(7) Parkinson, B. A.; Heller, A.; Miller, B. *Appl. Phys. Lett.* **1978**, *33*, 521.
(8) Ellis, A. B.; Bolts, J. M.; Kaiser, S. W.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 2848.
(9) Chang, K. C.; Heller, A.; Schwartz, B.; Menezes, S.; Miller, B. *Science* **1977**, *196*, 1097.
(10) Ellis, A. B.; Kaiser, S. W.; Bolts, J. M.; Wrighton, M. *J. Am. Chem. Soc.* **1977**, *99*, 2839.
(11) Hodes, G.; Manassen, J.; Cahen, D. *Nature (London)* **1976**, *261*, 403.
(12) (a) Kohl, P. A.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 7531. (b) Frank, S. N.; Bard, A. J. *Ibid.* **1975**, *97*, 7427.
(13) Stirn, R. J.; Yeh, Y. C. M. *Appl. Phys. Lett.* **1975**, *27*, 95.
(14) Gerischer, H. *J. Electroanal. Chem.* **1975**, *58*, 263.
(15) (a) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050. (b) Brosset, D.; Ai, B.; Segui, Y. *Appl. Phys. Lett.* **1978**, *33*, 87.
(16) Kohl, P. A.; Bard, A. J. *J. Electrochem. Soc.* **1979**, *126*, 59.
(17) Janz, G. J.; Tomkins, R. P. T. "Nonaqueous Electrolytes Handbook", Vol. II; Academic Press: New York, 1973; and references cited therein.
(18) Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *J. Am. Chem. Soc.* **1978**, *100*, 7264.
(19) Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas, O.; Legg, K. D.; Nadjo, L.; Palazzotto, M. C. *J. Electroanal. Chem.* **1978**, *87*, 429.
(20) Lenhard, J. R.; Rocklin, R.; Abruna, H.; Willman, K.; Kuo, K.; Nowak, R.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 5213.
(21) Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S. *J. Electroanal. Chem.*, **1979**, *100*, 283.
(22) Bolts, J. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5257.
(23) Merz, A.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 3222.
(24) Van de Mark, M.; Miller, L. *J. Am. Chem. Soc.* **1978**, *100*, 3223.
(25) Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979**, *101*, 739.
(26) Laviron, E. *J. Electroanal. Chem.* **1972**, *39*, 1.
(27) Ginley, D. S.; Butler, M. A. *J. Electrochem. Soc.* **1978**, *125*, 1968.
(28) Gatos, H. C.; Lavine, M. C. *J. Phys. Chem. Solids* **1960**, *14*, 169.
(29) Birintseva, T. P.; Pleskov, Yu. V. *Sov. Electrochem. (Engl. Transl.)* **1965**, *1*, 236.
(30) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

An ab Initio Molecular Orbital Study of 2- and 4-Monosubstituted Pyridines

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Abstract: Ab initio molecular orbital calculations have been performed to investigate the structural, energetic, and electronic properties of the 2- and 4-R-pyridines, with R including the isoelectronic saturated groups CH_3, NH_2, OH, and F and the unsaturated groups C_2H_3 (vinyl), CHO, and CN. The equilibrium geometry of the pyridine ring is essentially unchanged in the equilibrium structures of the 2- and 4-R-pyridines, independent of the nature of the substituent and its position. In all cases, the 2-R-pyridines are more stable than the corresponding 4-R-pyridines. Except for substitution of F in the 4 position, substitution in the 2 or 4 position of a π donating group has a stabilizing effect in pyridine relative to benzene, while substitution of the π withdrawing groups CN in the 2 or 4 position or CHO in the 4 position has a destabilizing effect relative to benzene. Analyses have also been made of substituent effects on electron distributions, n and π orbital energies, and dipole moments of the substituted pyridines.

Introduction

Recent developments in experimental methods have led to the determination of the strengths of organic bases in the gas phase.[1-3] Comparisons of the gas-phase and solution data have highlighted the important role which the solvent may play in mediating the intrinsic strength of a base toward a particular acid,[4-6] and have emphasized the need for reexamining the traditional theoretical arguments concerning base strengths. Ab initio molecular orbital calculations on free bases and on associated acid-base pairs are particularly well suited for providing some of the fundamental data required for this reexamination.

An important series of organic bases for which experimentally measured base strengths in the gas phase are now available are the monosubstituted pyridines.[6] While a few ab initio molecular orbital studies of these bases and their association with acids have been reported,[6-8] there has not yet been a systematic study of the structural, energetic, and electronic properties of these bases; therefore, such a study has been initiated in this laboratory. Pyridine has already been investigated,[9] and the present study is concerned with a set of 2- and 4-monosubstituted pyridines (2- and 4-R-pyridines) with the substituents including the isoelectronic saturated groups CH_3, NH_2, OH, and F and the unsaturated groups C_2H_3 (vinyl), CHO, and CN. This study has three specific aims: (1) to determine the equilibrium structures of the 2- and 4-R-pyridines and to analyze substituent effects on these structures, especially on the geometry of the pyridine ring; (2) to compare the relative stabilities of the 2- and 4-R-pyridines and the energetic effects of substitution in pyridine relative to benzene; (3) to investigate substituent effects on electron distributions, n and π orbital energies, and dipole moments, which are important properties that influence base strengths.

