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An Ab Initio Molecular Orbital Study of Pyridyl Radicals

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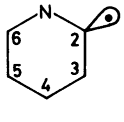
Synopsis. Open-shell RHF and UHF ab initio calculations were carried out for 2-, 3-, and 4-pyridyl radicals in order to determine their molecular structures and relative energies. The minimal STO-3G basis set was used for the structure optimization, while the 4-31G basis set was used for the energy evaluation. The 2-pyridyl radical has the lowest energy, although the energy differences among these three isomers were very small. The possibility of a Π-ground state in pyridyl radicals was rejected.

Pyridyl radicals are typical aryl radicals and are derived formally from the homolytic cleavage of the CH bond of pyridine. Three isomers, 2-, 3-, and 4-pyridyl radicals, have been detected by ESR,[1,2] and the reactivity of 2-pyridyl has recently been discussed.[3] An interesting aspect from the theoretical point of view is the relative energies of the three isomers, since the interaction between the singly-occupied molecular orbital (SOMO) and the nonbonding orbital at the nitrogen atom can be expected to affect the stability of these radicals. Another interesting point is to examine the possibility of the Π-ground state, in which the π_4 orbital is occupied by the unpaired electron, although ESR has suggested the Σ-ground states for these radicals.[2] There have been only a few theoretical studies of pyridyl radicals;[2,4] all of them are semiempirical calculations applied to idealized or assumed molecular structures. In the present study, the molecular structures of three pyridyl radicals, **2**—**4** were optimized by ab initio MO methods, and their relative energies were compared.



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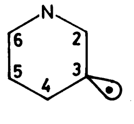

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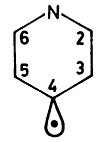

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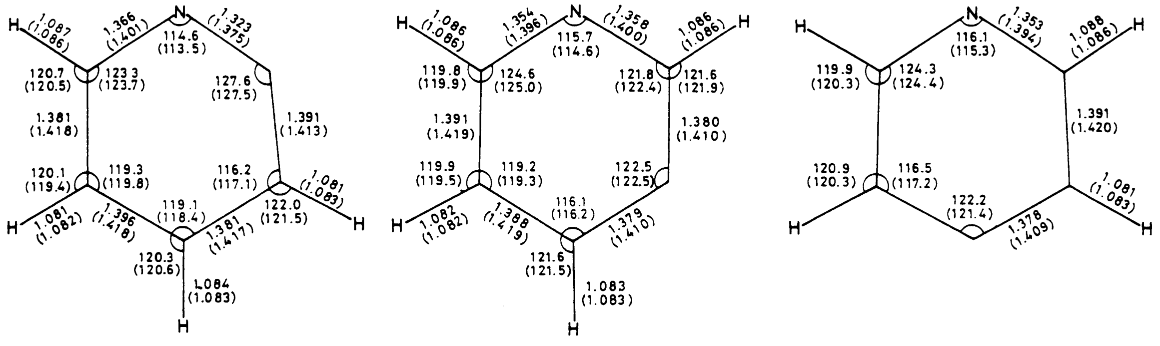
The open-shell RHF and UHF methods were employed. The RHF orbitals are appropriate for understanding the orbital shape, while the UHF orbitals involve the spin-polarization effect. The molecular structures were optimized with the STO-3G basis set,[5] and the energies were calculated with the 4-31G basis set.[6]

The RHF calculation showed that the SOMO of each radical is localized mainly on the carbon atom at the radical center; the atomic-spin populations at the carbon atoms in **2**, **3**, and **4** are 0.879, 0.918, and 0.916 respectively. The molecular structures optimized by RHF and UHF (in parentheses) calculations are shown in Fig. 1. The CC and CN bonds calculated by the UHF method are longer than those calculated by the RHF method by 0.02—0.05 Å. The RHF N-C(2) bond length in **2**, 1.323 Å, is very short in comparison with those in **3** and **4**, which are in the range of 1.35—1.36 Å. This is caused by the interaction between the nitrogen nonbonding orbital and the unpaired electron at the adjacent carbon atom in **2**. This interaction is also reflected in the calculated orbital energies of the SOMO and the nonbonding orbital. As may be seen from Fig. 2, the SOMO energy of **2** is higher than those of **3** and **4**, while the nonbonding orbital of **2** lies lower than those of **3** and **4**. These facts indicate an appreciable interaction between the two orbitals in 2-pyridyl.

The 2-pyridyl radical has the lowest energy of the three isomers, as is shown in Table 1. The energy differences among the three isomers, however, are not large. The origin of the stability of **2** is not clear, although the interaction between SOMO and the nonbonding orbital may contribute to some extent.

