

Indirect Electrochemical Oxidation of Picolines. Ab-initio Treatment

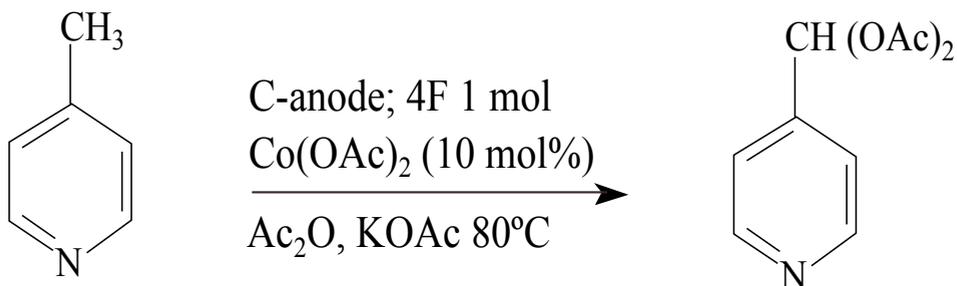
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ABSTRACT. The structures of 2-picoline, 3-picoline and 4-picoline (neutral and intermediate cationic species) have been optimized using 6-311G* basis set at RHF and UHF levels. The results of MO-calculations were interpreted in terms of energies and coefficients of their molecular orbitals (HOMO and LUMO), stabilization energy, and dipole moments. The computed electronic charge density of HOMO was located on CH₂⁺ group of 2- and 3-picoline cationic species, which prevented the formation of aldehyde diacetate. On the other hand, all charge densities of HOMO in cationic 4-picoline were mainly localized on the ring with no charge density on CH₂⁺ group. The CH₂⁺ group of 4-picoline cationic species could eventually be easily attacked by acetate to form aldehyde diacetate. The results of MO calculations confirmed the suggested oxidation mechanism reported.

Introduction

The rapid advances currently being made in the synthesis and applications of picolines and its N-oxides have led to a growing need for a simple and yet comprehensive theoretical framework within which the chemical and physical properties of this electron rich and biologically important compound can be understood. The structural features of picolines and its N-oxides are currently the subject of extensive investigations and a wide range of activities^[1-5]. Direct electrochemical oxidation of picolines is only possible at high oxidation potential under acidic conditions yielding pyridine carboxylic acids. Using at Pt, Pb, PbO₂ anode in a divided cell, 4-picoline is transformed to pyridine-4-carboxylic acid^[6,7].

An indirect electrochemical process for the selective oxidation of 4-picoline and its N-oxide with *in situ* electro generated Cobalt (III) in an undivided cell using graphite anode (yield 45-68%) have been studied^[8].



Under those experimental conditions, it was difficult to oxidize 2-picoline, 3-picoline. The theoretical study of such oxidation processes is rather rigorous from the viewpoint of quantum chemistry, due to a great number of species (*e.g.* oxidizing mediator, supporting electrolyte, oxidizing molecule, solvent). However, quantum chemical methods can provide qualitative, but even semi-quantitative, useful information for better understanding of the way such oxidation process can occur.

In the present work, we try to apply quantum mechanical calculation to explain why 4-picoline gives pyridine-4-aldehyde diacetate, while 2-picoline, 3-picoline would not give the corresponding pyridine aldehyde diacetate. For this purpose quantum mechanical calculations using 6-311G* at the level of RHF and UHF appeared in order to find a correlation between quantum chemical properties, such as orbital energies, ionization energy, dipole moment, electronic charge densities and the oxidation efficiency.

Computation Procedure

Ab-initio MO calculations were carried out at the Hartree-Fock level using the diffuse and split G-311G* basis set for comparison at some points in our work. All calculation reported were performed using the Games software package^[9]. The molecular geometries of the studied compounds were fully optimized using the gradient minimization technique^[10]. In all cases the global minimum on the potential energy surface is characterized by having zero gradient norms and by diagonalizing the matrix of the second derivatives. In case of a neutral molecule, RHF (restricted Hartree-Fock Hamiltonian) was used. In this approach, a single set of molecule orbital was used. Alternatively, in case of cationic species, UHF (unrestricted Hartree-Fock Hamiltonian) was used.