Method of Calculation

Wave functions for the singlet ground electronic states of the 2- and 4-R-pyridines have been expressed as single Slater determinants Ψ:

$$\Psi = |\psi_1(1)\bar{\psi}_1(2) \ldots \psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)}!$$

each consisting of a set of doubly occupied molecular orbitals (MOs). The MOs ψ_i are expressed as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation):

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu$$

with the expansion coefficients $c_{\mu i}$ determined variationally by solving the Roothaan equations.[10] The basis set used for the MO expansions is the minimal STO-3G basis set with standard scale factors.[11]

The 2-R-pyridines were assumed to have C_s symmetry. In these molecules, an in-plane hydrogen atom (H′) bonded to X (X is the first-row atom of the substituent bonded to C_2; see Figure 1) has been oriented so that X–H′ is s-cis to N_1–C_2. For the 4-R-pyridines, the pyridine ring was assumed to have C_{2v} symmetry, with the C_4–X bond to the substituent coincident with the C_2 symmetry axis of the ring. When R is NH_2, F, or CN, the overall molecular symmetry is C_{2v}; in all other cases,

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Table I. Structures of 2-R-Pyridines[a]

	bond distances, Å							bond angles, deg									
	1-2	2-3	3-4	1-6	5-6	4-5	CH[b]	612	123	234	165	345	456	23H	34H	16H	65H
R = H[c]	1.35	1.39	1.39	1.35	1.39	1.39	1.08	116	124	119	124	118	119	120	121	116	120
	(1.3402)	(1.3945)	(1.3944)				(1.08)	(116.8)	(123.9)					(120.2)		(115.9)	
CH_3	1.36	1.39	1.39	1.35	1.39	1.38	1.08	115	124	119	125	119	118	120	121	115	120
NH_2	1.36	1.40	1.38	1.35	1.39	1.39	1.08	115	124	119	125	119	118	120	121	115	120
OH	1.36	1.39	1.38	1.35	1.39	1.39	1.08	115	124	119	125	119	118	119	120	115	120
F	1.36	1.39	1.38	1.35	1.39	1.39	1.08	115	124	119	125	119	118	119	120	115	120
C_2H_3	1.36	1.40	1.39	1.35	1.39	1.39	1.08	115	124	119	125	118	119	120	121	116	120
CHO	1.36	1.39	1.39	1.35	1.39	1.38	1.08	115	124	119	125	119	118	119	121	115	120
CN	1.36	1.39	1.39	1.35	1.39	1.38	1.08	115	124	119	125	119	118	120	120	115	120

Substituent Geometries[d]

R = H	C_2-H	1.08	N_1-C_2-H	116	F	C_2-F	1.35	N_1-C_2-F	116
CH_3	C_2-C	1.53	N_1-C_2-C	116	C_2H_3	C_2-C	1.51	N_1-C_2-C	113
	C-H[e]	1.09	H-C-H[e]	109		C-C	1.31	C_2-C-C	126
NH_2	C_2-N	1.40	N_1-C_2-N	115		C-H[f]	1.08	C-C-H[f]	122
	N-H′	1.01	C_2-N-H′	119	CHO	C_2-C	1.52	N_1-C_2-C	116
	N-H″	1.01	C_2-N-H″	122		C-O	1.22	C_2-C-O	123
OH	C_2-O	1.39	N_1-C_2-O	117		C-H′	1.10	C_2-C-H′	114
	O-H′	0.99	C_2-O-H′	104	CN	C_2-C	1.47	N_1-C_2-C	116
						C-N	1.16		

[a] Underlined variables and values are determined by symmetry or geometry constraints, and have not been directly optimized. [b] Ring C-H distances assumed equal. [c] Computed structure from ref 9. Experimental data in parentheses from ref 12. [d] Hydrogens labeled H′ are bonded to X such that X-H′ is s-cis to N_1-C_2 with respect to the C_2-X bond. [e] C-H bond distances and H-C-H angles assumed equal. [f] C-H bond distances and C-C-H bond angles assumed equal.

the molecule has C_s symmetry. Bond lengths and bond angles in the 2- and 4-R-pyridines have been optimized cyclicly and independently to ±0.01 Å and ±1°, respectively. All calculations performed in this study were carried out in double precision on an IBM 370/148 computer.

