dipole electron-nuclear relaxation in complexed molecules. For the case of Cr(III) chelates we can see that the simple approach to the translational diffusion and outer sphere mechanisms, using eq 8, is reasonable as far as a specific PARR and molecules of similar size are concerned.

The paramagnetic relaxation reagents under investigation in this study seem to be suitable for applications in ^{15}N NMR spectroscopy using organic solvent systems. If a uniform decrease in ^{15}N spin-lattice relaxation times is required, both $Cr(acac)_3$ and $Cr(dpm)_3$ seem to be a good choice, the latter one being preferable if the compound studied contains acidic hydrogens. On the other hand, the Gd(III) chelates offer an interesting possibility of selective relaxation rate enhancement for basic and sterically accessible sites. Efficiency of the spin-labeling for the case of competing sites is conveniently defined in terms of the ratio of T_1^e's. Under favorable conditions (predominantly dipolar T_1's in diamagnetic solution, similar T_1^{dd} for the different sites of interest) spin-labeling effects can be easily monitored utilizing the differential quenching of the nuclear Overhauser enhancement.

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Banana and Nonbanana Bonds of the Carbonyl Group

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Abstract: Using substituted aldehydes, the effect on the form of the C=O repulsion-localized MOs of the presence of oxygen lone pairs and π conjugating substituents (CH_2^+, BH_2, CH_3, NH_2, OH, F) is examined. Generally, the banana model is correct, although for NH_2 and CH_2^+ substituents nonbanana results are obtained. Oxygen protonation, coupled with NH_2 and OH conjugation, also yields nonbanana bonds. The CO_π, O_{lp} repulsion integral is very sensitive to polarization of the CO π orbital and, more than any other factor, forecasts the form of the final LMOs.

Introduction

The carbonyl group continues to attract theoretical attention because of its prominence in enzyme bioprocesses as a ligating group for metal ions and as the site of nucleophilic attack in amino acid hydrolysis[1] and for its utility in 1,2-addition reactions with organometals.[2] Polarizability plays a key role in the chemistry of the C=O function and is particularly dependent on the nature of the carbon substituents. As coordination of a Lewis acid to an oxygen lone pair is an important aspect of enhancing the reactivity of C=O, this too has justifiably received considerable experimental and theoretical attention.

With regard to conceptualization of the electronic structure of the carbonyl group and the implications thereof for reaction properties of that group, previous descriptions have invoked simple Lewis structures to reflect π_{CO} polarization or relied on canonical σ and π MO descriptors. Extensive π_{CO} polarization implies extensive, if not dominant, lone-pair character

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Table I. Atomic Coordinates (Å) of XCHO

Compd	*X*	*Y*	*Z*
*F*CHO			
O	0.0	0.0	0.0
C	0.0	0.0	−1.1900
F[a]	0.0	1.1517	−1.8847
H	0.0	−0.9401	−1.7475
*HO*CHO			
O	0.0	0.0	0.0
C	0.0	0.0	−1.2450
O[a]	0.0	1.0838	−1.9843
H[a]	0.0	1.8335	−1.4008
H	0.0	−0.9231	−1.8151
H_2NCHO			
O	0.0	0.0	0.0
C	0.0	0.0	−1.2430
N[a]	0.0	1.1189	−1.9858
H[a]	0.0	2.0138	−1.5509
H[a]	0.0	1.0658	−2.9794
H	0.0	−0.8063	−1.9824
H_2BCHO			
O	0.0	0.0	0.0
C	0.0	0.0	−1.2200
B[a]	0.0	1.3516	−2.0000
H[a]	0.0	2.3816	−1.4050
H[a]	0.0	1.3510	−3.1900
H	0.0	−0.9405	−1.7630
H_3CCHO			
O	0.0	0.0	0.0
C	0.0	0.0	−1.2155
C[a]	0.0	1.2454	−2.0524
H[a]	0.0	2.1298	−1.4221
H[a]	0.8803	1.2794	−2.6875
H[a]	−0.8803	1.2794	−2.6875
H	0.0	−0.9781	−1.7488
H_2CCHO$^+$			
O	0.0	0.0	0.0
C	0.0	0.0	−1.2200
C[a]	0.0	1.2287	−1.9294
H[a]	0.0	2.1692	−1.3864
H[a]	0.0	1.2287	−3.0154
H	0.0	−0.9405	−1.7630

