# Ab Initio Study of Pyridyl Cations, Anions, and Radicals

Osamu KIKUCHI,* Yuji HONDO, Yukihiro YOKOYAMA, Kenji MORIHASHI, and Mitsunobu NAKAYAMA
Department of Chemistry, University of Tsukuba, Tsukuba 305
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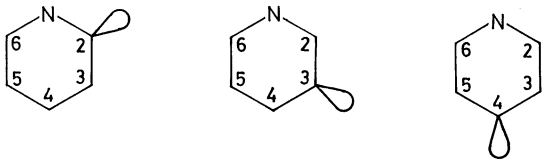
**Synopsis.** Ab initio calculations were carried out for the 2-, 3-, and 4-pyridyl cations, anions, and radicals in order to examine their molecular structures and relative energies among three isomers. The 4-31G//3-21G calculations have predicted that 2-pyridyl cation, 4-pyridyl anion, and 2-pyridyl radical are most stable among the isomers.

Pyridyl is derived formally from pyridine by the CH bond cleavage, and three types of species, cations, anions, and radicals, exist depending on the number of electrons involved in the carbon centered orbital. For the radical, 2-, 3-, and 4-pyridyl radicals have been detected by ESR,[1,2] and the reactivity of 2-pyridyl has been discussed.[3] The pyridyl anions and cations have been considered as the intermediates in chemical reactions.[4-7] Only a few theoretical works have been reported on these species.[8,9] In this note, we report the molecular and electronic structures of pyridyl cations, anions, and radicals determined by ab initio calculations and compare the relative stability among the 2-, 3-, and 4-isomers.

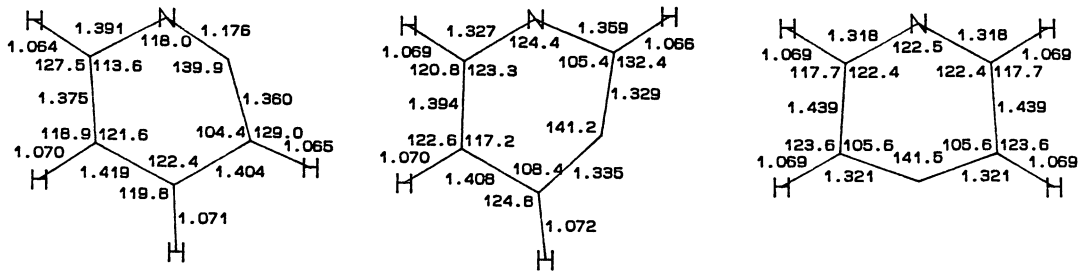


2 3 4

The closed-shell SCF method was used for the cations and anions, while the open-shell RHF method was used for the radicals. The molecular structures were optimized with the 3-21G basis set[10] under the restriction of the planarity for all species. All calculations were carried out using ABINIT program written in our group. The optimized molecular structures are shown in Figs. 1—3 and the relative energies among the isomers are listed in Table 1.

**Pyridyl Cations.** The calculated bond angles at the cationic carbon center of pyridyl cations are almost constant, 140°—142°, in three isomers. These bond angles are close to that calculated for the phenyl cation by Bernardi et al.[11] as is shown in Fig. 4-b. Since 2-pyridyl cation is isoelectronic with *o*-benzyne, it is interesting to compare the structures between them. Fig. 4-c is the structure of *o*-benzyne reported by Scheiner et al.[12] As may be seen from Fig. 4-c, the distortion of the carbon skeleton from hexagon is not large in *o*-benzyne, while a significant distortion is observed in the 2-pyridyl cation. This is due to the large bond angle at the carbon center in 2-pyridyl cation which is adjacent to the nitrogen atom and has the strong cationic character.

The 2-pyridyl cation is calculated to be more stable than the other isomers. This may simply be understood by the interaction between the cationic center and the nitrogen lone-pair electrons in 2-pyridyl. In spite of this large interaction, the large positive charge remains at the cationic carbon atom in 2-pyridyl; the value of +0.704



2 3 4

Fig. 1. Molecular structures of pyridyl cations optimized with the 3-21G basis set. Bond lengths are shown in Å and bond angles are in degrees.

Table 1. 4-31G//3-21G Energies (au) of Three Isomers of Pyridyl Cations, Anions, and Radicals[a]

| | Pyridyl cations | Pyridyl anions | Pyridyl radicals |
|---|---|---|---|
| **2** | −245.398005 ( 0.0) | −245.643669 (10.0) | −245.682080 (0.0) |
| **3** | −245.353832 (27.7) | −245.654192 ( 3.4) | −245.675981 (3.8) |
| **4** | −245.357490 (25.4) | −245.659626 ( 0.0) | −245.678910 (2.0) |

a) Values in parentheses are relative energies among three isomers in kcal mol$^{-1}$.