Results and Discussion

Structures. The computed equilibrium structures of the 2- and 4-R-pyridines are reported in Tables I and II, respectively. Table I also reports the computed[9] and the experimental[12] structures of pyridine, which are in excellent agreement. As evident from these structures, replacement of a C-H group in benzene by a nitrogen atom leads to a decrease in the 1-2 bond distance, decreases in the 6-1-2, 2-3-4, and 3-4-5 bond angles, and an increase in the 1-2-3 bond angle, with a resultant elongation of the pyridine ring as measured by the 1-4 distance. This geometry of the pyridine ring is essentially preserved in the monosubstituted 2- and 4-R-pyridines. No more than a 0.01-Å change in bond lengths nor more than a 2° change in bond angles of the pyridine ring occurs upon substitution, independent of the nature of the substituent and its position.

Although only small changes in bond lengths and bond angles occur upon substitution in pyridine, some generalizations can be made concerning these changes. In the 2-R-pyridines, the N_1-C_2 bond distance always increases by 0.01 Å relative to pyridine, while the N_1-C_6, C_5-C_6, and C-H bond distances remain unchanged. Substitution in the 2 position of NH_2, the strongest π electron donating group, or C_2H_3, a weak π donating group which conjugates well with the pyridine ring, leads to an increase of 0.01 Å in the adjacent C_2-C_3 bond. In the 4-R-pyridines, bond distances in the ring are insensitive to substitution except when the substituents are once again NH_2 and C_2H_3, in which cases the C_2-C_3 distance decreases while the C_3-C_4 distance increases by 0.01 Å. In 4-vinylpyridine, a 0.01-Å decrease also occurs in the N_1-C_2 distance.

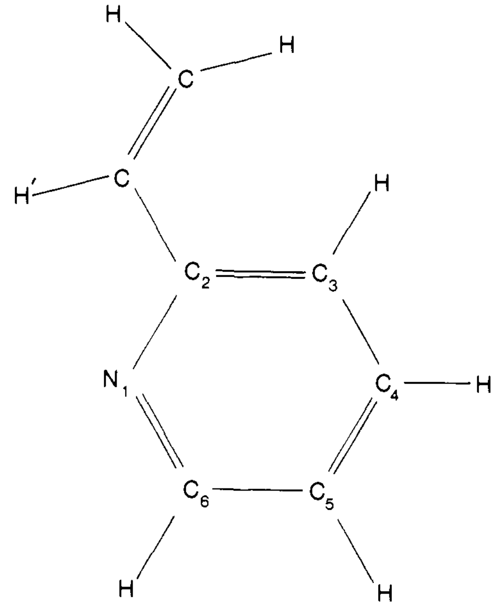

Figure 1. The structure of 2-vinylpyridine.

Substitution in the 2 position leads to changes in bond angles, including a 1° decrease in the C_6-N_1-C_2 angle and a 1° increase in the C_5-C_6-N_1 angle. In addition, in all 2-R-pyridines except 2-vinylpyridine, the C_3-C_4-C_5 angle increases while the C_4-C_5-C_6 and N_1-C_6-H angles decrease by 1° relative to pyridine. In 2-vinylpyridine, these angles are unchanged.[13] In the 4-R-pyridines, changes in internal angles occur only in 4-methyl- and 4-vinylpyridine, in which cases the C_2-C_3-C_4 angle increases by 1°, while the C_3-C_4-C_5 angle decreases by 2°.

Stabilities. Table III presents the relative stabilities (ΔE_1) of the 2- and 4-R-pyridines, calculated as the energy of the isomerization reaction

$$\text{2-R-pyridine} \rightarrow \text{4-R-pyridine} \qquad (1)$$

The positive values obtained for ΔE_1 indicate that the 2 isomer is more stable than the 4 in all cases. To understand the preference for substitution in the 2 position, and also the energetic effects of substitution in pyridine relative to benzene as pre-

Table II. Structures of 4-R-Pyridines[a]

	bond distances, Å				bond angles, deg				
	1-2	2-3	3-4	CH	612	123	234	32H	23H
R = H	1.35	1.39	1.39	1.08	116	124	119	120	120
CH_3	1.35	1.39	1.39	1.08	116	124	120	120	120
NH_2	1.35	1.38	1.40	1.08	116	124	119	120	120
OH	1.35	1.39	1.39	1.08	116	124	119	119	121
F	1.35	1.39	1.39	1.08	116	124	119	119	121
C_2H_3	1.34	1.38	1.40	1.08	116	124	120	120	119
CHO	1.35	1.39	1.39	1.08	116	124	119	119	121
CN	1.35	1.39	1.39	1.08	116	124	119	119	120

Substituent Geometries

R = CH_3	C_4-C	1.53	H-C-H[b]	108
	C-H[b]	1.09		
NH_2	C_4-N	1.40	C_4-N-H	121
	N-H	1.01		
OH	C_4-O	1.39	C_4-O-H	105
	O-H	0.99		
F	C_4-F	1.35		
C_2H_3	C_4-C	1.50	C_4-C-C	126
	C-C	1.31	C-C-H[c]	121
	C-H[c]	1.08		
CHO	C_4-C	1.52	C_4-C-O	123
	C-O	1.22	C_4-C-H	115
	C-H	1.10		
CN	C_4-C	1.46		
	C-N	1.16		

[a] The pyridine ring was assumed to have C_{2v} symmetry. See footnotes *a* and *b* in Table I. [b] C-H bond lengths and H-C-H bond angles assumed equal. [c] C-H bond lengths and C-C-H bond angles assumed equal.