[a] Refers to the atoms of substituent X.

for this bond pair and this is a characteristic readily diagnosed by a localized molecular orbital analysis of the canonical molecular orbitals. The implications of "lone pair" character for the π_{CO} bond pair are far reaching: the barrier to inversion at oxygen for an out-of-plane transition state is lowered by such lone-pair character; the ease with which the CO group acts as a Lewis base through the π pair is intimately related to the lone-pair character of π_{CO}; both of these aspects of CO chemistry are deeply involved in the mechanism for 1,2 addition of organometals; finally, the electrophilicity of the carbonyl carbon is directly related to the degree of π_{CO} lone pair character. Electron-donating substituents should enhance the lone-pair character of π_{CO}, as should Lewis acid coordination of an oxygen lone pair.

Earlier reports from this group[3] have focused on the question of the change in C=O electronic structure upon protonation of oxygen and its relation to the lone pair and π pair donor nature of C=O. Those studies have examined XCHO examples, where X = H, CH_3, in terms of canonical and localized orbital models. In this work we examine the nature of the localized orbitals as a function of π donor (X = NH_2, OH, F) and π acceptor (X = BH_2, CH_2^+) substituents.

From a purely theoretical point of view the C=O group affords a good test of the generally accepted notion that an X=Y moiety will yield bent or "banana" bands on localization.[4] Not examined previously is the condition implicit to this

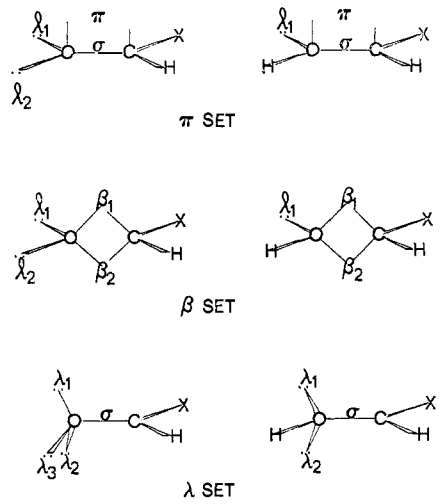


Figure 1. Idealized localized MOs for the carbonyl group.

generalization that the other valence electron pairs about X, Y not be localization-mixed with the X=Y π component. In the situation of all bond pairs about X=Y and no XY π conjugation with the X, Y substituents, localization seems to result in XY_π/XY_σ mixing only. No attention has been given, other than to H_2CO and CH_3CHO as mentioned above, to the question whether XY_π/Y_{lp} mixing may ever become substantial. If so, then it may be asked whether the localized MOs must show exclusively either π,σ or π,lp mixing or is a hybrid possible; furthermore, what is the effect on the localized MOs of the presence of π conjugating substituents at Y (or X)? Finally, is it possible that "canonical" σ,π LMOs are preferred to the banana LMOs? The present report examines examples under which all such localization results are obtained.

Calculation Methods

The geometries (see Table I) for XHCO (X = F, OH, NH_2, CH_3) were taken from ref 5; for X = BH_2, the nominal B–H and B–C bond lengths were obtained from "Table of Selected Bond Lengths" in the same reference and interbond angles of 120° were assumed. The protonated adduct structures were built from undistorted XHCO geometries having the proton in the molecular plane; H···H^+ cis structures with an H^+OC angle of 120° and a O–H^+ bond length of 1.04 Å were considered.