Results and Discussion

Electrochemical Results

The selectivity and effectiveness of the indirect electrochemical oxidation of 4-picoline in presence of Co (OAc)₂ were optimized toward the formation of pyridine-4- aldehyde diacetate by testing the effect of solvent electrolyte, presence of Cu²⁺ and oxygen^[8]. The following mechanism was proposed:



The acetoxy substituent would then lead to an easier side-chain oxidation by electron transfer through Co (OAc)₃ giving the end product. On the other hand, several trials were carried out to apply this method for the oxidation of 2-picoline, 3-picoline, it was entirely difficult to obtain the corresponding pyridine aldehyde diacetate.

Quantum Chemical Results

Tables (1, 2, 3, and 4) and Figures (1, 2, and 3) present the equilibrium bond lengths, bonds angles, net charge, bond order, heat of formation, total energy, dipole moment, % of P₂ on HOMO and charge density map (HOMO) for the studied picolines. Among the values given in tables and figures, one can reveal the following:

TABLE 1. Equilibrium bond lengths, A and bond angles degree for studied picolines using 6-311G* basis sets.

Compound	Bond length, A							Bond angle degree		
	N-C ₃	N-C ₅	C ₃ -C ₂	C ₂ -C ₁	C ₁ -C ₆	C ₅ -C ₆	C ₁ -C*	< 543	< 432	< 321
2-picoline	1.319	1.325	1.394	1.375	1.386	1.378	1.508	123.38	118.44	121.131
3-picoline	1.321	1.316	1.386	1.388	1.379	1.385	1.5	116.460	117.975	124.451
4-picoline	1.321	1.316	1.380	1.390	1.384	1.386	1.5079	116.23	117.01	123.85

TABLE 2. Bond order and net charge for studied picolines using 6-311G* basis sets.

Compound	Bond order							Net charge 'e						
	N-C ₃	N-C ₅	C ₃ -C ₂	C ₂ -C ₁	C ₁ -C ₆	C ₅ -C ₆	C ₁ -C*	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C*
2-picoline	1.319	1.325	1.394	1.375	1.386	1.378	1.508	-0.04	0.034	-0.002	-0.316	0.135	-0.057	0.12
3-picoline	1.321	1.316	1.386	1.388	1.379	1.385	1.5	0.15	-0.37	0.31	-0.355	0.26	-0.23	0.104
4-picoline	1.321	1.316	1.380	1.390	1.384	1.386	1.5079	-0.17	-0.05	0.128	-0.239	0.128	-0.57	0.160

TABLE 3. Heat of formation, ΔH_f , total energy, E_T , dipole moment, μ and energy difference for neutral molecule (A) and intermediate cationic species (B).

Compound	ΔH_f , k cal mol ⁻¹		E_T , eV		μ , D	
	A	B	A	B	A	B
2-picoline	19.75	234.94	-285.799	-284.920	-11.21	2.87
3-picoline	20.49	230.00	-285.696	-284.928	2.489	4.137
4-picoline	20.86	241.71	-285.616	-284.903	3.114	6.183

TABLE 4. % P_z of each atom in HOMO-MO for investigated compounds.

Compounds	% P_z													
	N		C ₁		C ₂		C ₃		C ₄		C ₅		CH ₃	CH ₂ ⁺
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
2-picoline	-	-	21.0	-	26.5	15.6	-	-	25.3	9.6	23.7	26.9	3.4	47.9
3-picoline	-	-	23.4	9.2	29.9	-	-	17.3	29.2	9.0	22.0	12.4	4.0	53.0
4-picoline	-	2.8	23.6	20.5	26.8	26.6	-	-	25.9	26.6	23.6	20.5	-	-

1 – Total energy of 4-picoline is less stable than 2- and 3-picoline by 114.7 and 50.6 k cal mol⁻¹ respectively.

2 – Cationic species of 4-picoline is less stable than 2- and 3-picoline cationic species by 10.6 and 15.6 k cal mol⁻¹.

3 – The instability of 4-picoline (neutral and cationic) would enable the molecule to react with acetate forming aldehyde diacetate (c.f. mechanism step 4).

4 – The stabilization energy ΔE^* ($E_A - E_B$) of 4-picoline is less than 2 and 3-picoline by 104 and 64.6 cal mol⁻¹ respectively. Again, the instability of 4-picoline enables molecule to react with acetate to form aldehyde diacetate.