Table III. Relative Stabilities and Isodesmic Energies (kcal/mol)

	ΔE_1[a]	ΔE_2[b]	
		2-R-pyridine	4-R-pyridine
R = CH_3	0.6	1.3 (1.5)	0.7 (0.9)
NH_2	2.0	4.1 (4.3)	2.1 (2.3)
OH	6.2	7.2 (8.7)	1.0 (2.5)
F	2.8	2.8 (3.2)	0.0 (0.4)
C_2H_3	0.6	1.4 (5.7)	0.8 (5.1)
CHO	1.2	0.2 (2.9)	−1.0 (1.7)
CN	0.1	−2.1 (−2.0)	−2.2 (−2.1)

[a] ΔE_1 is the energy of the isomerization reaction (1). [b] ΔE_2 is the energy of the isodesmic reaction (2) with benzene. Uncorrected values are in parentheses.

sented in the next section, it is advantageous to consider the electron distribution in pyridine, and substituent effects on π electron densities in monosubstituted benzenes.

It is well known that the nitrogen atom is a π electron acceptor in pyridine. As a result, the π electron densities at C_2, C_4, and C_6 are less than in benzene, whereas the densities at C_3 and C_5 are greater. Therefore, it should be expected that introduction of a π electron donor at the 2 or 4 position of pyridine should stabilize the molecule, whereas a π electron acceptor should have a destabilizing effect. Moreover, since the presence of a π electron donating group in a monosubstituted benzene increases the π electron density at the ortho position more than the para,[14] it may be expected that substitution of a π donating group at the 2 position in pyridine should be more favored than at the 4 since the nitrogen atom can better accommodate an increased π density. The positive ΔE_1 values for reaction 1 when the substituent is a π donating group are consistent with these expectations. Moreover, the ΔE_1 values are larger when the substituent is one of the strong π donating groups NH_2, OH, and F, and smaller when the substituent is CH_3 or C_2H_3, which are weak π donating groups. There are undoubtedly other factors which influence the relative stabilities of these 2- and 4-R-pyridines. In particular, interaction between the pyridine nitrogen and the in-plane hydrogen (H′) bonded to X should be important in stabilizing the 2 isomer relative to the 4. In the case of 2-hydroxypyridine, this hydrogen is most acidic, and the N-H′ interaction is a contributing factor in stabilizing 2-hydroxypyridine by 6.2 kcal/mol relative to 4-hydroxypyridine.[15]

As indicated above, π electron withdrawing substituents like CHO and CN should be expected to have a destabilizing effect on substituted pyridines. It might also be anticipated that σ and π withdrawal from the 2 position would be more unfavorable than from the 4 since the substituent in the 2 position would directly compete with nitrogen for electron density. However, π electron withdrawal from the 2 position further polarizes the π density of the ring toward the nitrogen and the substituent. As a result, when the substituent is the weaker π withdrawing group CHO, the π density at the nitrogen atom remains unchanged in 2-pyridinecarboxaldehyde relative to pyridine, while it decreases in 4-pyridinecarboxaldehyde. The greater total and π electron density at the nitrogen and a favorable interaction between the pyridine nitrogen and H′ in the 2 isomer contribute to the 1.2 kcal/mol increased stability of the 2 isomer relative to the 4. On the other hand, when the substituent is the stronger π withdrawing group CN, the stabilities of the 2 and 4 isomers differ by only 0.1 kcal/mol. In this case, the greater loss of total electron density by nitrogen tends to offset the smaller loss of nitrogen π density in 2-cyanopyridine compared with 4-cyanopyridine.[16]

Isodesmic Energies. Another way of analyzing the energetics of substitution is to compare the effect of substitution in pyridine relative to benzene. This can be done by computing the energy ΔE_2 for the isodesmic reaction[17]

$$(C_5H_4N)R + C_6H_6 \rightarrow C_5H_5N + C_6H_5R \qquad (2)$$

A positive value of ΔE_2 implies that the substituent stabilizes pyridine relative to benzene. Unfortunately, the energies of the corresponding monosubstituted benzenes[14] which are available for calculating ΔE_2 have not been obtained for fully optimized

