A theoretical approach to zwitterionic derivatives of 4-vinylpyridine

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4-Vinylpyridine and a quaternized derivative were calculated by the modified neglect of differential overlap (MNDO) method to obtain values related to their geometry, energetic magnitudes and dipole moments for the closed-shell molecules and the corresponding free radicals. A discussion of the chemical behaviour of all structures is presented and some evidence for a possible free-radical pathway for polymerization is analysed.

(Keywords: 4-vinylpyridine; MNDO method; zwitterion; quaternization; free radicals; polymerization)

INTRODUCTION

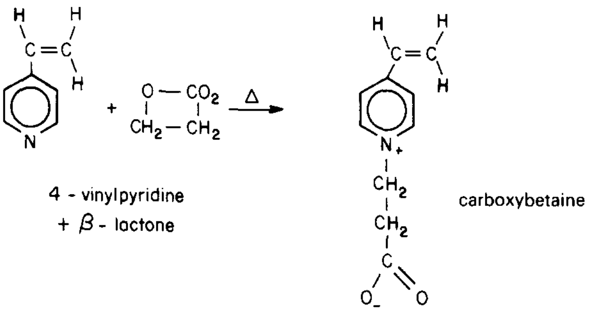
Monosubstituted pyridines are organic bases with known nucleophilic properties and, most importantly, they have a strong tendency to polymerize[1–3]. Zwitterionic derivatives of 4-vinylpyridine may produce polymers with real charges, with interesting properties that include an increase in ionic strength in aqueous solution[4]. In addition, a number of molecular characteristics make them particularly interesting as surfactants or detergents.

Pyridinic derivatives often have a complicated chemical structure, with active sites where polymerization may take place. It is therefore important to predict theoretically the more feasible pathway of the polymerization reaction, if specific characteristics of conformation and stability of the final products (macromolecules) are sought. Prediction of possible reaction mechanisms is valuable in experimental characterization as well.

Vinylpyridine isomers have been studied in relation to their base strength in both gas phase and solution[4], with further attention given to their chemical characteristics[5]. As Barone *et al.*[5] pointed out, the conformational characteristics of conjugated molecules are determined by a balance between steric and conjugative effects (double bonds conjugated to aromatic rings), and this kind of analysis represents one of the most difficult tasks for semiempirical methods. Moreover, the zwitterionic derivatives obtained after quaternization of the vinylpyridine group are larger molecules where straightforward computations by more reliable *ab initio* methods are extremely expensive. In the present investigation, attention is given to a carboxylic derivative of 4-vinylpyridine obtained after quaternization, by using the locally modified version of the MNDO method. These calculations included total optimization of the molecular structures of the closed-shell molecules and of the free radicals produced in the polymerization process. The program was computed on a 7800 Burroughs computer using standard parameters[6].

CLOSED-SHELL MOLECULAR CALCULATIONS

In this section we address results of the calculations corresponding to 4-vinylpyridine and the carboxylic derivative obtained after the quaternization reaction:



The relevant geometrical parameters and net charges for 4-vinylpyridine and the quaternized molecule are shown in *Figures 1–3*. Calculations in *Figure 3* considered a planar position of the vinyl group with respect to the aromatic ring. This equilibrium structure corresponds to the minimum energy or maximum stability of the compound molecule[5]. These results show that the negative charge expected on the carboxylic group is split over the two oxygen atoms, but the positive charge on the nitrogen atom is not localized, due to the aromaticity of the ring in the quaternized derivative. These results also show that the distribution of the nitrogen charge over the ring causes the reactivity of this atom to be lower than expected. As a consequence, enhanced reactivity is induced on the carbon and hydrogen atoms of the ring. In addition, the first carbon atom of the vinyl group shows a small negative value in both cases but it is slightly larger in the quaternized molecule.

Another interesting aspect related to the chemical properties of the quaternized molecule lies in the possible sites for nucleophilic and electrophilic reactions. The two

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more likely positions for nucleophilic reactions are the carbon of the carboxylic group and some of the acid hydrogen atoms. However, this possibility is small due to the repulsive effect of the strong negative charge of the carboxylic group. Furthermore, it is also well known that a nucleophilic reaction on the aromatic ring is out of the question. On the other hand, the more likely places for electrophilic reactions are obviously the positions of the carboxylic group, the nitrogen atom and the carbon of the vinyl group attached to the ring. The last position is important in the context of this study because of the possibility of polymerization through the vinyl group.