5 – The heat formation of ΔH_f of 2-picoline, 3-picoline and 4-picoline are of the same order of magnitude with almost no significance difference. On the other hand, the heat of formation of the intermediate cation manifested a dramatic change from the neutral molecule; 4-picoline cationic species seemed to be greater than 2- and 3-picoline cationic species by 37 and 41 k cal mol⁻¹ respectively. Thermodynamically, 4-picoline cationic species seems to be the favorable species in the reaction medium to react with acetate.

6 – The dipole moment, which is the most common desired measure of electron distribution in a molecule, was calculated for the studied compounds and their cationic species. The data obtained (c.f. Table 3) showed that 4-picoline cationic species was highly polar than 2- and 3-picoline cationic species by 3.31

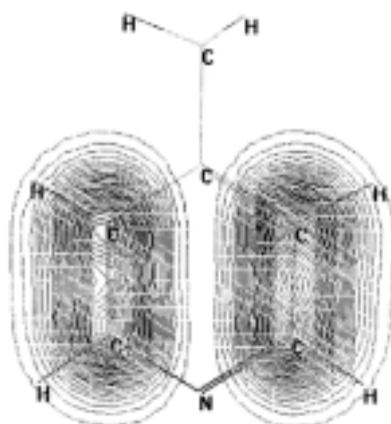
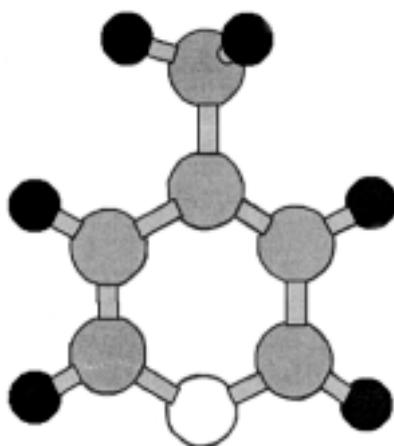


FIG. 1. Equilibrium geometry and charge density map (HOMO) for 4-picoline.

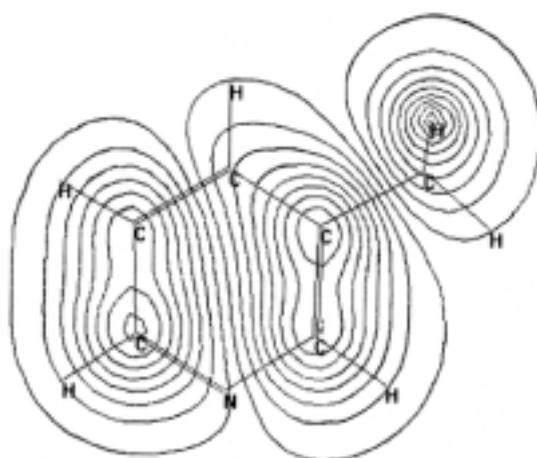
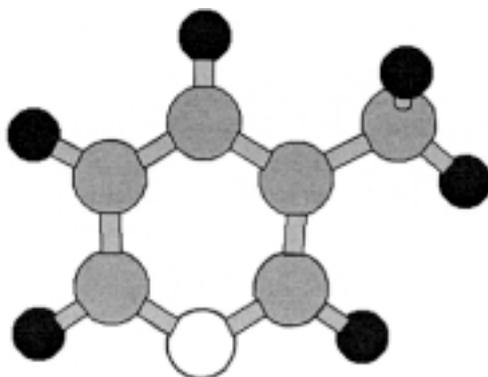


FIG. 2. Equilibrium geometry and charge density map (HOMO) for 3-picoline.