Table IV. Mulliken Population Data for Substituted 2- and 4-R-Pyridines

		π densities						total densities	
		N_1	C_2	C_3	C_4	C_5	C_6	N_1	ring[a]
R = H		1.048	0.988	1.004	0.967	1.004	0.988	7.241	41.075
CH_3	(2)	1.069	0.956	1.025	0.960	1.020	0.979	7.248	41.030
	(4)	1.060	0.982	1.022	0.941	1.022	0.983	7.247	41.026
NH_2	(2)	1.144	0.929	1.094	0.941	1.069	0.959	7.280	40.979
	(4)	1.105	0.965	1.091	0.915	1.091	0.965	7.268	40.977
OH	(2)	1.131	0.957	1.059	0.944	1.046	0.964	7.284	40.938
	(4)	1.084	0.967	1.076	0.947	1.054	0.968	7.255	40.935
F	(2)	1.095	0.988	1.049	0.950	1.028	0.969	7.258	40.877
	(4)	1.069	0.973	1.042	0.976	1.042	0.973	7.246	40.876
C_2H_3	(2)	1.061	0.973	1.013	0.963	1.012	0.983	7.243	41.020
	(4)	1.050	0.991	1.011	0.956	1.008	0.991	7.245	41.024
CHO	(2)	1.048	0.996	0.988	0.966	0.996	9.986	7.238	40.998
	(4)	1.039	0.989	0.997	0.979	0.986	0.988	7.233	40.995
CN	(2)	1.038	1.036	0.985	0.963	0.983	0.982	7.217	40.894
	(4)	1.028	0.986	0.983	1.021	0.983	0.986	7.224	40.891

[a] Includes all atoms except those in the substituent.

structures, but for standard-model geometries.[18] Since the standard-model geometry of benzene is its optimized geometry, the error introduced into ΔE_2 from using a standard-model energy for the substituted benzene will bias ΔE_2 in a positive direction. Before any meaningful comparisons can be made from the available data it is necessary to estimate the magnitude of this error. This can be done by analyzing the effect of geometry optimization on the energies of pyridine and substituted 4-R-pyridines, as indicated below.

It should be noted that the only significant difference between the standard-model and the optimized geometries of pyridine is in the internal angles of the ring. Although these differ in the two geometries by no more than 4°, the optimized molecule is computed to be 6.6 kcal/mol more stable than the standard-model pyridine, and this is a significant difference. Therefore, a set of 4-R-pyridines has been constructed using the optimized geometry of pyridine for the ring and the standard-model geometry for the substituent. Since the pyridine ring geometry is essentially unchanged by substitution, the difference between the energies of this structure and the fully optimized structure for a particular 4-R-pyridine should be a good estimate of the difference between the energies of the corresponding standard-model and fully optimized substituted benzene, assuming that the geometry of the benzene ring also remains essentially unchanged by substitution. This energy difference is then an estimate of the correction to be applied to the computed value for ΔE_2. The data obtained show that the correction is dependent on the substituent. When R is CH_3, NH_2, F, or CN, the correction is quite small at 0.2, 0.2, 0.4, and 0.1 kcal/mol, respectively. However, when R is OH, C_2H_3, or CHO, it increases to 1.5, 4.3, and 2.7 kcal/mol, respectively.[19] The corrected and the uncorrected values of ΔE_2 are reported in Table III.

The corrected ΔE_2 values indicate that substitution in the 2 position of the π electron donors CH_3, NH_2, OH, F, and C_2H_3 stabilizes pyridine relative to benzene, as anticipated. Except for F, substitution of these same groups in the 4 position also has a stabilizing effect in pyridine.[20] The effect of F substitution at the 4 position in pyridine appears to be similar to the effect of F substitution in benzene. On the other hand, substitution of the strong π withdrawing group CN in the 2 or 4 position or of the weaker π withdrawing group CHO in the 4 position of pyridine has a destabilizing effect relative to benzene. The small corrected ΔE_2 value for 2-pyridinecarboxaldehyde and the large estimated error for benzaldehyde make somewhat tentative the prediction that CHO substitution in the 2 position of pyridine has a small stabilizing effect relative to benzene.

Other Properties. It is well known that substituents on an aromatic ring alter the electron density of the ring. For pyridine, the changes depend on the nature and position of the substituent, as shown by the Mulliken population data[21] reported in Table IV. The saturated substituents and the unsaturated group C_2H_3 are π electron donating and σ electron withdrawing groups relative to H, with the σ effect being stronger than the π. The substituents CHO and CN withdraw both σ and π electron density relative to H. Thus, for the entire set of 2- and 4-R-pyridines, the pyridine ring loses total and σ electron density upon substitution.

