# Proton Affinities and Preferred Protonation Sites in 3- and 4-Substituted Pyridines. Prediction from 1s Orbital Energies

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**Abstract:** We have carried out an ab initio study of 21 3- and 4-substituted pyridine derivatives, using a STO-3G minimal basis set. The linear correlation found between $N_{1s}$ orbital energies and experimental PA for these compounds is different from the one obtained for anilines, indicating that relaxation energy is sensitive to details of local bonding at the nitrogen atom. There exists a linear correlation between the n orbital energies, if this orbital is centered on the ring nitrogen, and experimental PA. A similar correlation exists for the minimum value of the molecular electrostatic potential. No correlation was found between PA values and the net charge at the ring nitrogen. Cyanopyridines are predicted to undergo protonation on the ring nitrogen. 4-Nitropyridine can protonate either on the ring nitrogen or on the oxygen atoms. The lactam form of 4-hydroxypyridine is a much stronger base than the lactim one.

## I. Introduction

The influence of solvent is an important factor when studying the strength of a base. This problem is particularly interesting in the case of pyridine (and its derivatives) since it has been proven[1] that external effects are responsible for the fact that ammonia is a stronger base than pyridine in water solution, while the gas-phase proton affinity of the latter is substantially greater. This anomaly in base strength motivated a considerable number of papers[2-5] on the protonation of pyridine derivatives and the possible correlations between gas-phase proton affinities—that can be measured with high accuracy using different techniques[6]—and the enthalpy or free-energy change corresponding to the protonation process in solution. Such correlations were good for 3- and 4-substituted derivatives; but they failed, to some extent, for 2-substituted derivatives, probably owing to a less effective solvent intervention between the charged center and the 2-substituted derivatives, as pointed out by Aue et al.[2]

Another difficulty is to identify the protonation site (which could be only determined by means of sequential deuterium exchange reactions for a very limited number of benzene derivatives[7]) or to predict the proton affinity of a given compound. This kind of information is generally obtained through molecular orbital studies, as the calculated energy change for the "isodesmic" proton reaction[8-10] seems a suitable way to obtain such information. Another powerful method is the evaluation of the corresponding molecular electrostatic potential,[11,12] but, in general, the computed proton affinity depends on the basis set used and seems quite sensitive to geometry constraints.[12,13]

We have proposed[14-16] a very economical way to predict the preferred protonation site and the intrinsic proton affinity of any position, which proved to be very useful for a wide set of benzene derivatives. This method, based on the correlation between experimental proton affinities and calculated $C_{1s}$, $O_{1s}$, or $N_{1s}$ orbital energies, can be applied to any system, if the relaxation energy involved in the removal of a core electron[15,17] can be considered practically constant for all compounds in the series. Using this assumption we have estimated carbon proton affinities of nonaromatic compounds with considerable success.[16]

In this paper we shall try to extend this treatment to the evaluation of proton affinities of pyridine derivatives, in order to contribute to a better understanding of the effects of the substituent on their gas-phase proton affinities, and in some cases to interpret data in solution, since for those pyridines containing basic sites other than the ring nitrogen it is not well established[5] where protonation takes place. In some cases, as in cyanopyridines, it was postulated that both nitrogens can be protonated in the gas phase.

## II. Predicted Proton Affinities for 3- and 4-Substituted Pyridines

For our study we have selected 3- and 4-substituted pyridines exclusively, since, as was pointed out in the previous section, correlation between data in solution and gas-phase proton affinities is poor for 2-substituted derivatives.[2] Furthermore, it has been found that hydrogen bond basicities of 3- and 4-substituted pyridines correlate with their gas-phase proton affinities and no correlation was found for 2-substituted pyridines.[5]

To avoid prohibitive geometry optimizations we have used the experimental geometry for pyridine.[18] As experimental structures are available only for a very reduced number of its derivatives, we have adopted the following geometrical model: the aromatic ring was that of the parent molecule in all cases; the experimental structure of the substituent in the corresponding benzene derivative[19] was adopted, except for isocyanopyridines, in which case values taken from the corresponding aliphatic compounds[20] were used.