Since the SOMO of **2** lies higher than those of **3** and **4**, the Π state of 2-pyridyl, in which the σ_{18} electron is



2 **3** **4**

Fig. 1. Molecular structures of pyridyl radicals optimized by open-shell RHF and UHF methods with STO-3G basis set. The UHF values are in parentheses. The optimization was performed under restriction of the planarity of molecular structure. Bond lengths are shown in Å, and bond angles are in degrees.

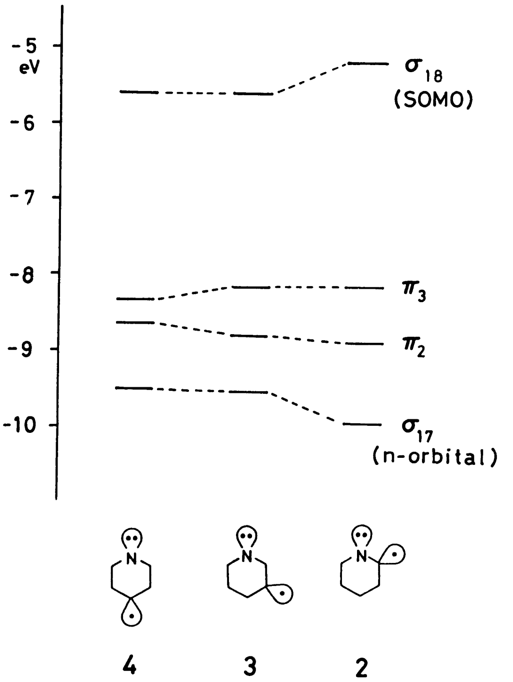


Fig. 2. Higher four occupied molecular orbitals of pyridyl radicals calculated by open-shell RHF method with STO-3G basis set. The σ_{18} orbital is the singly-occupied orbital.

Table 1. Calculated Energies (au) of Three Isomers of Pyridyl Radicals[a)]

	RHF 4-31G//STO-3G	UHF 4-31G//STO-3G
2-Pyridyl (**2**)	−245.67930(0.0)	−245.68987(0.0)
3-Pyridyl (**3**)	−245.67319(16.0)	−245.68667(8.4)
4-Pyridyl (**4**)	−245.67617(8.2)	−245.68804(4.8)

a) Values in parentheses are relative energies in kJ mol^{-1}.

excited to the π_4 orbital, may be expected to lie low. The Π state of 2-pyridyl was thus examined. The optimized structure is shown in Fig. 3. The structure of the Π state of 2-pyridyl is very different from that of the Σ state in Fig. 1. The N–C$_2$ bond, 1.221 Å, is extremely short, while the N–C$_2$–C$_3$ bond angle is very large. These facts suggest that the N–C$_2$ bond may be written formally as a triple bond, $-N^+\equiv C-$. The Π state was calculated to lie 376 kJ mol^{-1} above the Σ-ground state (STO-3G energy difference). It is thus concluded that the Π state is not expected for the ground state of 2-pyridyl, even if the substitution and/or environmental effects are changed.

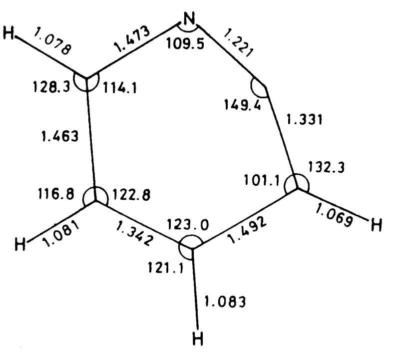


Fig. 3. Molecular structure of the excited Π state of 2-pyridyl radical optimized by open-shell RHF method with STO-3G basis set.

The calculated spin distribution of pyridyl radicals did not agree with the experimental values estimated from the ESR spectra. The proton hyperfine coupling constants[7)] of 2-pyridyl, for example, were calculated by means of the RHF method to be very small (0.4—2.1 G (1G=10^{-4} T)); experiments have shown the coupling constants of 10 and 6 G to two protons.[2)] The UHF method gave larger values: $a(H_3)=36$, $a(H_4)=-30$, $a(H_5)=33$, $a(H_6)=-33$. The disagreement may come from the method of calculation. The UHF values are generally larger than the experimental values because of the failure of the spin-polarization contribution.[8)]

All the calculations were carried out with the ABINIT program written by our group. The work was supported by the University of Tsukuba Project Research.

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7) Estimated by the use of $a(H)=507\times\rho_H$.

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