and −0.18766, respectively) and, in contrast to II (−0.27748) are lower than the charge on the methylene group in the IV molecule (−0.24022). This indicates the greater CH acidity of the methyl groups in 1,2-dialkylquinolinium and 1,2-dialkylisoquinolinium salts as compared with 1,2-dialkylpyridinium salts, i.e., the anhydro bases can be formed at a higher rate from the first two series of salts. These data are in agreement with the basicities of the anhydro bases [5], which change in the same direction as the increase in the charge on the methylene group: −0.18254 (15.01), −0.18766 (15.62), and −0.24022 (19.8) for I, III, and IV, respectively (the experimental pK_a values [5] are indicated in parentheses). It should be noted that the CH acidity of the methyl group in the 3 position of the isoquinoline ring is the minimum value, and anhydro base II will

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*The numbering of the atoms (which does not correspond to the generally accepted nomenclature) presented in the structural formulas was used for convenience in comparing I-IV.

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TABLE 1. Electron Density Distribution in the Investigated Systems

	s—r	Compound					
		Ia	II	III	IVa	V	VI
π-Electron bond orders	1—2	0,3196	0,3147	0,3240	0,3206	0,3225	0,3262
	2—3	0,4194	0,4697	0,3889	0,4339	0,4561	0,3656
	3—4	0,8352	0,6859	0,5723	0,8047	0,6998	0,5755
	4—5	0,4214	0,4321	0,4195	0,4946	0,4038	0,3876
	5—6	0,5784	0,6920	0,8456	0,8114	0,7731	0,9188
	1—6	0,3432	0,4425	0,3809	0,4024	0,0172	0,0113
	2—7	0,8412	0,8078	0,8552	0,8295	0,8218	0,8636
	8—9	0,6847	0,7723	0,6774	—	0,7771	0,6729
	9—10	0,6472	0,5420	0,6471	—	0,5300	0,6526
	10—11	0,6761	0,7736	0,6824	—	0,7862	0,6751
	6—7	0,0741	0,1810	0,1716	0,1469	0,3284	0,1405
	5—8	0,6048	0,4872[b]	0,6192[c]	—	0,4833[b]	0,6245[c]
	6—11	0,6262	0,4838[d]	0,6086[e]	—	0,4579[d]	0,6215[e]
Residual π-electron charges on the atoms	1	+0,2078	+0,2636	+0,2286	+0,2422	+0,1021	+0,1052
	2	+0,0199	+0,0052	+0,0184	+0,0143	+0,0363	+0,0344
	3	−0,0059	−0,0438	−0,0174	−0,0219	+0,0033	−0,0051
	4	+0,0124	+0,0098	+0,0091	+0,0207	−0,0056	−0,0072
	5	−0,0374	−0,0596	−0,0960	−0,0825	+0,0025	+0,0076
	6	+0,0437	+0,0985	+0,0518	+0,0674	+0,0360	−0,0182
	7	−0,1825	−0,2775	−0,1877	−0,2402	−0,1023	−0,1304
	8	+0,0057	−0,0003	+0,0073	—	+0,0029	+0,0065
	9	−0,0194	+0,0136	−0,0058	—	−0,0022	+0,0054
	10	+0,0112	−0,0106	+0,0085	—	+0,0056	+0,0003
	11	−0,0555	+0,0011	−0,0166	—	−0,0067	+0,0012

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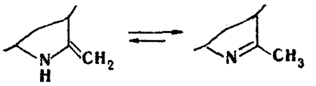
[a] Our calculation of the electron density distribution is in good agreement with the earlier calculations [3, 4]; however, long-range bond orders are not presented in the papers cited. [b] This is the order of the 4—8 bond. [c] This is the order of the 3—8 bond. [d] This is the order of the 5—11 bond. [e] This is the order of the 4—11 bond.

consequently be the most difficult-to-form base. Constants of the tautomeric equilibrium type were calculated [5] on the basis of the experimental pK_a values:



This equilibrium is shifted to the right as the CH acidity of the methyl groups decreases. This shift in the tautomeric equilibrium is in agreement with the positive π-electron charge on the nitrogen atoms in I-IV, which change in the same direction as the negative charge on the methylene groups (Table 1).