All calculations were carried out using a STO-3G minimal basis set,[21] and only in a special case, which will be discussed later, was a geometry optimization attempted.

We have used eq 1, 2, and 3 of ref 16 to predict ring, oxygen, and nitrogen proton affinities of all compounds studied here. The results obtained are presented in Table I. In all cases the theoretically predicted proton affinity for any position is much smaller than the experimental one, except for 4-nitropyridine. Nevertheless, the intrinsic proton affinities at the ring nitrogen follow the same sequence as the experimental values. This seems to indicate that the relaxation energy involved in the protonation of pyridines is quite different from that involved in the protonation of anilines, which makes eq 3 of ref 16 only qualitatively valid when applied to pyridines. Mills et al.[22] showed that proton affinity values are sensitive to details of local bonding at the nitrogen site, and primary, secondary, and tertiary amines yield different equations. This fact can be also responsible for the lack of correlation between $N_{1s}$ orbital energies and PA in the case of diazines, pointed out by Del Bene.[3] Therefore, it is not too surprising that the correlation

**Table I.** Predicted Proton Affinities for 3- and 4-Substituted Pyridines (kcal/mol)

| substituent | positions | | | | | | | exptl PA |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7[f] | |
|---|---|---|---|---|---|---|---|---|
| H | 205.3 | 147.1 | 169.1 | 160.4 | 169.1 | 147.1 | | 218.1[a] |
| 3-CH₃ | 206.3 | 153.7 | | 167.4 | 171.6 | 153.2 | | 220.5,[b] 220.8[a] |
| 4-CH₃ | 207.7 | 149.6 | 176.5 | | 176.5 | 149.6 | | 221.3,[b] 222.1[a] |
| 3,5-(CH₃)₂ | 207.2 | 158.9 | | 174.4 | | 158.9 | | 223.6[c] |
| 3-CF₃ | 199.5 | 126.0 | | 141.6 | 155.0 | 129.1 | | 210.0[a] |
| 4-CF₃ | 198.7 | 132.2 | 150.4 | | 149.3 | 131.9 | | 210.3,[a] 210.6[c] |
| 4-F | 204.4 | 136.1 | 164.9 | | 164.9 | 136.1 | | 214.2[d] |
| 3-CN | 196.4 | 115.9 | | 130.4 | 147.1 | 120.7 | 198.0 | 206.8,[a] 207.2[b] |
| 4-CN | 195.6 | 125.1 | 139.5 | | 139.5 | 125.1 | 196.4 | 207.6,[a] 208.3[b] |
| 4-N(CH₃)₂ | 217.6 | 157.9 | 198.5 | | 198.4 | 157.6 | 197.5 | 232.7,[a] 233.4[b] |
| 3-NH₂ | 205.6 | 160.6 | | 174.3 | 170.7 | 162.8 | 203.7 | 218.1–219.3[c] |
| 4-NH₂ | 212.1 | 149.6 | 183.9 | | 183.9 | 149.6 | 202.5 | 226.5–228.2[c] |
| 3-F | 200.7 | 141.5 | | 155.1 | 157.9 | 143.5 | | 211.5,[a] 212.5[c] |
| 3-OH | 202.8 | 151.5 | | 166.7 | 164.6 | 154.1 | 189.3 | |
| 4-OH | 208.8 | 143.4 | 176.3 | | 174.7 | 141.6 | 187.9 | |
| 3-CCH | 202.4 | 137.0 | | 151.5 | 162.8 | 139.2 | 211.1 | |
| 4-CCH | 202.7 | 140.5 | 160.7 | | 160.7 | 140.5 | 207.3 | |
| 4-NO₂ | 192.8 | 117.9 | 132.1 | | 132.1 | 117.9 | 201.2 | 201.1 ± 2,[e] 206.2[d] |
| 4-NO | 197.7 | 131.5 | 150.5 | | 147.4 | 130.9 | 164.9 | |

[a] Reference 4. [b] Reference 5. [c] Reference 2. [d] Reference 24. [e] Reference 1. [f] Position 7 corresponds always to the substituent.

found for aromatic amines will not be quantitatively valid for pyridines.

