QUANTUM-CHEMICAL DESCRIPTION OF THE RECYCLIZATION REACTIONS OF QUATERNARY PYRIDINIUM SALTS

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Recently we have reported the base-catalyzed recyclization of 1,2-dialkylpyridinium salts to alkylanilines [1-3]. Apart from its preparative significance, this reaction is the simplest model of the isomerization of heteroaromatic to carbocyclic structures. In several cases it takes place under mild conditions and competitive isomer formation can occur [1, 2]. We have now attempted to provide a quantum-chemical interpretation of this rearrangement.

A formal quantum-chemical framework for the description of reactions of this type with the LCAO SCF MO method in the π-electron approximation can be provided by bonding perturbation theory. Moreover, since these reactions are intramolecular processes, the perturbation can be equated with intramolecular bonding and the reactivity index is then represented by the bond orders between the chemically nonbonded atoms [4]. A positive bond order means an energy gain in bond formation and a negative bond order, the opposite.

$$\Delta E = P_{ik}\Delta\beta. \tag{1}$$

In the context of Vysotskii's method for dealing with the effects of substitution on the physicochemical properties of a molecule [5-7] the presence of functional groups requires use of two-parameter perturbation theory. The quantities that quantitatively specify the effect of functional groups on the rate and course of the recyclization reactions are the mutual atom–bond polarizabilities ($\pi_{j,ik}$) and

$$P_{ik} = P_{ik}^0 + \sum_j \pi_{j,ik}\Delta\alpha_{\text{sub}}, \tag{2}$$

where P_{ik}^{0} are the bond orders in the unsubstituted molecule and j is the number of the atom to which the substituent is added. The substituent is characterized by $\Delta\alpha_{\text{sub}}$, whose values for various functional groups are linearly related to the Taft σ^* constants and have been tabulated [5-7].

We assume that recyclization proceeds via the anhydro bases. This has experimental support: we have isolated one of the intermediate anhydro bases, 1-methyl-2-(2-oxopropylidene)-5-nitropyridine, recorded its UV and NMR spectra, and shown that in alkaline medium it subsequently recyclizes to N-methyl-p-nitroaniline [3]. Consequently, for the quantum-chemical description of these recyclization reactions using the parametrization and procedures developed earlier [5-8], we required calculations on the anhydro bases, whose excess atomic charges and bond orders are summarized in Table 1. Table 2 collects the mutual atom–bond polarizabilities in compounds (I), (II), and (V). The numbering of the atoms is shown in the structural formulas.

This parametrization has been successfully used for work on the UV and NMR spectra of aromatic hydrocarbons, azines, and oxazolium and oxadiazolium cations [5-8]. We checked that it is applicable to the anhydro bases by calculating the proton chemical shifts and the energy of the lowest singlet–singlet transition of 1-methyl-2-(2-oxopropylidene)-5-nitropyridine. The calculation gave the following values (experimental figures [3] in parentheses): 3H 9.49 (8.63), 4H 7.13 (7.58), 6H 8.17 (8.36), CH 5.25 (5.26) ppm; and $\lambda_{\max}$ 407 (405) nm. The reasonable agreement between the calculated and experimental figures demonstrates the reliability of the calculated electron density distributions, which are at the basis of the

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TABLE 1. Electron Density Distributions

	pq	Compound					
		I	II	III	IV	V	VI
π-electron bond orders	1—2	0,3206	0,3231	0,0271	0,6145	0,3210	0,4819
	2—3	0,4339	0,4154	0,4516	0,6747	0,4163	0,4705
	3—4	0,8047	0,8195	0,7931	0,6618	0,8488	0,7395
	4—5	0,4946	0,4526	0,4893	0,6618	0,3663	0,6043
	5—6	0,8114	0,8884	0,8094	0,6747	0,9290	0,6384
	1—6	0,4024	0,0178	0,3935	0,6145	0,0152	0,6992
	2—7	0,8295	0,8468	0,8871	−0,2133	0,8485	0,7121
	5—7	0,1743	−0,0211	0,0764	−0,0302	−0,0062	0,2916
	6—7	0,1469	0,2528	0,2441	−0,2133 0,3840*	0,2004	−0,0999 0,1761†
Excess π-electron charges on the atoms	1	+0,2422	+0,1032	+0,1471	+0,0593	+0,1016	−0,2508
	2	+0,0143	+0,0344	−0,0133	−0,0837	+0,0335	+0,0298
	3	−0,0219	+0,0029	−0,0691	+0,0058	−0,0199	−0,1147
	4	+0,0207	−0,0076	+0,0201	−0,0440	+0,0076	−0,0260
	5	−0,0825	+0,0062	−0,1172	+0,0058	−0,0014	−0,1907
	6	+0,0674	−0,0223	+0,0793	−0,0837	+0,0048	+0,0274
	7	−0,2402	−0,1167	−0,0468	+0,1405	−0,1262	−0,4750

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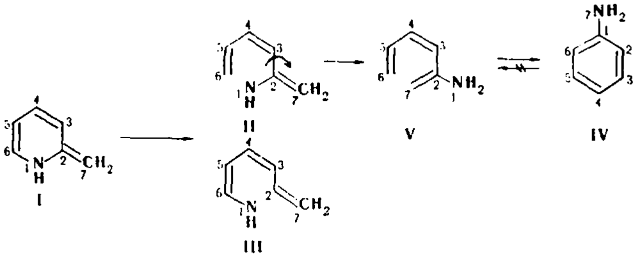
*Bond order between atoms 1 and 7.