The computed equilibrium structures, relative energies and dipole moments for 4-vinylpyridine and the quaternized molecule are shown in *Table 1*. Comparison with values obtained in ref. 5 for 4-vinylpyridine depicts very good agreement. It is necessary to emphasize that previous computations were performed using basically *ab initio* methods for the most significant fragments.

Among the greatest differences in molecular values obtained for 4-vinylpyridine and the quaternized molecule, we observe the dramatic change in the value of the dipole moment due to the presence of the charges. Its magnitude is 22.61 D with a mean contribution of 18.42 D on the y axis.

Figure 4 depicts the molecular-orbital interaction diagram pictorially, i.e. the highest occupied, lowest unoccupied molecular-orbital region (HOMO–LUMO region). This figure shows that the last electron is delocalized around the region between the oxygen atoms of the carboxylic group, particularly in the hybrid orbitals sp_2 in the x–y plane (HOMO region). With respect to the LUMO orbitals these correspond to the delocalized set of p_z orbitals of the ring and the vinyl group, with results that show lower specific magnitudes of the vinyl group. In contrast, in the vinylpyridine case both HOMO and LUMO orbitals of the ring and vinyl groups have similar weights in relation to their wavefunction coefficients.

Ionization potentials (*IP*) for both molecules were calculated following Koopman's theorem, yielding values of 9.464 eV for 4-vinylpyridine and 7.457 eV for the quaternized molecule. This difference is caused by the

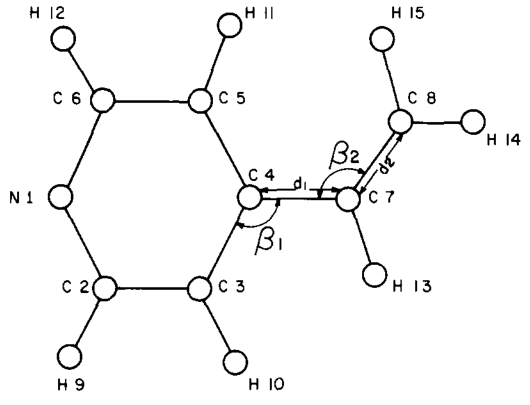

Figure 1 4-Vinylpyridine

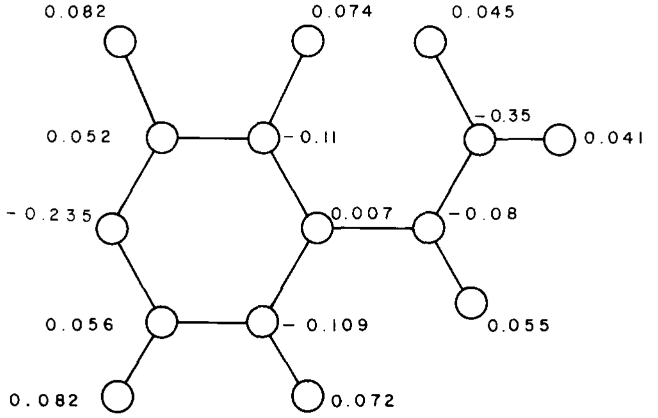

Figure 2 Net charges on 4-vinylpyridine

Table 1 Final results for 4-vinylpyridine (4VP) and quaternized molecule (QM)

	4VP		
	This work	Previous work[5]	QM
d_1 (C4–C7) (Å)	1.471	1.496	1.467
d_2 (C7–C8) (Å)	1.353	1.310	1.347
β_1 (C7–C4–C3) (deg)	123.9	123.8	124.28
β_2 (C8–C7–C4) (deg)	126.3	127.6	128.40
Total energy (eV)	−1199.98	-	−2281.84
ΔH_f (kcal mol^{-1})	47.035	-	33.887
Dipole moment (D)	2.221[a]	2.270	22.61
IP (eV)	9.46[b]	9.42	7.46

[a] Exp. value = 2.0[7]
[b] Exp. value = 9.42[8]