The predicted oxygen proton affinity of 4-nitropyridine is in very good agreement with (one of) the experimental values (see last column of Table I), indicating that this compound can be an oxygen base; this point will be discussed later in more detail.

## III. Correlation between N₁ₛ Orbital Energies and PA in Pyridines

From the previous section, it seems clear that a correlation different from that found for anilines[16] must hold between N₁ₛ orbital energies and experimental PA for pyridines. To obtain a reliable correlation we have selected, for this study, those pyridine derivatives for which experimental proton affinity values, measured in diffferent ways, differ by less than 1.0 kcal/mol. These are the first ten compounds listed in Table I. The linear correlation between their experimental proton affinities (PA in kcal/mol) and their ring nitrogen 1s orbital energies ($E_{N_{1s}}$ in au) obeys the equation

$$PA = 385.55 E_{N_{1s}} + 6133.20 \quad r = 0.982$$

$$\sigma_{PA} = 1.4 \text{ kcal/mol} \quad (1)$$

and has been plotted in Figure 1.

It is important to note that 3- and 4-cyanopyridines satisfy very well this correlation, which can be interpreted as an evidence that these compounds protonate on the ring nitrogen. This conclusion is ratified if the following facts are considered.

The N₁ₛ orbital energy for cyanobenzene is −15.347 au,[14] and that corresponding to the nitrogen atom of the -CN group in 3- and 4-cyanopyridine are −15.365 and −15.372 au, respectively. The experimental proton affinity of cyanobenzene[23] is 195.1 kcal/mol; therefore, the PA values for protonation on the -CN group in 3- and 4-cyanopyridine must be even lower, and in consequence, according to our results, protonation must take place on the ring nitrogen, preferably.

We have calculated, with eq 1, the PA values of compounds (11–19 in Table I) which were not used to obtain this equation. These results are shown in Table II. The predicted values agree reasonably well with experimental ones. The calculated PA values for 3- and 4-aminopyridines, for which experimental determination is difficult owing to their low volatility,[2] fall within experimental error (see Figure 1). In the particular case
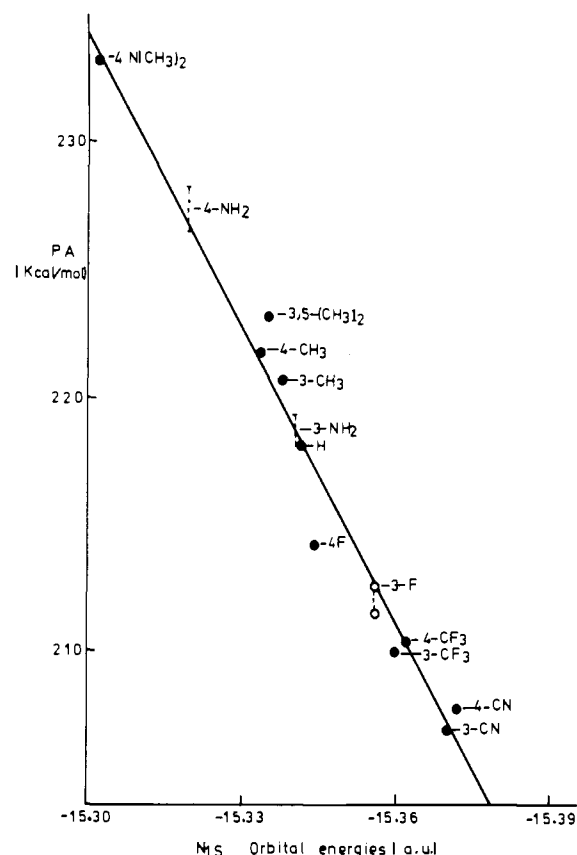


**Figure 1.** Correlation of experimental PA and the N₁ₛ orbital energy of the ring nitrogen, for 3- and 4-substituted pyridines. 3-F, 3-NH₂, and 4-NH₂ derivatives are included in the figure, but they were not used to obtain eq 1 (see text).

of 3- and 4-hydroxypyridines, the experimental PA values are not available, but our results agree reasonably well with those corresponding to 3- and 4-methoxypyridine (220.1 and 224.3 kcal/mol,[4] respectively).