Some interesting but not unexpected patterns of changes in electron populations of atoms in the ring are observed upon substitution. In both the 2- and 4-R-pyridines, the total and the π electron densities of atoms N_1, C_3, and C_5 increase when R is a π donor. The π densities of atoms C_4 and C_6 in the 2-R-pyridines and C_2 and C_6 in the 4-R-pyridines decrease when R is a π donating group except in 4-vinylpyridine. The total electron density of the atom directly bonded to the substituent (C_2 in the 2 isomer and C_4 in the 4) always decreases relative to pyridine. The π density of this atom also decreases except when the substituent is F, CHO, or CN.

The electronic effects of substituents also alter n and π orbital energies, as evident from the data of Table V. To understand the changes which occur in the two highest energy π and the highest energy σ occupied orbitals, the nature of these orbitals in pyridine should be considered. The highest occupied π orbital in pyridine has a_2 symmetry, with a node through N_1 and C_4. The second π orbital has b_1 symmetry, with large coefficients for the p-π atomic orbitals on N_1 and C_4. The energies of the a_2 and b_1 orbitals are -8.18 and -8.71 eV, respectively. The highest occupied σ orbital in pyridine has a_1 symmetry, with an energy of -9.20 eV. This is the n orbital associated with the nitrogen lone pair of electrons.

The data of Table V show that substitution of a π donating group in the 2 position destabilizes the highest occupied π orbital. While this orbital no longer has a node at the nitrogen, it is similar to the pyridine a_2 orbital, but is also delocalized onto the substituent. Both delocalization and π donation by the substituent lead to the destabilization of the highest occupied π orbital. On the other hand, when the substituent is CHO or CN, π electron withdrawal from the 2 position tends to stabilize the highest occupied π orbital. In 2-pyridinecarboxaldehyde, the π withdrawing effect and the effect of delocalization are apparently balanced, with the result that the energy of the highest occupied π orbital is the same as in pyridine. In 2-cyanopyridine, the π withdrawing effect is dominant, so that only in this case does substitution stabilize the highest occupied π orbital.

In the 4-R-pyridines, the highest occupied π orbital is also

Table V. Orbital Energies (eV) and Dipole Moments (D) of Substituted Pyridines

	2-R-pyridine				4-R-pyridine			
	1st π	2nd π	n	μ	1st π	2nd π	n	μ
R = H	−8.18[a]	−8.71[a]	−9.20	2.06	−8.18[a]	−8.71[a]	−9.20	2.06
CH_3	−7.84	−8.61	−9.14	1.85	−8.11	−8.33	−9.06	2.37
NH_2	−6.39	−8.52	−9.04	1.69	−6.74[b]	−8.10	−8.78	3.50
OH	−7.29	−8.87	−9.56	1.36	−7.74[b]	−8.36	−9.19	2.11
F	−7.89	−9.04	−9.55	2.70	−8.33[b]	−8.49	−9.43	1.11
C_2H_3	−7.28	−8.63	−9.26	1.92	−7.62[b]	−8.23	−9.14	2.30
CHO	−8.18	−8.93	−9.04	2.39	−8.42	−8.67	−9.24	1.45
CN	−8.60	−9.37	−10.10	4.90	−8.86	−9.03	−9.92	1.34

[a] The first and second π orbitals of pyridine have a_2 and b_1 symmetry, respectively. [b] The highest occupied π orbital corresponds to the pyridine b_1 orbital.

destabilized relative to pyridine except when the substituent is F, CHO, or CN. However, substitution in the 4 position has very different effects on the energies of the a_2 and b_1 orbitals. Substitution of a π donor alters the a_2 orbital energy to a relatively small extent, destabilizing this orbital by 0.08 eV in 4-aminopyridine and stabilizing it by 0.31 eV in 4-fluoropyridine. There is little (in molecules with C_s symmetry) or no (in molecules with C_{2v} symmetry) delocalization of the pyridine a_2 orbital onto the substituent. On the other hand, the b_1 orbital of pyridine is greatly affected by substitution at the 4 position, becoming highly delocalized onto the substituent. As a result, the b_1 orbital is destabilized in all 4-R-pyridines except 4-cyanopyridine, in which case it is stabilized but by only 0.32 eV. Substitution destabilizes the b_1 orbital to the extent that in 4-amino-, 4-hydroxy-, 4-fluoro-, and 4-vinylpyridine the b_1 orbital is the highest occupied molecular orbital. This implies that the nature of the first π ionization is dramatically different in these molecules than in the remaining 4-R-pyridines and the 2-R-pyridines. Although the highest occupied π orbital in a 2-R-pyridine is less stable than the highest occupied π orbital in the corresponding 4-R-pyridine, the b_1 orbital in the 4-R-pyridine is less stable than the b_1 orbital in the corresponding 2-R-pyridine.