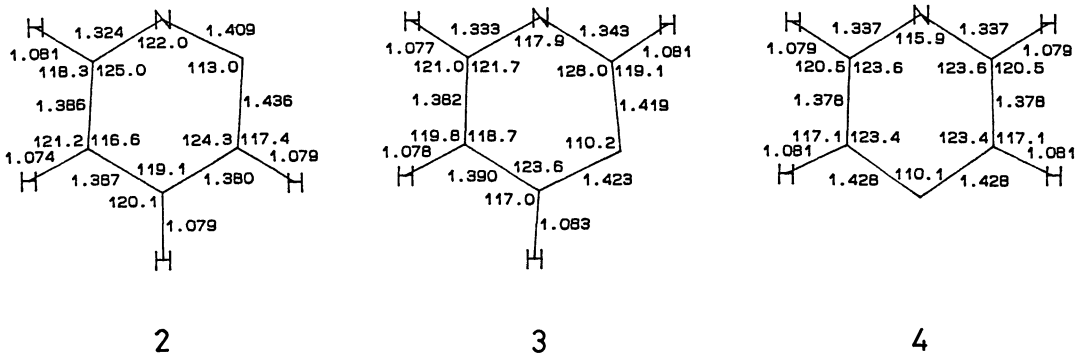



Fig. 2. Molecular structures of pyridyl anions optimized with the 3-21G basis set. Bond lengths are shown in Å and bond angles are in degrees.

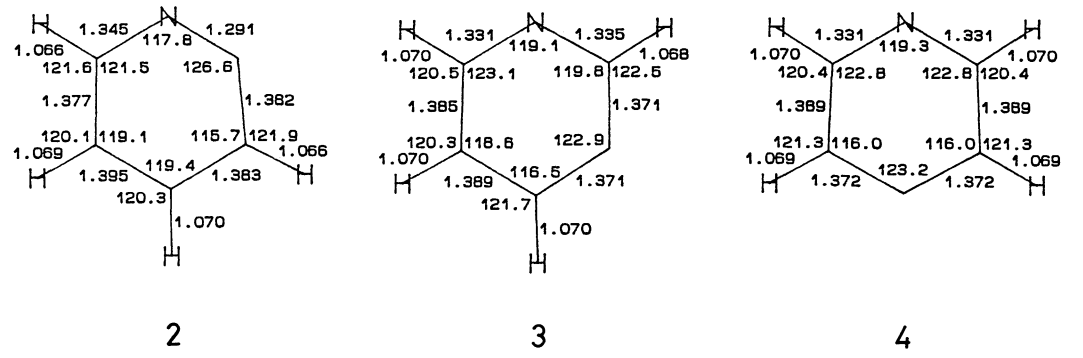



Fig. 3. Molecular structures of pyridyl radicals optimized with the 3-21G basis set. Bond lengths are shown in Å and bond angles are in degrees.

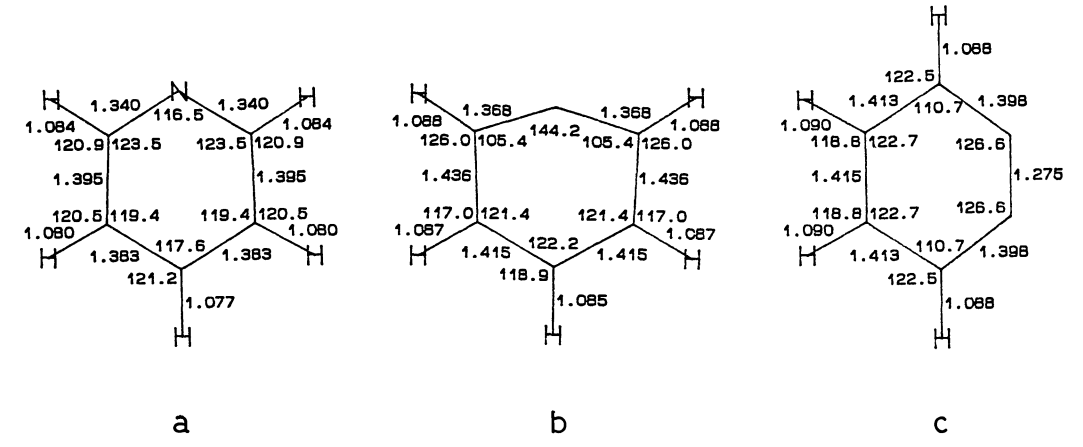



Fig. 4. Molecular structures of a) pyridine from experiment,[13] b) phenyl cation optimized with MCSCF/STO-3G,[11] and c) *o*-benzyne optimized with MP2/DZ+P.[12]

may be compared with those of the cationic centers in other isomers, +0.189 (3-pyridyl) and +0.410(4-pyridyl). This indicates that the stabilization expected in 2-pyridyl is due to the electrostatic interaction.

**Pyridyl Anions.** The angle at the anionic carbon atom is 110°—113° for three isomers. As may be understood from Fig. 2 and Fig. 4-a, the local structure around the nitrogen atom in 3- and 4-isomers is not largely disturbed by deprotonation of pyridine. In the case of 2-pyridyl anion, a remarkable distortion is observed at the anionic center. This is due to the repulsive interaction between two lone-pair electorns at the adjacent nitrogen and carbon atoms. This interaction makes the 2-pyridyl anion unstable. The 4-pyridyl

anion is calculated to be most stable, although the energy differences among three isomers are not large.

The 6-31G*//AM1 calculations gave the same trend in the relative stabilities among three anions, although AM1 calculations gave incorrect results for the relative energies of these anions.[9]

**Pyridyl Radicals.** Although the 4-31G//STO-3G calculations of pyridyl radicals have been reported earlier,[8] it may be worth to show the structures and energies obtained by the same level of calculations as for the cations and anions. The molecular structures (Fig. 3) and the relative stabilities of three isomers (Table 1) are parellel to the 4-31G//STO-3G results.

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