†Bond order between atoms 1 and 3.

calculation of the spectral properties. Conclusions regarding the subsequent chemical transformations of the anhydro bases should therefore be possible.

Thus Table 1, which summarizes the bond orders in the anhydro base (I), implies that the weakest π bonds between directly bonded atoms 1-2 and 1-6, i.e., they may well be broken during the reaction. In addition between nonbonded atoms 5 and 7 and 6 and 7 there are high positive bond orders, which suggests the possibility of formation of a chemical bond between them (the energies of the C—N and C—C σ bonds that are broken and formed, respectively, are similar to and lower than the C—H and N—H bond energies). Thus anhydro base (I) could recyclize either to aniline (IV) or to 1-aminomethylenecyclopentadiene or 1-methylene-3-aminocyclopentadiene. However, breaking of bonds 1-6 (structure II) or 1-2 (structure III) causes considerable weakening of the bonding between atoms 5 and 7 and simultaneous strengthening of that between atoms 6 and 7 (Table 1). Consequently, anhydro base (I) can recyclize only to aniline, but this recyclization is relatively improbable since bond orders 1-2 and 1-6 are still reasonably high, and this reaction will require activation of the anhydro base by, for example, introduction of functional groups.



In fact, using Vysotskii's model [5-7] of the substituents with Eq. (2) and the mutual atom—bond polarizabilities of Table 2, we see that the introduction of methyl groups into positions 1, 1 and 4, 1 and 6, or 1, 4, and 6 in the molecule of (I) causes a considerable reduction in bond order 1-6. It may even become negative (−0.1189; −0.1989; −0.4069; −0.4150, respectively), i.e., the breaking of this bond leads to an energy gain. Simultaneously bond order 6-7 increases (0.4282; 0.5710; 0.6510; 0.7950) while bond order 5-7 diminishes (−0.0652; −0.1320; −0.4268; and −0.2288). These results unambiguously reveal the course of recyclization. As would be expected, breaking of bond 1-6 (Tables 1 and 2) results in reduction in the negative bond orders 1-6, strengthening of bonds 1-2, and slight weakening of bonds 6-7. Bond orders 6-7 remain high (~0.3), which is consistent with Dewar's concepts [4] and accounts for the recyclization of these salts to anilines. The result of introducing two methyl groups in positions 1 and 3 or 1 and 5 is that bond 1-2 in compound (I) weakens more than bond 1-6, while bonds 5-7 and 6-7 are not strengthened as much as in preceding cases.

TABLE 2. Mutual Atom-Bond Polarizabilities ($\pi_{j,ik}$)

Molecule	ik	Substituent position, j					
		1	3	4	5	6	7
I	1—2	-0,110	0,031	-0,002	0,028	-0,025	-0,187
	2—3	0,002	0,026	0,005	0,016	0,019	-0,065
	3—4	-0,013	0,012	-0,015	-0,018	-0,022	0,046
	4—5	0,037	-0,029	0,006	0,039	0,038	-0,082
	5—6	-0,063	0,030	0,001	0,039	-0,071	0,049
	1—6	0,174	-0,069	0,027	-0,128	0,096	-0,075
	2—7	-0,048	-0,010	-0,001	-0,027	-0,005	0,147
	5—7	0,080	-0,031	-0,066	-0,027	0,121	-0,008
	6—7	-0,094	0,088	-0,048	0,132	-0,074	0,027
II	1—2	0,140	0,004	-0,010	0,008	-0,030	-0,161
	2—3	-0,018	-0,015	-0,001	-0,003	-0,003	0,047
	3—4	0,005	0,002	0,008	0,002	0,011	-0,029
	4—5	-0,001	0,004	0,001	-0,005	-0,015	0,015
	5—6	0,000	-0,002	-0,003	-0,001	0,018	-0,011
	1—6	0,019	0,040	0,009	0,018	0,022	-0,104
	2—7	-0,044	0,008	0,004	-0,001	0,014	0,051
	5—7	-0,013	-0,019	-0,068	-0,005	0,201	-0,051
	6—7	-0,009	-0,028	0,001	-0,017	-0,011	0,057
	1—2	0,137	-0,027	0,011	-0,002	0,007	-0,174
	2—3	-0,020	-0,005	-0,002	0,000	-0,002	0,037
	3—4	0,006	0,014	0,002	-0,001	-0,000	-0,022
	4—5	-0,002	-0,006	-0,002	-0,002	0,006	0,005
	5—6	0,001	0,003	0,001	0,002	-0,004	-0,002
	1—6	0,014	0,021	0,010	0,009	0,013	-0,069
	2—7	-0,041	0,014	-0,004	0,001	-0,002	0,063
	5—7	-0,003	-0,023	-0,048	-0,071	0.212	-0,044
	6—7	-0,008	-0,013	-0,009	-0,003	-0,008	0,041

This can evidently result in ring opening with elimination of the amine molecule [9]. The introduction of any other electron-donating group (instead of the methyl) should have the same results.

