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QUANTUM-CHEMICAL INVESTIGATION OF THE RECYCLIZATION OF 1,2,4,6-TETRAMETHYL-3-NITROPYRIDINIUM IODIDE

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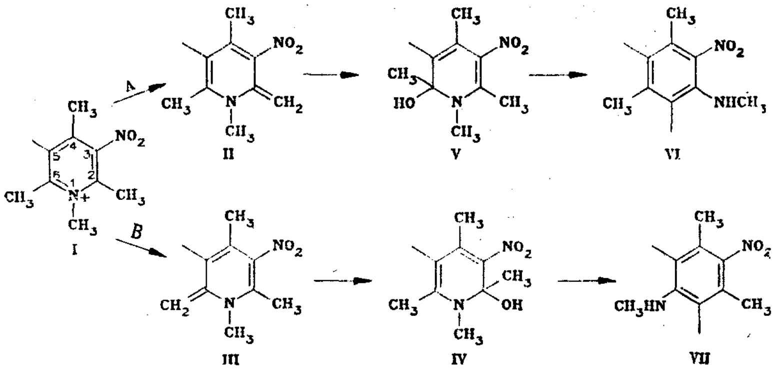
The recyclization of 1,2,4,6-tetramethyl-3-nitropyridinium iodide was examined within the framework of the CNDO/2 (complete neglect of differential overlap) approximation. The electronic structures of the starting, final, and intermediate structures of two competitive processes were evaluated. The primary formation of one of the products was explained.

Two competitive processes (A and B), which, according to [1], take place through the formation of the corresponding anhydro bases II and III, are possible in the recyclization of 1,2,4,6-tetramethyl-3-nitropyridinium iodide.



The aim of the present research was to ascertain the possibility of description of the recyclization within the CNDO/2 (complete neglect of differential overlap) approximation [2]. The calculations were made by means of the program in [3] with an EC-1022 computer. It has been shown [4, 5] that it is sufficient to use the "averaged" geometrical parameters to esti-

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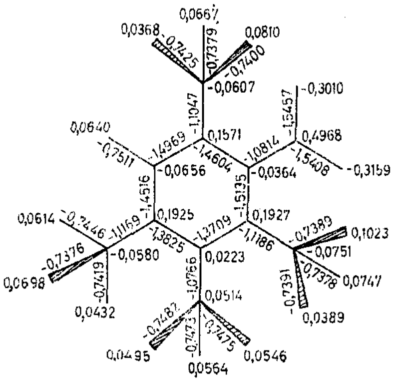

Fig. 1. Charges on the atoms and resonance energies of the bonds (in atomic units) of the 1,2,4,6-tetramethyl-3-nitropyridinium ion (the types of atoms at the nodes are designated in the recyclization scheme).

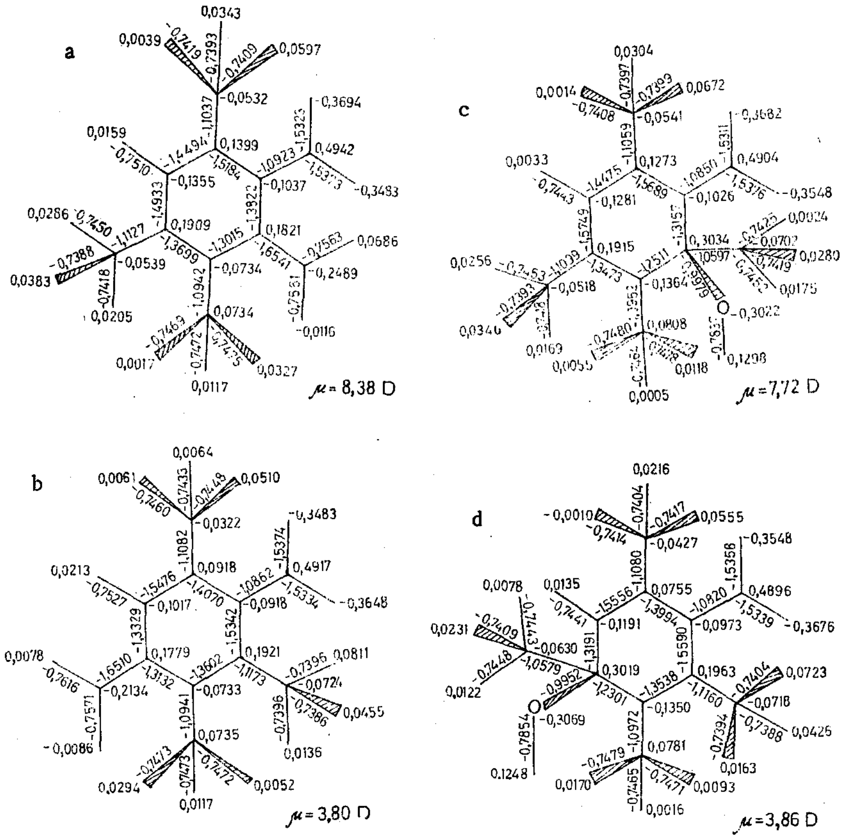

Fig. 2. Electronic structures: *a*) anhydro base II; b) anhydro base III; c) structure IV; d) structure V.

mate the electronic structures of various nitro compounds within the CNDO/2 approximation. All of the calculations of I-VII were therefore carried out in the standard geometry. Complete information regarding the electronic structures of the molecules is presented in Figs. 1-3, in which, as the energy characteristics of the bonds, we used their resonance energies (E_{AB}^{R}) [6] as the most reliably estimable values within the framework of the CNDO/2 method.