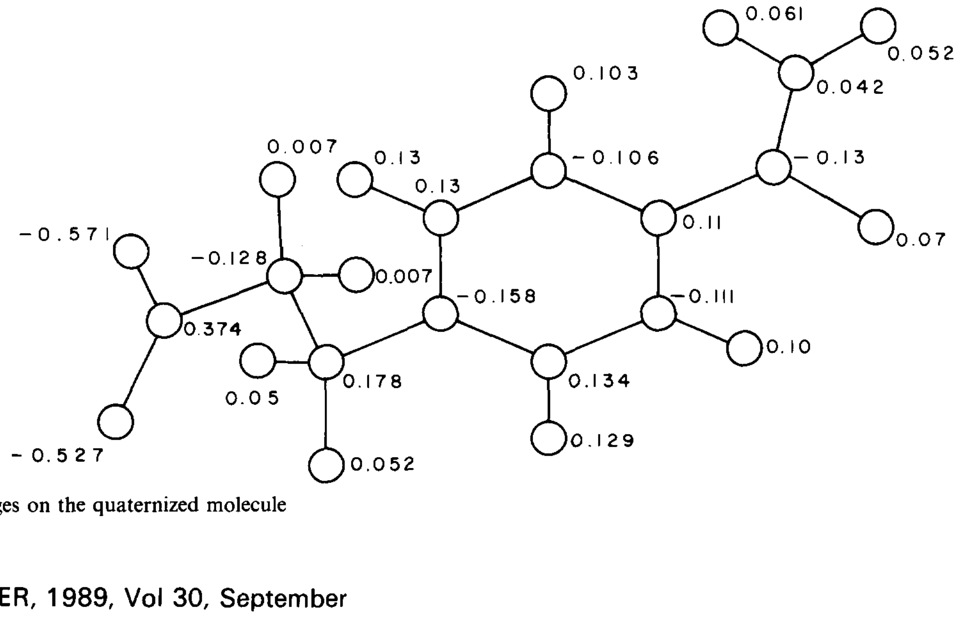

Figure 3 Net charges on the quaternized molecule

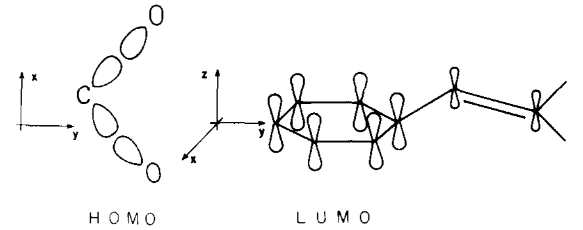

Figure 4 HOMO–LUMO representations for the quaternized molecule

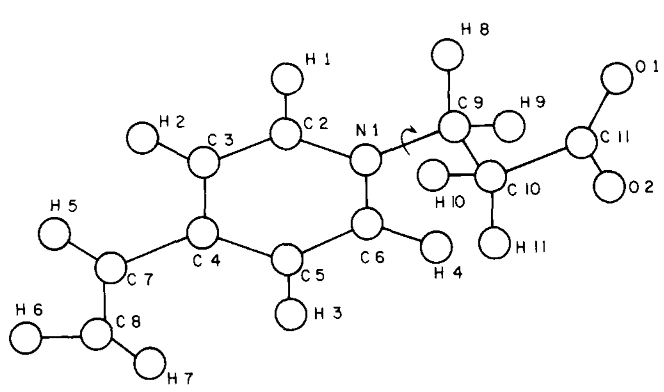

Figure 5 Rotational barrier in the quaternized molecule

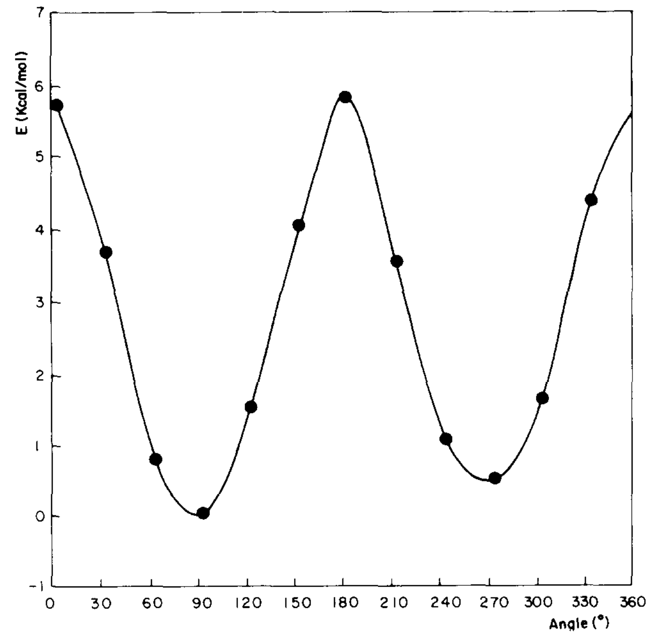

Figure 6 Potential energy curves *versus* torsional angle for the quaternized molecule

real charge density of the carboxylic group and the change in the HOMO diagram after quaternization.