Since ring opening during the rearrangement entails disruption of the aromatic character of the pyridine ring, the ease of this opening and the development of a new bond should be due to the aromatic character of the starting structures. In view of this, a study of the aromatic character of I-III as compared with nonannelated structure IV seems of interest. We selected the induced ring π-electron currents and the relative π-electron diamagnetic susceptibilities [6, 7], the method of calculation of which within the bonded approximation of perturbation theory in the MO LCAO self-consistant field (SCF) method was developed in [8], as a quantitative criterion of the aromatic character. The results of the corresponding calculation are presented in Table 2. It follows from Table 2 that the aromatic character of the investigated compounds with respect to $\chi^{\pi}/\chi^{\pi}_{C_6H_6}$ changes in the order III $\geqslant$ I > II > IV. This scale of the aromatic character is close to the scale constructed from experimental data on the tautomeric equilibrium constants [5], viz., I = III > IV $\geqslant$ II. Let us note that the scale of the aromatic character constructed from the $\chi^{\pi}/\chi^{\pi}_{C_6H_6}$ values coincides completely with the scale constructed from the dispersion of the charges (Table 2), which according to [6] are one of the criteria of aromatic character. The scale of aromatic character with respect to the dispersion of the bond orders, which are a measure of the quinoid character, does not coincide with the scales of aromatic character with respect to the diamagnetic susceptibilities and the dispersions of the charges (Table 2). Let us note

TABLE 2. Aromatic Character of the Anhydro Bases

Compound	Orders of the bonds formed	Magnetic criteria			Dispersion of the bond orders		Dispersion of the π - e⁻ charges		Energy for ring cleavage, eV
		ring π -electron currents		χ^{π}/χ^{π} C_6H_5	over the entire system	over the 2-methylene-dihydropyridine ring	over the entire system	over the 2-methylene-dihydropyridine ring	
		J_1	J_2						
I	0,0741	0,1235	0,8950	1,0038	0,0336	0,0420	0,00763	0,01167	1,04
II	0,1810	0,1155	0,4475	0,5593	0,0287	0,0440	0,01473	0,02308	1,15
III	0,1716	0,1380	0,8949	1,0263	0,0244	0,0270	0,00913	0,01429	1,03
IV	0,1469	0,1431		0,1429	0,0961	0,0961	0,01840	0,01840	1,10