The molecular orbitals were obtained according to the INDO prescription.[6] The calculations avoiding π conjugation between the CO group and the substituent X, called *noco* calculations, were undertaken by zeroing those off-diagonal Fock matrix elements that lead to π interaction of X with C=O.

The localized orbitals were obtained by the Edmiston and Ruedenberg procedure as adapted[7] to the set of INDO molecular orbitals. This iterative procedure was carried out with an intraorbital repulsion energy gradient convergence criterion of 10^{-4}. Three idealized CO configurations (see Figure 1) were studied in the following way: the set having the CO σ–π configuration (hereafter called the π set) is obtained by dividing the canonical MOs into two sets, σ (in plane) and π (out of plane), with separate localization of each set. Working from this partially localized set of σ and π orbitals for each molecule, the β molecular orbitals for the CO group were obtained from the localized π set through the unitary transformation

$$\begin{vmatrix}\beta_1\\ \beta_2\end{vmatrix} = \begin{vmatrix}1/\sqrt{2} & 1/\sqrt{2}\\ -1/\sqrt{2} & 1/\sqrt{2}\end{vmatrix}\begin{vmatrix}\sigma\\ \pi\end{vmatrix}$$

The same transformation applied to the π and lp MOs of the protonated carbonyls yielded a set of localized MOs called the

Table II. Intraorbital Repulsion Energy Curvature

Compd	Final set ν^a	Final set Vector[b]	Ideal π set ν^c	Ideal π set Vector[d]
	π Donors			
10. FCHO	−0.0381		0.0811	
18. $FCHOH^+$	−0.0082		0.1531	(π,l)
7. FCHO noco	−0.0475		0.0720	
13. $FCHOH^+$ noco	−0.0311		0.1353	(π,l)
12. HOCHO	−0.0119		0.0857	
21. $HOCHOH^+$	−0.0156	(λ_1,λ_2)	0.1899	$(\lambda,l)^e$
6. HOCHO noco	−0.0426		0.0658	
16. $HOCHOH^+$ noco	−0.0195		0.1474	(π,l)
19. H_2NCHO	−0.0269		0.1072	$(\pi,l_1)(\pi,l_2)$
22. H_2NCHOH^+	−0.0472	(λ_1,λ_2)	0.2143	$(\pi,l)^e$
8. H_2NCHO noco	−0.0411		0.0667	
17. H_2NCHOH^+ noco	−0.0121		0.1522	(π,l)
9. H_3CCHO	−0.0368		0.0661	
20. H_3CCHOH^+	−0.0008		0.1624	(π,l)
5. H_3CCHO noco	−0.0412		0.0620	
14. H_3CCHOH^+ noco	−0.0229		0.1435	(π,l)
	π Acceptors			
2. H_2BCHO	−0.0143		0.0202	
11. H_2bchoh^+	−0.0391		0.1187	
4. H_2BCHO noco	−0.0380		0.0574	
15. H_2BCHOH^+ noco	−0.0220		0.1438	(π,l)
1. H_2CCHO^+	−0.0682	(σ,π)	−0.0682	
3. H_2CCHO^+ noco	−0.0380		0.0457	

[a] The least negative eigenvalue corresponds in all cases (except X = F and H_2NCHOH^+) to mixing of LMOs centered at oxygen. For X = F, $\nu = 0.000$ for mixing of F lone pairs. For H_2NCHOH^+, $\nu = -0.0243$ corresponds to N_{1p}, CN_σ mixing. [b] The direction of least curvature is dominated by a component $>1/\sqrt{2}$ for one orbital pair (β_1,β_2, except where given). [c] Reported are the largest eigenvalues with vectors dominated by oxygen center LMOs. In all instances a positive eigenvalue dominated by σ/π mixing at the substituent is found (H_2CCHO^+ is the exception). [d] Unless otherwise given, the vector is dominated by $\pi\sigma$ mixing with a coefficient >0.8. Other entries mean that π,σ and that entry both have coefficients >0.5 and <0.8. [e] Entry contribution is greater than the π,σ contribution.