Finally, *Figures 5* and *6* show the rotational barrier of the carboxylic group around the bond joining this group with the ring. In these figures, the aromatic ring lies in the x–y plane and depicts two energy maxima at 0° and ~190° with a magnitude of 5.9 kcal mol^{-1} for both maxima. The difference in the magnitudes of the minima amounts to 0.432 kcal mol^{-1}, and they are located at 90° and 270°. The Boltzmann populations for these conformers are 0.517 and 0.482, respectively.

These results suggest the presence of strong interactions between the carboxylic group and the aromatic ring in some conformations. The repulsion produced at 0°, for example, eliminates any possible intramolecular association between the aliphatic group and the ring.

FREE-RADICAL CALCULATIONS

This study was aimed at elucidating possible reactive sites of free-radical precursors of specific polymers of interest. Polymerization via free radicals is very sensitive to the reactive sites of the molecules involved. Therefore, it is important to analyse the possible synthetic pathways of this reaction.

Calculations were performed using the same method with total geometrical optimization and a multiplicity of 2 for both free radicals. *Table 2* shows the results for both 4VP and the quaternized molecule. Comparison with the values in *Table 1* shows dramatic differences in the values of the heats of formation and the dipole moments.

Differences in the magnitudes and sign of the heat of formation allow us to conclude that the free radicals should be more stable than the corresponding closed-shell molecules. This fact suggests that any reaction mechanism will necessarily involve a free-radical pathway. Another argument to assess this possibility lies in the molecular-orbital diagrams. In fact, the HOMO diagram presented in *Figure 7* shows an increase in the specific magnitudes of the p_z orbitals of the vinyl group, reflecting higher values of the corresponding wavefunction coefficients in comparison with the p_z orbitals of the ring. This contrasts with results of the closed-shell quaternized molecule, where the vinyl group had lower magnitude. Specifically, the p_z atomic orbital of C8, where the additional electron is located, gives the largest probability for a free-radical propagation through the vinyl group. An eigenvalue analysis confirms the strong probability of bond formation when this electron is shared.

The dipole moment decreases in the quaternized molecule when free radicals are formed. This result is in contrast with the case of 4-vinylpyridine, where an increase of almost five times is observed. In the quaternized molecule, the high value of the dipole

Table 2 Free radicals

	4VP	QM
d_1 (C4–C7) (Å)	1.429	1.451
d_2 (C7–C8) (Å)	1.367	1.348
β_1 (C7–C4–C3) (deg)	123.6	123.87
β_2 (C8–C7–C4) (deg)	130.1	129.2
Total energy (eV)	−1200.81	−2285.39
ΔH_f (kcal mol^{-1})	27.8	−48.01
Dipole moment (D)	10.87	15.92

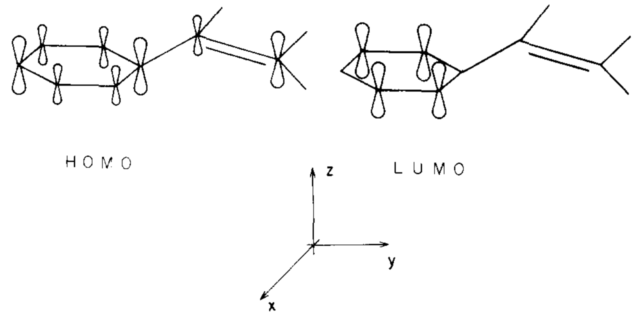

Figure 7 HOMO–LUMO representations: free radicals of the quaternized molecule

moment is due to the presence of opposite charges located in the carboxylic group and in the ring. The presence of a new negative charge density located in the vinyl group diminishes the dipole moment. In the case of 4-vinylpyridine, there is no previous situation of real charges and the magnitude of the moment only reflects the presence of a negative charge placed on the vinyl group. The opening and contraction of the bond joining the ring with the vinyl group also reflects the effect caused by the charge.

CONCLUSIONS

A theoretical MNDO calculation of quaternized derivatives of 4-vinylpyridine for both the closed-shell molecules and free radicals shows molecular values that suggest possible reaction mechanisms and stability of the structures. The electronic distribution and energetic data for the radicals suggest a relatively high stability, particularly in the case of the zwitterionic compounds. Therefore, a free-radical mechanism for polymerization through the vinyl group is quite feasible. This appears to be the case according to preliminary experimental observations in our laboratory. Unfortunately the process is too fast to allow isolation for the monomer to be properly analysed. Work is in progress in order to surmount this problem experimentally. A theoretical study combined with experimental observation of the corresponding reaction will be the subject of a forthcoming publication.

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