It should also be noticed that the ring nitrogen PA for 4-nitropyridine is very close to that calculated for oxygen protonation, and in agreement with one of the experimental values, but much lower than the other (see Table I); therefore, in this case theoretical results indicate that protonation can occur

**Table II.** Theoretical Values of the Intrinsic Proton Affinities of the Ring Nitrogen, Obtained Using Equation 1

| substituent | PA (theor), kcal/mol | substituent | PA (theor), kcal/mol |
|---|---|---|---|
| 3-F | 212.6 | 4-NO$_2$ | 202.9 |
| 3-NH$_2$ | 218.7 | 3-CCH | 214.7 |
| 4-NH$_2$ | 226.7 | 4-CCH | 215.1 |
| 3-OH | 215.2 | 4-NO | 209.0 |
| 4-OH | 222.6 | | |

either on the ring nitrogen or on one of the oxygen atoms of the -NO$_2$ group. This result must be taken with caution, since the agreement between the oxygen PA and one of the experimental values could be fortuitous, as it is possible that oxygen protonation of nitro compounds follows a relation different from that obtained in ref 16.

## IV. n Orbital Energies as Measure of PA

The ionization potential of a base is a measure of its n donor ability. Beauchamp showed[24] that there exists a correlation between experimental ionization potentials and proton affinities; a similar correlation should hold between n orbital energies and PA values. It seems that such correlation would be only possible if the nature of the n orbital does not change from one compound to another.[3] Moreover, a good linear correlation must exist between the energy of the n orbital and the minimum value of the corresponding molecular electrostatic potential evaluated at that center, since the value of this potential must reflect the donor ability of the center considered.

To investigate if the nature of the n orbital does not change in all 3- and 4-pyridine derivatives we have evaluated the molecular electrostatic potential of each compound using the equations of ref 25. The value of the corresponding minimum (placed at the ring nitrogen) is plotted vs. the n-orbital energy, corresponding to the ring nitrogen in Figure 2. Clearly, the correlation is very good for all compounds with only two exceptions: 4-nitro- and 4-nitrosopyridine.

These exceptions are due to the fact that the interaction between the n orbitals on the two nitrogen atoms (and also on the oxygen atoms) results in a n orbital that is not completely localized on the ring nitrogen and therefore does not reflect the basicity of this center. It is also evident that in all other cases the n orbital is fundamentally localized on the ring nitrogen and therefore its energy can be used as a measure of the proton affinity of each compound.

Figure 3 shows that the correlation between experimental PA and n-orbital energies of the ring nitrogen is very good for all compounds whose experimental PA is known, except for 4-nitropyridine, for the reasons previously indicated.

A least-squares fitting of the data plotted in this figure leads to the equation

$$PA = 519.49\epsilon_n + 393.36 \quad r = 0.987 \quad \sigma_{PA} = 1.2 \text{ kcal/mol} \tag{2}$$

where the experimental proton affinity (PA) is in kcal/mol and the n orbital energy ($\epsilon_n$) is in au.

3-Cyanopyridine is predicted to be a stronger base than 4-cyanopyridine when any of the three indexes (1s orbital energies (Figure 1), molecular electrostatic potentials (Figure 2), or n orbital energies (Figure 3)) are used, in disagreement with experimental evidence. However, it should be remembered that experimental PA values for these compounds have little accuracy[2] and the difference between them is very small (of the order of 1 kcal/mol).