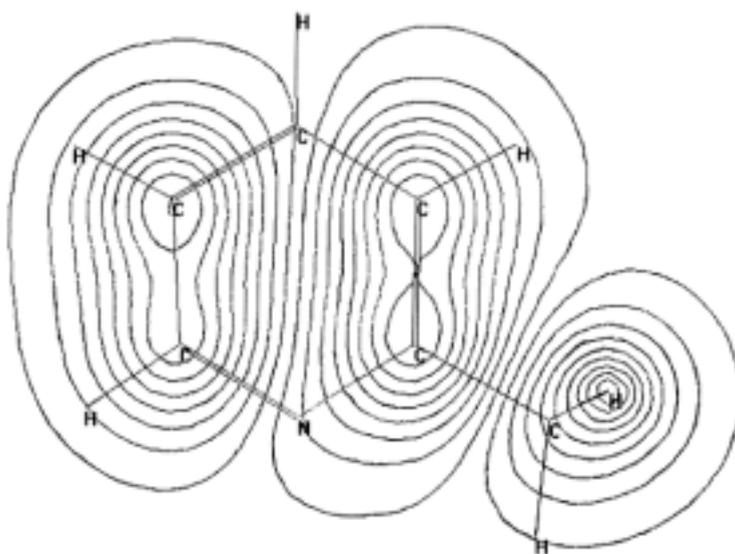
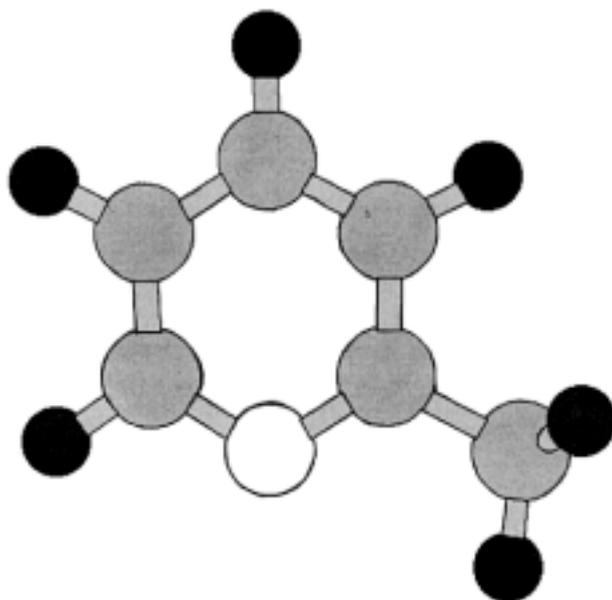


FIG. 3. Equilibrium geometry and charge density map (HOMO) for 2-picolinic.

D and 2.05 D, respectively. Then, the high value of the dipole moment of 4-picoline would lead to a better stabilization of the cation especially in a protic solvent like acetic acid.

7 – With the framework of UHF, two sets of molecular orbitals are usually obtained, namely, α - and β - molecular orbitals and the charge density located on each center in case of cation would be the same of the two molecular orbitals.

8 – CH_2^+ group of 2- and 3-picoline contributes 47.9% 53% from the total electronic charge density of HOMO, respectively. On the other hand no charge density was located at the CH_2^+ group of 4-picoline cation species. This shows that the presence of relatively high charge density 2- and 3-picoline would prevent the formation of acetoxy substituents (*c.f.* Figs. 1, 2 and 3).

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الأكسدة غير المباشرة لمركبات البيكولين باستخدام كيمياء الكم

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المستخلص. تم دراسة التركيب الإلكتروني لمركبات البيكولين وذلك لإيجاد أفضل شكل هندسي لهذه المركبات باستخدام قاعدة الدوال من النوع 6-311G* وقد تمت الحسابات على الجزئي المتعادل وكذلك الكاتيون الموجب وقد نوقشت نتائج الحسابات بمداريه الجزئية في ضوء كل من الطاقة الكلية، معاملات المدارات الجزئية، طاقة الثبات، عزم الازدواج وأخيراً فجوه الطاقة.

وبتحليل كثافة السحابة الإلكترونية لأعلى مدار مشغول في حالة الكاتيون الموجب وجد أن معظم السحابة الإلكترونية توجد على (CH_2^+) في مركبات 2-، 3- بيكولين وهي تمنع تكوين ألدهيد داى أستيت وعلى الجانب الآخر وجد أن معظم السحابة الإلكترونية في 4- بيكولين موزعة على الحلقة ولا توجد أي سحابة إلكترونية على مجموعه المثلين الكاتيونيّة (CH_2^+) مما أدى إلى قابلية الاتحاد مع مجموعة الأستينات لتكوين داى أستينات ألدهيد. وكانت نتائج حساب المدارات الجزئية مؤكدة لميكانيكية التفاعل المقترحة من الكيمياء الكهربائية.