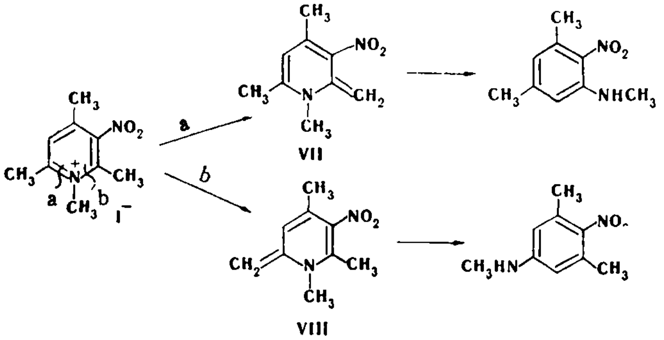
However, if the N-alkyl group is preserved, the introduction of electron-accepting groups has the opposite effect. Thus the introduction of a nitro group into position 3 or 5 greatly weakens bond 1-6 (−0.2562 and −0.3745) and increases the distant bond orders 6-7 (0.6042 and 0.6915), which also promotes the recyclization of 1-alkylnitropicolinium salts to N-alkylnitroanilines. This conclusion is fully compatible with experiment [1, 2].

Since the effect of several substituents can be described additively in first-order perturbation theory [5-7], the simultaneous introduction of electron-donating substituents into positions 1, 4, and 6, and of electron-accepting substituents into positions 3 and 5 preserves the essential features of the reaction, in agreement with experiment [1, 2]. When several close-lying functional groups are present, their interaction (higher orders of perturbation theory) and steric factors have to be taken into account.

Bond 1-6 can be broken thermally or by the hydroxide ion; in the second case the position of attack is controlled by the maximum positive π-electron charge (at position 6) and by addition at this position, which can also be described in our method as the introduction of an extra substituent that insubstantially modifies the bond orders and mutual polarizabilities. Moreover, after breaking of the C—N bond a necessary condition for cyclization should be rotation about any of the C—C bonds. The calculation shows that ring opening is energetically favored only by rotation about the C_2—C_3 bond (energy reduction of 1.38 eV), which is fully compatible with Sliwa and Tartar's results [10]. The bond orders and mutual polarizabilities also change slightly (see compound (V) in Tables 1 and 2).

Quaternization of the nitrogen atom is an important condition for these recyclizations. Calculation on the 2-picolinium cation for example gives a negative bond order 6-7 with high positive bond orders 1-6 and 1-2 and distant orders 5-7 and 1-3 (compound (VI) in Table 1), which in our method suggests that recyclization of this compound to aniline is impossible. However, the reverse recyclization of aniline (IV) to picoline is also relatively improbable, since bond orders 1-2 and 1-6 are similar to the other bond orders of the benzene ring, while bond order 5-7 is negative (Table 1).

The presence of methyl groups in positions 2 and 6 in the pyridinium salt results in competitive isomer formation [1, 2]



Here the formation of two different anhydro bases (VII) and (VIII) should be feasible, depending on the rates of abstraction of the proton from different methyl groups (on the carbon acidity, which is controlled by the excess π-electron charge on these groups). We have already described methods for examining the recyclization of anhydro bases (VII) and (VIII) to anilines. Thus the first stage of calculations on these reactions should be the evaluation of the carbon acidity of the methyl groups in the reactant molecules, which can be done from the excess π-electron charges on the methylene groups in compounds (VII) and (VIII). Calculation shows that the excess π-electron charge on the methylene group in compound (VII) is 0.05232 less than in (VIII), suggesting that the carbon acidity of the ortho-methyl group toward the nitro group is higher than that of the para-methyl group. This accounts for the preferential recyclization of 1,2,4,6-tetramethyl-3-nitropyridine iodide by pathway a [1, 2]. The same result can be derived by evaluating the carbon acidity in the case of addition of the proton to the 1-methyl-2,6-dimethylene-3-nitropyridine anion.

In almost all cases bond orders 1-6 and 1-2 are quite small, and, consequently, exchange of the amino group is possible during the recyclization process, which is consistent with experiment [2].

Thus, in summary we remark that the distant positive π-electron bond orders between chemically nonbonded atoms reliably describe the recyclization reactions of 1,2-dialkylpyridinium salts to anilines.

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