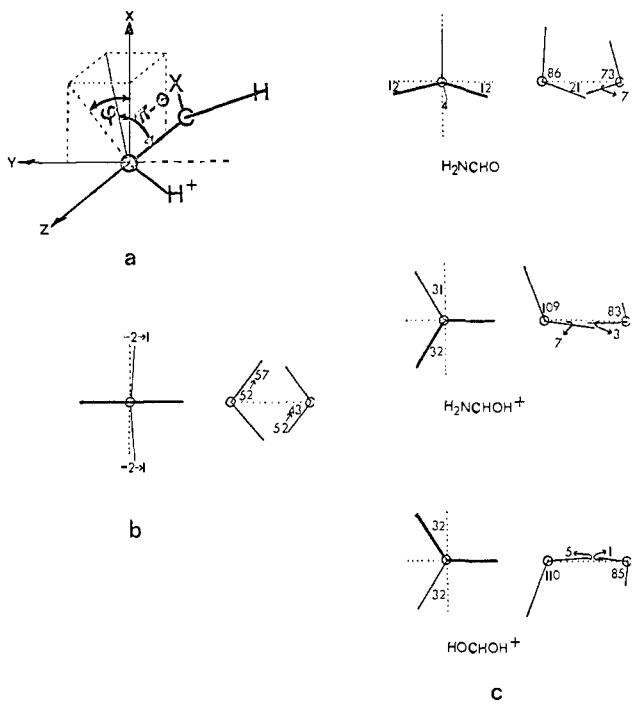


Figure 2. Views from the $+z$ and $-y$ directions of the fully localized CO MOs (π donor substituents): (a) defines the coordinate system and hybrid axis angles; (b) is a generalization for all cases but those in (c); (c) the NH_2CHO, NH_2CHOH^+, and $HOCHOH^+$ cases.

λ set in Figure 1.[8] For the unprotonated compounds, the λ set is obtained from the two oxygen lone pair and CO_π orbitals by the (also unitary) transformation

$$\begin{vmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \end{vmatrix} = \begin{vmatrix} \sqrt{2/3} & 1/\sqrt{6} & 1/\sqrt{6} \\ -1/\sqrt{6} & 1/\sqrt{6}+1/2 & 1/\sqrt{6}-1/2 \\ -1/\sqrt{6} & 1/\sqrt{6}-1/2 & 1/\sqrt{6}+1/2 \end{vmatrix} \begin{vmatrix} \pi \\ l_1 \\ l_2 \end{vmatrix}$$

Further localization of the β and π sets yielded the same set of completely localized MOs as did localization of the canonical and randomized canonical MOs. That convergence to true maxima (to second order) on the intraorbital repulsion energy surface had taken place in all cases was established by evaluating the second-order derivatives, $D_2(ij, mn) = \partial^2 D/\partial A_{ij}\partial A_{mn}$, of the intraorbital repulsion energy D at the point of convergence. All elements $D_2(ij, ij)$ were negative and diagonalization of the supermatrix constructed from the second derivatives yielded all negative eigenvalues (for the fluorinated compounds zero was the value assumed by the least negative eigenvalues, indicating that the intraorbital energy D is insensitive to couplings (rotations around the C–F axis) of the three fluorine lone pairs). See Table II. Although there always exists the possibility of multiple maxima in D space, the second-order derivative analysis and the nondependence of the final MOs on the starting set of MOs establishes the appropriateness of the final localized MOs.

