INDO[1] CONFIGURATIONAL ENERGY DIFFERENCES.   THE SIGMA PI PROBLEM.

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We wish to present the results of our investigations of the energies of the sigma and pi electronic structures of pyrryl (1) and formyloxy (2) radicals.   These results, like the

previous ones[2] on formamido (3), show that the configurations converged upon in the standard INDO method are not always of lowest energy.   The present analysis includes the examination of three configurations of each system with partial geometric optimization.   The results of these studies give a rather different picture for the ground states than that of a recent study[3] which neglected both the configurational and geometric problems.

Using the standard INDO method and standard geometries[3] for 1 and 2, one arrives at the SCF limit in pi ($^2A_2$) and sigma ($^2A_1$) configurations respectively.   However, a systematic population scheme[2] shows that these configurations correspond to the second excited state for both 1 and 2 (Fig. 1 and 2).   The question of which is the adiabatic ground state requires a search for the minimum in total energy for each configuration.   Figures 1 and 2 give the results of such a search in a restricted[4] geometric space.   Table 1 summarizes the calculated properties for each species in its (partially) optimized geometry.

The pi ($^2A_2$) state of formyloxy shows little deviation in geometry from standard bond lengths and bond angles.   The $^2B_2$ sigma state prefers small O-C-O angle with little change in bond length.   The vacancy resides in an orbital which is antibonding with respect to the two oxygen atoms.   The geometric change is thus in accord with the 0, 0 σ bond order change

which increases as the O,O distance decreases. The $^2A_1$ sigma state prefers large O-C-O angle

and slightly lengthened H-C distance. Here the vacancy resides in an O, O σ bonding orbital

while the antibonding level is doubly occupied so that the bond order argument also applies.

It is the $^2A_1$ sigma configuration of $\underline{2}$ which is C_{2v} correlated with the ground state of

carbon dioxide and hydrogen atom by continual opening of the O-C-O angle and lengthening the

H-C distance. The $^2A_2$ pi configuration correlates with an excited state of carbon dioxide

in this topological domain. The decarboxylation of the apparent ground state of the formyloxy

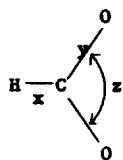species is thus energeticly forbidden by the (crossing) noncrossing[5] rule.

Our interest in this problem was partially generated by the recognition that the isotope

effects[6] for concerted perester decompositions could also be explained by nonconcerted reactions

which involved acyloxy intermediates of $^2A_1$ electronic structure. The hyperconjugation of the

H atom (high a_H, lengthened C-H bond) of this species suggests the possibility that the ground

states of acyloxy species might change from pi ($^2A_2$) to sigma ($^2A_1$) on replacement of the

H of $\underline{1}$ by a radical stabilizing group. However, calculations on acetoxy ($\underline{2}$, CH_3 for H) and

isobutyroxy radicals ($\underline{2}$, $(CH_3)_2CH$ for H) showed the difference in these two configurations was

rather insensitive to this substitution. The formation of sigma acyloxy radical intermediates

from peresters is rather unlikely if the INDO energies[9] are taken as the criterion.

The geometric preference of the pyrryl configurations also agree with bond order changes.

The ground state sigma ($^2A_1$) level is only slightly distorted from the geometry of pyrrole.[4a]

The two Π configurations deviate according to the Π bond order changes which depend on which

Π orbital contains the vacancy. The lower energy of the sigma state corresponds to the 4n+2

rule in allowing the aromatic sextet to remain unperturbed. An acyclic analogy would certainly[7]

have a Π ground state.

The vertical ordering of the two pi configurations above pyrrole geometry is quite sur-

prising. This order ($^2B_1$ ∿1.3eV below $^2A_2$) corresponds, in Huckel Theory, to a Coulombic

integral of nitrogen which is less bonding ($\alpha_N = \alpha_c + h\beta$, h≤o) than that for carbon. We have

previously pointed[2] out that the experimental NH_2 potential surface requires changes in α_N

in this same direction as the H-N-H angle decreases. This effect is a result of the two

electron repulsion differences for a neutral nitrogen atom. Calculations on pyrrole radical

cation give the opposite order ($^2B_1$ ∿.4eV above $^2A_2$) at the same geometry in agreement with

assignment in the photoelectron spectrum.[8]

Table I

INDO Configurational Energies at Optimized[4] Geometries.

Config.	x	y	z	$E_{rel}(\frac{kcal}{mole})$	$a(O_e)$	$\mu(D)$
$^2A_2(\Pi)$	1.09Å	1.30Å	120°	0.	-24[a]	1.73
$^2A_1(\Sigma)$	1.14Å	1.28Å	132°	37.	+172[a]	2.37
$^2B_1(\Sigma)$	1.09Å	1.29Å	83°	22.	-11[a]	3.74
$^2A_1(\Sigma)$	1.40Å	1.40Å	1.40Å	0.	53[b]	1.04
$^2A_2(\Pi_a)$	1.39Å	1.43Å	1.37Å	7.0	-3[b]	2.23
$^2B_1(\Pi_s)$	1.38Å	1.37Å	1.43Å	9.2	10[b]	1.92

a) Hyperfine coupling constant to carbon.   b) Hyperfine coupling constant to nitrogen.

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4. The optimizations assume that C_{2v} symmetry is maintained. With that restraint they are complete for formyloxy but quite incomplete for pyrryl for which the angular and C-H coordinates have been held nearly constant at the experimental values of pyrrole.[4a]

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8. P. Derrick, L. Asbrink, O. Edquist, B-Ö Jonsson and E. Lindholm, Int. J. Mass. Spect. and Ion Phys., __6__, 191 (1971).

9. As pointed out in ref. 2, the problem of the relevance of the configuration obtained by standard "aufbau" population schemes is a general one. Also, the INDO ordering of the configurational energies is not necessarily the correct one.

FIGURE 1

FIGURE 2