A similar situation is found in the case of 3- and 4-CF$_3$ derivatives, but again the difference between their experimental
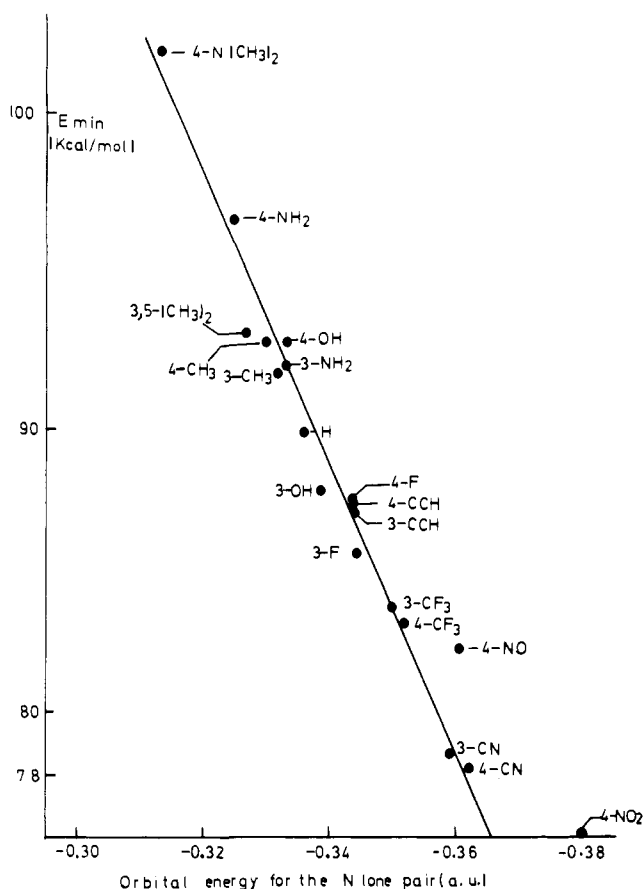


**Figure 2.** Minimum value of the molecular electrostatic potential, evaluated at the ring nitrogen, vs. energy of the n orbital on the same atom.
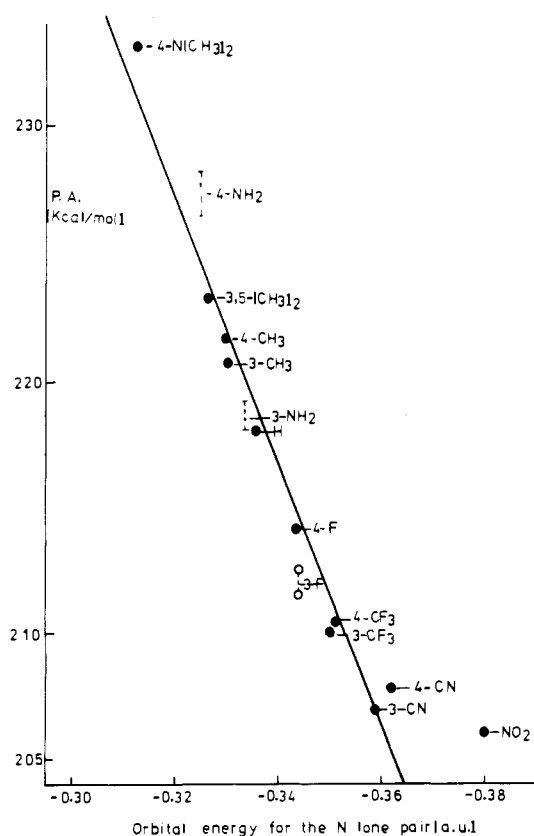


**Figure 3.** Experimental PA of 3- and 4-substituted pyridines vs. the energy of the n orbital on the ring nitrogen.
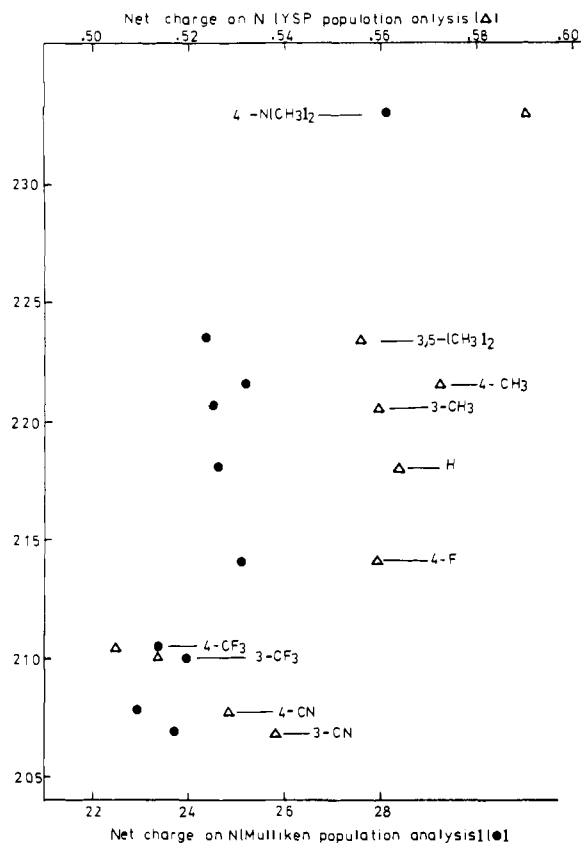
**Figure 4.** Experimental PA of 3- and 4-substituted pyridines vs. the net charge at the ring nitrogen, obtained using Mulliken and YSP population analyses.