After the final localized orbitals were obtained, special consideration was given to the four MOs localized at oxygen: the angles θ and ϕ were calculated as $\theta^i(O) = \cos^{-1}[p_{zi}(O)/\{p_{xi}^2(O) + p_{yi}^2(O) + p_{zi}^2(O)\}^{1/2}]$, $\phi^i(O) = \tan^{-1}[p_{yi}(O)/p_{xi}(O)]$, where the superscript i identifies one of the four localized orbitals, O stands for oxygen, and p_x, p_y, p_z refer to the LCAO coefficients of the oxygen hybrid in the ith localized orbital. Vectors showing the angles $\pi-\theta$ and ϕ for the LMO hybrids at oxygen are drawn in Figure 2. The vector lengths at carbon and oxygen reflect the carbon and oxygen atomic densities. The latter quantities are given in Table III

Table III. Atomic Densities for Localized Orbitals at Oxygen and X

Compd	MO[a]	O	C	X
FCHO	lp(2)	0.97	0.02	
	CO(2)	0.60	0.40	
	X(3)		0.01	0.99
$FCHOH^+$	lp(1)	0.98	0.02	
	OH(1)	0.67	0.02	
	CO(2)	0.69	0.31	
	X(3)		0.03	0.97
HOCHO	lp(2)	0.96	0.03	
	CO(2)	0.61	0.39	
	X(2)	0.97	0.02	
$HOCHOH^+$	lp(2)	0.90	0.09	
	OH(1)	0.66	0.01	
	CO(1)	0.60	0.40	
	X(2)		0.07	0.93
H_2NCHO	lp(2)	0.97	0.03	
	CO(σ)	0.54	0.46	
	CO(π)	0.71	0.28	
	X(1)	0.01	0.13	0.85
H_2NCHOH^+	lp(2)	0.92	0.07	
	OH(1)	0.65	0.01	
	CO(σ)	0.59	0.41	
	X		0.29	0.75
CH_3CHO	lp(2)	0.98	0.01	
	CO(2)	0.59	0.41	
	X(3)		0.01	0.99
CH_3CHOH^+	lp(1)	0.98	0.01	
	OH(1)	0.65	0.01	
	CO(2)	0.69	0.30	
	X(3)		0.03	0.96
H_2BCHO	lp(2)	0.99	0.01	
	CO(2)	0.55	0.42	0.03
H_2BCHOH^+	lp(1)	0.99	0.01	
	OH(1)	0.66	0.00	
	CO(2)	0.66	0.32	0.01
H_2CCHO^+	lp(2)	0.99	0.01	
	CO(σ)	0.60	0.39	
	CO(π)	0.37	0.48	0.15

[a] The number of LMOs of each type in parentheses. X designates conjugating pair(s) at the substituent.

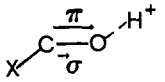
for the four MOs centered at oxygen and, where appropriate, for the π MO(s) centered at X.

Results and Discussion

Overview of X = π Donor Cases. Noting that the molecular plane (yz) is a true symmetry plane, the xy projections in Figure 2 reveal, with one exception (H_2NCHO), that the l_p MOs about oxygen reflect this symmetry. Symmetry about the xz plane in these projections, on the other hand, is not expected because the carbon substituents are not the same. More germane to the object of our study are the symmetries (or lack thereof) in the xz projections. Deviations of the simple LMO from the molecular symmetry forecast the occurrence of two symmetry-equivalent "resonance" structures such as has already been noted for boranes and benzene,[9] for example. In any one such structure the deviation is made up for by other LMOs so that the *total* electron density is, as required, fully symmetric.

On the question of the appropriateness of the π ideal structure, in every case a positive eigenvalue, weighted heavily for σ,π mixing, is indicated. Table II, columns 4 and 5, summarizes our findings. It is interesting to note that many of the orthogonal eigenvectors consist of both π,σ and π,l components, whereas the final LMOs exhibit only one or the other mixing to be important. This simply reflects the fact that the orthogonal vectors at the π structure do not correspond well with the most efficient direction to the surface maximum. Consequently, the π structure eigenvector is not a completely reliable indicator of the form of the final LMOs about oxygen.