The presence of substituents also affects the energy of the n orbital. As noted previously, the substituents which are π electron donating are also σ electron withdrawing. Since π donation tends to destabilize the n orbital by lowering the effective nuclear charge at the nitrogen while σ withdrawal tends to stabilize the n orbital by reducing the nitrogen electron density in the plane of the ring, changes in n orbital energies upon substitution of a π donating group reflect a competition between these two effects.[22] The effect of π donation is most evident in 2- and 4-aminopyridine, since the n orbital is destabilized by 0.16 and 0.42 eV, respectively, relative to pyridine. On the other hand, when the substituent is the strong σ and π electron withdrawing group CN, substitution leads to a stabilization of the n orbital by 0.90 and 0.72 eV in 2- and 4-cyanopyridine, respectively. However, it should be noted that the σ and π effects of substituents are not the only factors which influence n orbital energies. A comparison of n orbital energies of corresponding 2- and 4-R-pyridines shows that the largest differences occur when the substituents are OH and NH_2. These large differences may be attributed to the increased stability of the n orbital in the 2 isomer due to the interaction between the pyridine nitrogen and the substituent hydrogen (H′). Moreover, the data of Table V show that the n orbital in the 2 isomer is more stable than in the 4 in all 2- and 4-R-pyridines except for 2- and 4-pyridinecarboxaldehyde. In these isomers, interaction between the n orbital associated with the pyridine nitrogen and that associated with the carbonyl oxygen leads to two delocalized n orbitals, which have energies of −9.04 and −9.96 eV in the 2 isomer and −9.24 and −9.94 eV in the 4.

The dipole moments of the 2- and 4-R-pyridines are also reported in Table V. The change in the pyridine dipole moment upon substitution is readily understood from the polarity of the substituent and the orientation of the substituent dipole moment vector (as deduced from the corresponding substituted benzene) relative to the dipole moment vector of pyridine, and from the electron redistribution which occurs upon substitution. Substituents which enhance the dipole moment in the 2 isomer lower it in the 4, and those which lower the dipole moment in the 2 isomer enhance it in the 4. Among the 2 isomers, increases in the dipole moment occur when the substituents are F, CHO, and CN, with the enhancement being greatest in 2-cyanopyridine, which has a computed dipole moment of 4.90 D. Among the 4 isomers, the dipole moment of 3.50 D for 4-aminopyridine is largest. In 4-cyanopyridine, not only is the dipole moment reduced, but the dipole moment vector is reversed relative to pyridine.

Conclusions

Ab initio molecular orbital calculations have been performed to determine the structural, energetic, and electronic properties of the 2- and 4-R-pyridines, with R including the isoelectronic saturated groups CH_3, NH_2, OH, and F and the unsaturated groups C_2H_3, CHO, and CN. The data obtained support the following statements.

1. The equilibrium geometry of the pyridine ring is essentially unchanged in the equilibrium structures of the 2- and 4-R-pyridines, independent of the nature of the substituent and its position.
2. The 2-R-pyridines are more stable than the corresponding 4-R-pyridines in all cases. When the substituent is a strong π donor, the difference in the stabilities of the two isomers is greater than when the substituent is a weak π donor or a π electron withdrawing group. The largest difference in the stabilities of the isomers is found for the hydroxypyridines, in which case the interaction between the aromatic nitrogen and the hydroxyl hydrogen is important in stabilizing 2-hydroxypyridine.
3. Except for substitution of F in the 4 position, substitution of a π donor at the 2 or 4 position has a stabilizing effect in pyridine relative to benzene. Substitution of the strong π electron withdrawing group CN at the 2 or 4 position, or the weak π electron withdrawing group CHO at the 4 position, has a destabilizing effect in pyridine relative to benzene.
4. Although substitution of a π donating group increases the total and π electron densities of the aromatic nitrogen atom, substitution at the 2 or 4 position of pyridine leads to net decreases in the total and the σ electron densities of the ring.
5. The electronic effects of substituents are manifest in the changes in orbital energies which occur upon substitution. Substitution of a π donating group tends to destabilize the first and second π orbitals of the 2- and 4-R-pyridines relative to pyridine. In 4-amino-, 4-hydroxy-, 4-fluoro-, and 4-vinylpyr-

idine, the pyridine b_1 orbital is destabilized to the extent that it rather than the a_2 orbital is the highest occupied molecular orbital. On the other hand, only substitution of the strongest π electron donating group NH_2 leads to a significant destabilization of the pyridine n orbital.

6. The change in the dipole moment which occurs upon substitution in pyridine is determined by the polarity of the substituent and the orientation of the substituent dipole moment vector relative to that of pyridine, and by the electron redistribution in the molecule. Those substituents which enhance the dipole moment in the 2 isomer lower it in the 4, and vice versa. In 4-cyanopyridine, the dipole moment vector is reversed relative to pyridine.