PA (0.4 kcal/mol) is smaller than the error which affects our correlations.

## V. Correlation between Proton Affinities and Charge Densities

Davis and Shirley[26] have proposed an empirical method in which the proton affinity of a base is directly related to hydrogen charge density.

In the particular case of 3- and 4-substituted pyridines, where the n orbital is totally localized on the ring nitrogen, it is possible for the net charge on this atom to correlate with its intrinsic PA. In order to investigate this point we have evaluated the corresponding atomic charges using (a) the Mulliken population analysis[27] and (b) the population analysis proposed by Yáñez, Stewart, and Pople[28] (that we shall call YSP population analysis), that is not sensitive to the basis set used.

We present in Figure 4 the experimental PA of 3- and 4-substituted pyridines vs. the net charge at the ring nitrogen obtained with both methods. It is evident that there does not exist a direct relationship between these two magnitudes.

It seems clear that it is not the net charge, but the charge transferred to the proton, whose magnitude is directly related to the proton affinity of a given position, as was pointed out by Reynolds et al.[29] and Del Bene;[30] this method implies the calculation of both protonated and unprotonated systems.

## VI. Influence of Possible Isomerisms

Oxo derivatives of N-heteroaromatic compounds usually present a lactim-lactam tautomerism.[31] It is generally accepted[31] that, in the particular case of 4-XH-pyridines (where XH is a tautomeric group), these compounds exist in the lactam, rather than in the lactim, form. It is reasonable to assume that this tautomerism can strongly affect the basicity of such compounds.

In order to study this point in the case of 4-hydroxypyridine, we have calculated the corresponding lactam form, in which the hydrogen of the phenol group is attached to the ring nitrogen. As the pyridine ring will be distorted, in this case, we have used in our ab initio calculations the INDO fully optimized geometry[32] since it has been pointed out[33] that this method yields reliable geometries for this kind of compound.

Using the corresponding $O_{1s}$ orbital energy and eq 2 of ref 16 the predicted proton affinity is 234.4 kcal/mol, indicating that the lactam is much more basic than the lactim form (see Table II). Therefore, according to our results, when experimental conditions favor the existence of the lactam form, the PA value will be much higher than that measured when the lactim is the predominant form.

Another interesting isomerism is that of cyano- and isocyanopyridines. 3- and 4-cyanopyridines have been studied in previous sections. Here we present similar calculations for the corresponding isocyano derivatives, for which the NC bond length adopted was that of methyl isocyanide.[20] For both 3- and 4-substituted compounds the predicted PA values using eq 1 (208.7 and 207.4 kcal/mol, respectively) are a little higher than those of the corresponding cyano derivatives. It is also interesting to note that, in this case, the 4-substituted compound is predicted to be a stronger base than the 3-substituted one, in opposition to the theoretical results obtained from the cyano derivatives.

## VII. Conclusions

From our results we can conclude that the correlation between $N_{1s}$ orbital energies and experimental proton affinities for pyridines is different from the one obtained for anilines, indicating that the relaxation energy is sensitive to details of local bonding at the nitrogen atom.

There exists also a good linear correlation between the n orbital energy (whenever this orbital is fundamentally centered on the ring nitrogen) and experimental proton affinities. Consequently a parallel correlation exists for the minimum values of the corresponding molecular electrostatic potentials.