According to the data obtained (Fig. 1), the starting molecule can undergo nucleophilic attack in the 2 and 6 positions with virtually equal probabilities (maximum positive charges on the atoms in the ring). However, the energetics of the 1—2 and 1—6 bonds differ. The weakest link in the ring is the 1—2 bond. The formation of anhydro bases II and III leads to further

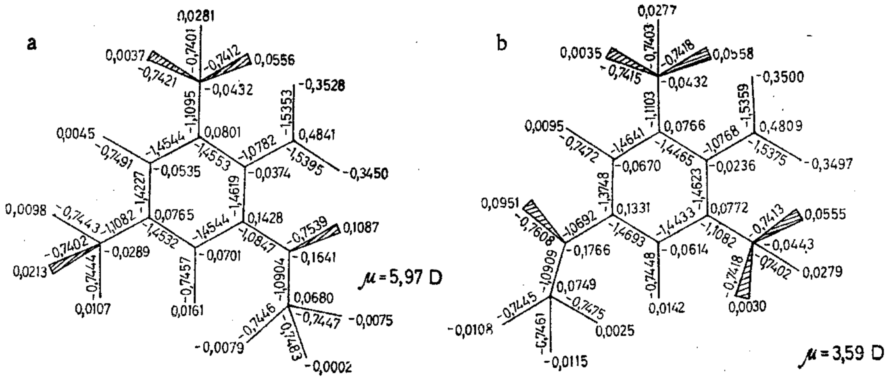

Fig. 3. Electronic structures: *a*) 3,5-dimethyl-2-nitro-N-methylaniline; b) 3,5-dimethyl-4-nitro-N-methylaniline.

weakening of the 1—2 and 1—6 bonds (Fig. 2, structures *a* and b); in the case of structure II the maximum change was obtained for the 1—2 bond, whereas in the case of III the maximum change was obtained for the 1—6 bond. Despite the fact that the changes in the energies of the 1—2 and 1—6 bonds are virtually identical when one compares processes I → II and I → III with one another, due to the inequality of E_{12}^R and E_{16}^R in starting structure I the weakest link in the ring was obtained for anhydro base II. Upon comparing anhydro bases II and III with one another one might arrive at the conclusion that the formation of the former is more favorable. This is also indicated by the greater (in absolute value) total energy of the system. If the strain energy is considered to be the sum of the resonance energies of the valence-unbonded atoms multiplied by the coefficients of the "two-center" approximation [7], we obtain 50.6 and 60.1 kcal/mole, respectively. An approximate estimate of the enthalpies of formation via the scheme in [7] gives —6 kcal/mole for structure II and +24.6 kcal/mole for structure III. In examining the electron density distributions in the anhydro bases let us note that one should expect attack by the nucleophile at the 6 position for structure II and at the 2 position for structure III (the maximum positive charges on the atoms in the ring). As a result, structures V and IV can be formed. According to Fig. 2, structures c and d, further weakening of the 1—2 and 1—6 bonds occurs but in a more complex manner. In fact, when one compares structures II and V, it is apparent that the strengths of the bonds decreased and, as it were, changed positions. The weakest bond in V is now the 1—6 bond. Cleavage of this bond makes realization of rotation of the $-C(CH_3)NCH_3$ group about the 2—3 bond to give the VI molecule possible. Nonvalence interactions are responsible for this rotation. The resonance energies of the 7—4, 7—5, and 7—6 bonds are negative. The maximum bonding was obtained for the 7—6 bond and was —0.0026 au. The positive energy $E_{14}^R = 0.0115$ au also promotes rotation of the fragment.

Upon comparing structures V and IV with one another one may arrive at the conclusion that structure V has greater stability. A lower value of the total energy was obtained for it. The strain energy is 50.5 kcal/mole (the strain energy for IV is 62.0 kcal/mole). The difference in the enthalpies of formation of structures V and IV is ~—5 kcal/mole.

Upon examining the entire process as a whole it is apparent that the formation of the VI molecule from anhydro base II is energically favorable, as is the formation of VII from III; opposite tendencies in the changes in the dipole moments of the structures are observed.

In conclusion, let us note that the CNDO/2 approximation can be recommended for the investigation of recyclization reactions. The formation and yields of the final products are directly interrelated with the electronic structures of the corresponding anhydro bases. In the case of ring cleavage the possibility of rotation of the molecular fragment is due to the energy of the nonvalence interactions; product VI is primarily formed in the case of 1,2,4,6-tetramethyl-3-nitropyridinium iodide. The results of the calculations do not contradict the data previously obtained within the π approximation [1] but supplement them substantially.

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