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References and Notes

(1) R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Eds., Wiley, New York, 1975, pp 31-77.
(2) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311 (1976).
(3) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
(4) E. M. Arnett in ref 1, pp 79-101.
(5) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 318 (1976).
(6) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5729 (1977).
(7) I. G. John, G. L. D. Ritchie, and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1601 (1977).
(8) W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5821 (1977).
(9) J. E. Del Bene, *J. Am. Chem. Soc.*, **97**, 5330 (1975); *Chem. Phys.*, **15**, 463 (1976).
(10) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(11) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(12) L. E. Sutton, *Chem. Soc., Spec. Publ., Suppl.*, **No. 18** (1965).
(13) The angle to the substituent (N_1-C_2-X) is also within ±1° of the N_1-C_2-H angle in pyridine except in 2-vinylpyridine, where it decreases by 3°.
(14) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).
(15) The N-H' interaction should probably not be labeled an intramolecular hydrogen bond. The O-H'· · ·N arrangement is far from linear (73°) and the N_1-H overlap population is negative, whereas in an inter- or intramolecular A-H· · ·B hydrogen bond the B-H overlap population is always positive.
(16) The relative orientation of component dipole moments of the ring and of the substituent has been invoked as a factor influencing the relative stabilities of 2- and 3-monosubstituted furans. (See I. G. John and L. Radom, *J. Am. Chem. Soc.*, **100**, 3981 (1978). However, this factor does not stabilize the 2-substituted pyridine when the substituent is F or CN, in which cases the component dipole moments are unfavorably oriented.
(17) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
(18) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(19) These large errors arise primarily from an overestimation of the C_4-X distance by the standard model and from variations in angular coordinates within the substituent from standard model values, as evident from Table II.
(20) It should be noted that a nonplanar aniline structure with a pyramidal nitrogen was found to be 2.7 kcal/mol more stable than the planar standard-model structure (see ref 14). With the pyramidal structure as a reference, the computed ΔE_2 value would be reduced to 1.6 kcal/mol, but would still remain positive for 2-aminopyridine. A more detailed study of the effect of NH_2 substitution on the relative stabilities of aniline and the aminopyridines would require that similar pyramidal structures be investigated for the aminopyridines.
(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(22) R. Ditchfield, J. E. Del Bene, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 703 (1972).

Intramolecular Electron Transfer from Pentacyanoferrate(II) to Pentaamminecobalt(III) Mediated by Various 4,4'-Bipyridines[1a]

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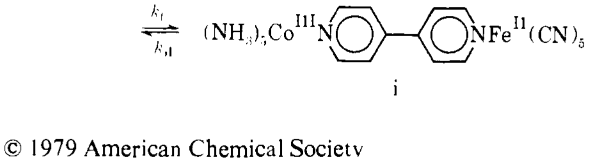
Abstract: The reactions of $Fe(CN)_5OH_2^{3-}$ with $Co(NH_3)_5L^{3+}$ (L = bis(4-pyridyl)methane, bis(4-pyridyl)ethane, bis(4-pyridyl)propane, bis(4-pyridyl)ethylene, and bis(4-pyridyl) ketone) produce binuclear complexes $(NC)_5Fe^{II}LCo^{III}(NH_3)_5$ that exhibit iron t_{2g} to ligand π^* charge transfer bands at (same order) 370, 365, 360, 500, and 555 nm. Comparison of these values with those for the corresponding $Fe^{II}(CN)_5L^{3-}$ complexes (370, 365, 360, 460, and 520 nm) suggests that the electron-withdrawing effect of the Co(III) moiety attached to the remote N is transmitted to the ring adjacent to the Fe(II) via π interactions, and that saturated hydrocarbon groups connecting the two pyridine rings insulate electronically the iron and cobalt centers. Rate constants for the formation and dissociation of the binuclear complexes have been measured and a dissociative mechanism is clearly indicated by the LFER of slope −1.0 between rate constants and equilibrium constants for the formation reactions. The rate constants for intramolecular electron transfer from Fe(II) to Co(III) in the binuclear complexes have been measured. At 25 °C, $\mu = 0.10$ M, the values are (same order of ligands) $<0.6 \times 10^{-3}$, 2.0×10^{-3}, 4.8×10^{-3}, 1.4×10^{-3}, and $<0.1 \times 10^{-3}$ s^{-1}. It is suggested that conjugation between the two pyridine rings is essential for electron transfer mediated by the ligand. When the two rings are separated by insulating methylene groups, electron transfer through the ligand is precluded, but ligands that permit close approach of the metal centers lead to intramolecular, outer-sphere electron transfer.

It was previously reported[2] that the redox reaction between 4,4'-bipyridinepentaamminecobalt(III) and aquopentacyanoferrate(II) proceeds via the *detectable* binuclear precursor complex i. The rate constants for the formation and dissociation of this intermediate (k_f and k_d in eq 1) and the rate constant for intramolecular electron transfer (k_{et} in eq 2) were measured.[2] In view of the importance of measuring intramo-



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