No correlation seems to exist between PA values and the net charge at the ring nitrogen.

Cyanopyridines are predicted to undergo protonation on the ring nitrogen. 4-Nitropyridine can behave as an oxygen or a nitrogen base, since the predicted PA for both centers (ring nitrogen and oxygen atoms) are very similar. Isocyanopyridines are predicted to be slightly stronger bases than the corresponding cyanopyridines.

Finally, the lactam form of 4-hydroxypyridine is a much stronger base than the lactim one.

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(32) INDO fully optimized geometry of the lactam form of 4-hydroxypyridine; N1C2 = 1.380, C2C3 = 1.349, C3C4 = 1.439, C4O7 = 1.289; N1C2C3 = 121.4, C2N1C6 = 119.1, C2C3C4 = 121.7, C3C4C5 = 114.7 (bond lengths in ångstroms and bond angles in degrees).

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# Vertical Excitation Energy to the Lowest ¹ππ* State of Acrolein

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**Abstract:** In acrolein the use of orthogonal orbital SCF procedures on the lowest ¹ππ* state results in a configuration which has a low energy but a high overlap with the ground-state wave function. Variationally correct nonorthogonal SCF procedures give a much higher energy estimate for this state. Configuration interaction calculations with the correct SCF orbitals in a basis set without Rydberg orbitals gives 7.52 eV for the best estimate of the excitation energy compared with the observed value of 6.5 eV.

## Introduction

Acrolein $CH_2=CH-CH=O$ is a molecule with interacting ethylenic and carbonyl chromophores. In a recent paper in this journal, Dykstra reported extensive SCF calculations on several excited states of acrolein.[1] This was followed by a CI calculation for the lowest states of symmetry different from the ground state.[2] While most of the results in these papers seem correct, the ΔSCF results for the lowest ¹A′ excited state produced energies much lower than CI results by other workers.[3,4] On the basis of these calculations, Dykstra concluded[1] that acrolein has a low-energy (3.52 eV) ¹ππ* excited state of the form ·$CH_2-CH=CH-O$·, although he later recognized that there might be some problem with this result because the SCF wave functions for the excited state and ground state have nonzero overlap.[2]

Dykstra's calculations were performed by minimizing the energy subject to the constraint that π and π* be orthogonal. We show here that this low energy is a rather extreme example of the well-known inapplicability of this SCF procedure to singlet states where both open shell orbitals are of the same symmetry.

## Procedure

Dunning's[5] [5s,3p] contraction of Huzinaga's[6] (9s,5p) Cartesian Gaussian basis plus a (2s,p,d) set of Rydberg functions[7] centered midway between the central carbon atoms were used. SCF calculations were done on the ground state and the lowest ¹ππ* state of acrolein at its equilibrium ground-state geometry.[8] At this geometry, the molecule has $C_s$ symmetry and both of these states are ¹A′.

The ¹ππ* state energy was calculated by two different SCF procedures. One used the normal SCF procedure where the singly occupied orbitals are constrained to be orthogonal and the absolute minimum in the energy is sought subject to this constraint.[9] This procedure is correct for finding the lowest energy state of any symmetry except ¹A′. The other method used the nonorthogonal SCF program developed by Davidson and Stenkamp.[10] In this procedure, the orbitals are not constrained to be orthogonal, but the π* orbital is constrained to be the second eigenfunction of its Fock operator.

Configuration interaction calculations were carried out by using all single replacements and selected double replacements from the dominant configuration. About 6000 configurations were included in most calculations. For the nonorthogonal SCF procedure, symmetrically orthogonalized π and π* orbitals were used for the CI. It is easily shown that symmetrical orthogonalization leads to the pair of orbitals u and v for which the ¹uv configuration has maximum overlap with the nonorthogonal SCF function and the contribution from the $u^2$ and $v^2$ configurations is minimum.[11]

## Results

The energies from these calculations are summarized in Table 1. The orthogonal SCF calculation gave a $\Delta E_{SCF}$ of 3.42