TABLE 3. Atom–Bond Mutual Polarizabilities of the Investigated Systems

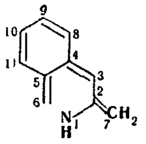
Compound	Position of the substituent	1–2	2–3	3–4	4–5	5–6	1–6	2–7	6–7
I	1	+0,115	−0,004	−0,002	+0,018	−0,025	+0,137	−0,045	−0,058
	3	+0,017	+0,009	+0,002	−0,009	+0,008	−0,027	−0,018	+0,034
	4	−0,005	+0,003	−0,007	+0,005	+0,001	+0,021	−0,001	−0,032
	7	−0,178	−0,019	+0,017	−0,048	+0,006	−0,037	+0,107	−0,004
II	1	+0,104	−0,002	−0,015	+0,025	−0,070	+0,207	−0,044	−0,136
	3	+0,042	+0,048	+0,021	−0,020	+0,042	−0,121	−0,065	+0,177
	6	−0,036	+0,018	−0,024	+0,024	−0,091	+0,141	−0,002	−0,156
	7	−0,183	−0,091	+0,058	−0,056	+0,058	−0,101	+0,169	+0,006
V	1	+0,140	−0,021	+0,005	−0,001	+0,000	+0,019	−0,042	−0,009
	3	+0,004	−0,022	+0,004	+0,001	−0,002	+0,063	+0,015	−0,005
	6	−0,049	−0,003	+0,012	−0,010	+0,026	+0,022	+0,023	−0,000
	7	−0,141	+0,060	−0,035	+0,011	−0,014	−0,135	+0,031	+0,070
III	1	+0,114	−0,001	−0,002	+0,028	−0,058	+0,157	−0,047	−0,070
	5	+0,030	+0,008	−0,005	+0,032	+0,053	−0,143	−0,022	+0,131
	6	−0,027	+0,015	−0,008	+0,029	−0,058	+0,081	+0,000	−0,041
	7	−0,180	−0,037	+0,007	−0,048	+0,021	−0,027	+0,119	−0,023
VI	1	+0,142	−0,016	+0,003	+0,000	−0,000	+0,012	−0,046	−0,005
	5	+0,010	−0,002	+0,001	−0,003	−0,003	+0,012	−0,003	−0,011
	6	−0,024	+0,000	+0,004	−0,012	+0,013	+0,014	+0,010	−0,009
	7	−0,179	+0,034	−0,011	−0,004	−0,004	−0,060	+0,068	+0,035

that the introduction of substituents in I-IV markedly increases their quinoid character, without, on the whole, changing the order of the dispersion of the bond orders cited above.

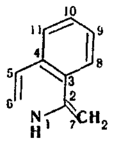
Let us note that the scale of aromatic character presented above does not correlate with the recyclization indexes: it does not correlate either with the long-range bond orders or the ring cleavage energies. This is evidently associated with the fact that only the pyridine ring participates in the recyclization, and the recyclization indexes (the long-range bond orders) must be compared with the aromatic character of the 2-methylene-1,2-dihydropyridine ring rather than with the aromatic character of the entire molecule. The aromatic character of the pyridine ring was estimated from the induced π-electron ring currents expressed in units of the current of the benzene ring. In this case the scale of the aromatic character of the 2-methylene-1,2-dihydropyridine ring has the form IV > III > I > II (Table 2). This scale is in good agreement with the long-range orders of the 6–7 bonds for II-IV, which, within the framework of the evolved scheme, characterize the ability to undergo recyclization and increase as the index of aromatic character decreases (Tables 1 and 2). Compound I deviates from this order; this is evidently associated with the fact that the C_6 atom is a nodal atom. Let us note that neither the energies of cleavage of the pyridine ring nor the orders of the bonds cleaved, especially the dispersions of the bond orders and charges of the 2-methylene-1,2-dihydropyridine ring (Tables 1 and 2) correspond to the scale constructed with respect to the π-electron currents.

The site of attack of the anhydro bases by the nucleophile is determined by the maximum positive π-electron charge, which is localized on the C_6 atom. Attack by the nucleophile at this position should lead to cleavage of the 1–6 bond, since this bond order is minimal (Table 1). In I the 6 position is sterically hindered with respect to attack by the nucleophile, and as a consequence of this the nucleophile will attack the 2 and 4 positions with cleavage of the 1–2 bond; this is in agreement with the experimental data [9]. Thus the rearrangement of the 1,2-dialkylquinolinium salt to naphthylamine with cleavage of the 1–6 bond and formation of a 6–7 bond is forbidden with respect to steric factors. However, cleavage of the 1–2 bond presupposes the formation of a benzene ring at the 8 position, since the corresponding long-range 7–8 bond order is 0.1296. However, a necessary condition for this rearrangement is rotation about the 4–5 bond, which, as demonstrated by the calculation, occurs with a 24 kcal/mole loss in energy. In II and III attack is directed to the 6 position, which determines cleavage of the 1–6 bond (Table 1), in agreement with the experimental data [10].

