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An Ab Initio Molecular Orbital Study of Lithiopyridines

Osamu Kikuchi,* Hideo Togo, and Naomichi Furukawa
Department of Chemistry, The University of Tsukuba, Sakura, Ibaraki 305

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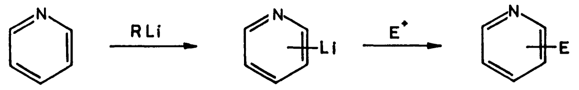
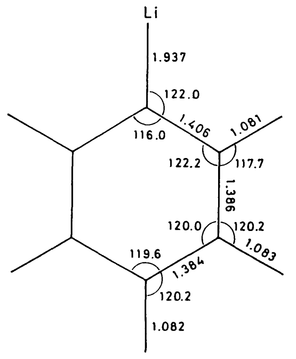
Synopsis. Ab initio molecular orbital calculations were performed for 2-, 3-, and 4-lithiopyridine monomers, and the molecular and electronic structures of lithiopyridines and their reactivity with electrophiles were examined.

Aryllithium compounds react with various electrophiles to afford the corresponding substituted compounds, and they are very important species for synthetic purposes.[1,2] Lithiopyridines are considered to be the intermediates in the following synthetic route to the substituted pyridines.[2] Since phenyllithium, **1**, is tetrametric in the solid phase and in solution,[3] lithiopyridines may exist in the aggregation state with a solvent in solution. However, the study of the lithiopyridine monomers is essential to understand the electronic properties of lithiopyridines. The present note will examine the molecular and electronic structures and reactivity of 2-, 3-, and 4-lithiopyridines on the basis of MO calculations.



The molecular structures of phenyllithium, **1**, and of lithiopyridines, **2**—**4**, were optimized by means of ab initio calculations with the STO-3G basis set[4] by assuming planar molecular structures. Their energies were obtained with the 6-31G basis set.[5] The molecular strcture of **1** is shown in Fig. 1, while those of **2**—**4** are shown in Fig. 2. The energies of **2**—**4** and some electronic properties of **1**—**4** are listed in Table 1.

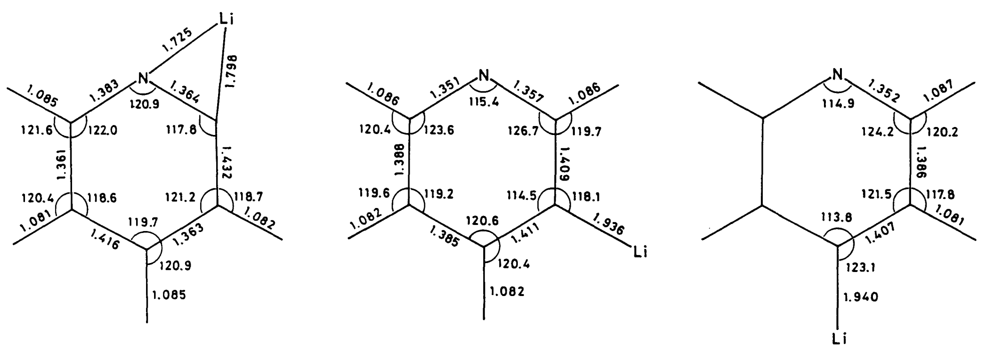
The molecular structures of **3** and **4** can be estimated from those of phenyllithium and pyridine; the STO-3G structure of pyridine has 1.352 Å for the CN bond and 115.6° for the CNC angle. The structures around the N atom in **3** and **4** resemble that of pyridine, while those around the C-Li bond resemble that of phenyllithium. The calculated C-Li bond lengths of **1**, **3**, and **4** are shorter than the C-Li bond in alkyllithium, 2.001,[6] and longer than those between the Li atom and the olefinic carbon atom, 1.776—1.863.[7] The structure of **2** was found to be very different from **3** and **4**; the interaction between the Li atom and the lone-pair electrons of the N atom is strong enough to give the bridged structure. A similar bridged structre has been reported for LiHNOH.[8] The energies of **3** and **4** are comparable and are higher than **2** by about 50 kJ mol^{-1}. The lower energy of **2** is due to the stabilization of the Li atom by the lone-pair electrons. As was pointed out above, lithiopyridines may be stabilized in solution by the Li-solvent interaction; the relative stabilities among the three isomers in solution can not, however, be estimated here.



1

Fig. 1. The STO-3G structure of phenyllithium. Bond lengths are in Å, and bond angles are in degrees.

Since the electrophilic substitution at the C-Li carbon atom is a typical reaction of lithiopyridines, the reactivity of **1**, **3**, and **4** with electrophiles was com-



2 **3** **4**

Fig. 2. The STO-3G structures of 2-lithiopyridine (**2**), 3-lithiopyridine (**3**), and 4-lithiopyridine (**4**). Bond lengths are in Å, and bond angles are in degrees.

Table 1. Energies and Some Electronic Properties of 2-, 3-, and 4-Lithiopyridines and Phenyllithium

Compound	Energy[a]	Q(Li)[b]	q(C)[c]	q_{π}(C)[d]	$\varepsilon_{\mathrm{HOMO}}(\pi)$[e]
2-Lithiopyridine (**2**)	−253.44542 (0.0)	0.088	5.932	0.678	−7.52
3-Lithiopyridine (**3**)	−253.42588 (51.5)	0.217	6.054	0.851	−6.68
4-Lithiopyridine (**4**)	−253.42633 (50.2)	0.228	6.035	0.816	−7.06
Phenyllthium (**1**)		0.190	6.042	0.849	−6.23

a) The 6-31G calculation for the STO-3G structures. The values are in atomic units, and the values in parentheses are relative energies in kJ mol^{-1}. b) Charge at the Li atom. c) Electron population at the carbon atom of the C-Li bond.
d) π-Electron population at the carbon atom of the C-Li bond. e) Orbital energy of the highest occupied π-orbital. The values are in eV.

pared. As may be seen from Table 1, the electron population on the C-Li carbon atom is in the order of **3**>**1**>**4**, while the π-electron population on the carbon atom in the order of **3**≅**1**>**4**. These findings suggest that the S$_E$2-type displacement of the Li atom occurs in **3** more easily than in **4**. The orbital energies of HOMO(π) of **3** and **4** are more negative than **1**; this indicates that the reactivity of **3** and **4** is lower than **1** for the orbital-controlled reaction. The calculated positive charges of the Li atom are in the order of **4**>**3**>**1**≫**2**. The small value in **2** is due to the participation of the lone-pair electrons of nitrogen.

All the calculations were performed on the FACOM M-380 computer at The University of Tsukuba using the ABINIT program written by our group. The work was supported by University of Tsukuba Project Research.

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