Cleavage of the 1–6 bond in the calculation (the corresponding resonance integral was assumed to be zero) leads to an increase in the order of the 6–7 bond of II (see V in Table 1) and to a certain decrease in this order in III (see VI in Table 1); however, this bond order remains large. Compounds II and III can consequently undergo recyclization to naphthylamine, although, as in the case of 2-picoline [1], it is necessary to activate the process for this sort of reaction by introduction of substituents in the molecules.



V



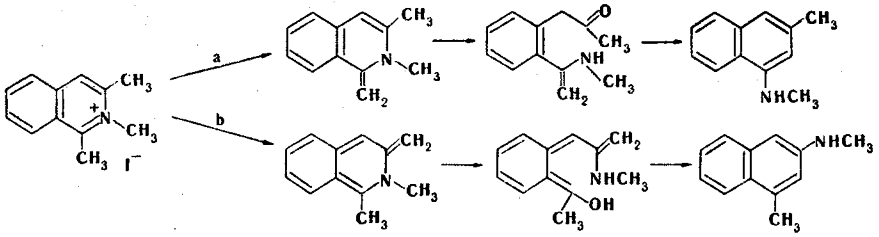
VI

The effect of substituents in the pyridine ring and the effect of the ring-opening hydroxide ion, which was modeled by means of the atom–bond mutual polarizabilities [1] (presented in Table 3), turn out to be similar to those for IV. The atom–bond mutual polarizabilities for II and III and their open forms V and VI are close to the mutual polarizabilities for IV and its open form [1]. In other words, the introduction of electron-donor substituents in the 1 or 1 and 6 positions and of electron-acceptor substituents in the 3 or 5 position should facilitate the rearrangement. Substituents in the benzene ring have little effect on the bond orders in the molecules, since the atom–bond mutual polarizabilities in the 8, 9, 10, and 11 positions do not exceed 0.02, whereas in the open molecules they decrease and do not exceed 0.008 (they are therefore not presented in Table 3). Since the order of the 6–7 bond in III is greater than in IV, whereas the order of the 1–6 bond is lower and the CH acidity of the 1,2-dialkylisoquinolinium ion is higher than in the case of the 1,2-dialkylpyridinium ion, one should expect higher yields of products of rearrangement of 1,2-dialkylisoquinolinium salts than in the case of 1,2-dialkylpyridinium salts. This is in complete agreement with the experimental data (see [10, 11]).

Regarding the recyclization of II one can state the following: since this compound has the maximum long-range order of the 6—7 bond and this bond order increases sharply with cleavage of the 1—6 bond, one should expect the maximum yields of recyclization products in the investigated series. However, the low CH acidities of 2,3-dialkylisoquinoline salts may lower the yields of the recyclization products, but they should remain rather high. Unfortunately, no experimental data on the recyclization of 2,3-dialkylisoquinolinium salts are yet available.

It should be noted that rotation about the 2—3 bond after cleavage of the 1—6 bond in II and III takes place with a gain in energy (a 2-4 kcal/mole decrease in energy). The energy gain in this case turns out to be smaller than for IV [1].

As in the case of 1,2,3-trialkylpyridinium salts, a competitive process is possible in the case of 1,2,3-trialkylisoquinolinium salts:



A comparison of the estimate of the CH acidities of the methyl groups in the 1 and 3 positions of isoquinoline was made as described in [1]. It was found that the CH acidity of the 1-methyl group is higher than that of the 3-methyl group.* One should consequently expect that reaction via pathway a is preferred.

Thus, the evolved method satisfactorily describes the recyclization of benzopicolinium salts to naphthylamines; the trend of the effect of annelation of the pyridine ring on the recyclization is the opposite of the trend of the aromatic character of the 2-methylene-1,2-dihydropyridine ring.

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*The fact that the 1-methyl group undergoes condensation with aldehydes more readily than the 3-methyl group serves as an indirect confirmation of the higher CH acidity of the 1-methyl group in isoquinoline [12].