On the whole, the presence of the oxygen lone pairs and π conjugation of X with the CO group do not yield other than the usual "banana" description of the CO double bond. Such a statement cannot be generalized, for in the cases of protonated formamide and formic acid there is a dominant preference for mixing of the CO_π and O_{lp} functions, *if conjugation of the NH_2 and OH lone pairs with the CO group is permitted.* It seems that CO_π,O_{lp} interorbital repulsion in these cases is greater than CO_π, CO_σ repulsion. This is likely due to pronounced CO_π polarization toward oxygen and a less important, synergically suppressed σ polarization toward oxygen (see later). The former tends to enhance the oxygen π, lp repulsion



while the π,σ synergism dampens the increase in π,σ repulsion.[10] This is most clearly reflected in the change, on protonation, of $(D_\lambda - D_\pi) \times 10^4$ and $(D_\beta - D_\pi) \times 10^4$ for formic acid ($-200 \rightarrow 171$ and $66 \rightarrow 40$) and for formamide ($-80 \rightarrow 262$ and $14 \rightarrow -29$), where D_i is the sum *intra*orbital repulsion for the ideal $i = \lambda$, β, and π models.

The case of formamide itself is interesting because it appears (figure 2) to be borderline in the sense of equally significant π,σ and π,lp repulsions. Again, when the synergic interaction of X with CO is blocked (see the noco set, Figure 2) a "normal" result is attained; thus, among the series of substituents examined here, NH_2 seems to strike a unique balance of π donor, σ acceptor character. Most interestingly, this balance between (π,l) and (π,σ) mixing is associated with *weak*, not strong, preference for each ideal. Specifically, $(D_\lambda - D_\pi)$ and $(D_\beta - D_\pi)$ are only -80×10^{-4} and 14×10^{-4}, the former three times and the latter five times smaller than the corresponding values for the next closest case, formic acid. Thus H_2NCHO is particularly indiscriminate about a favored LMO set.

Orbital Structure Preferences. To see the operation of the CO σ and π polarization effects within the proper theoretical framework, the following expressions can be derived to reveal the origin of favored status of one idealized structure against another:[8,11]

$$D_\beta - D_\pi = \sum_{i=1}^{2} \langle \beta_i\beta_i || \beta_i\beta_i \rangle - [\langle \sigma\sigma || \sigma\sigma \rangle + \langle \pi\pi || \pi\pi \rangle]$$

$$= 2K_{\sigma\pi} + J_{\sigma\pi} - \frac{1}{2}[J_{\sigma\sigma} + J_{\pi\pi}] \quad (1)$$

$$D_\lambda{}^+ - D_\pi = \sum_{i=1}^{2} \langle \lambda_i\lambda_i || \lambda_i\lambda_i \rangle - [\langle ll || ll \rangle + \langle \pi\pi || \pi\pi \rangle]$$

$$= 2K_{l\pi} + J_{l\pi} - \frac{1}{2}[J_{ll} + J_{\pi\pi}] \quad (2)$$

$$D_\lambda - D_\pi = \sum_{i=1}^{3} \langle \lambda_i\lambda_i || \lambda_i\lambda_i \rangle - \left[\sum_{j=1}^{2} \langle l_jl_j || l_jl_j \rangle + \langle \pi\pi || \pi\pi \rangle\right] = 2\bar{K}_{l\pi} + \bar{J}_{l\pi} - \frac{1}{2}[\bar{J}_{ll} + J_{\pi\pi}] + \ldots \quad (3)$$

In eq 2 the + superscript on D_λ identifies protonated species for which there is but one lone pair to mix with CO_π. Equation 3 reflects the fact that there are two lone pairs to mix with CO_π in the unprotonated species and that these are technically nonequivalent. For all practical purposes this asymmetry may be ignored[12] and eq 2 also applies to the unprotonated species. Equations 1 and 2 may be combined

$$D_\beta - D_\lambda = 2[K_{\sigma\pi} - K_{l\pi}] + [J_{\sigma\pi} - J_{l\pi}] - \frac{1}{2}[J_{\sigma\sigma} - J_{ll}] \quad (4)$$

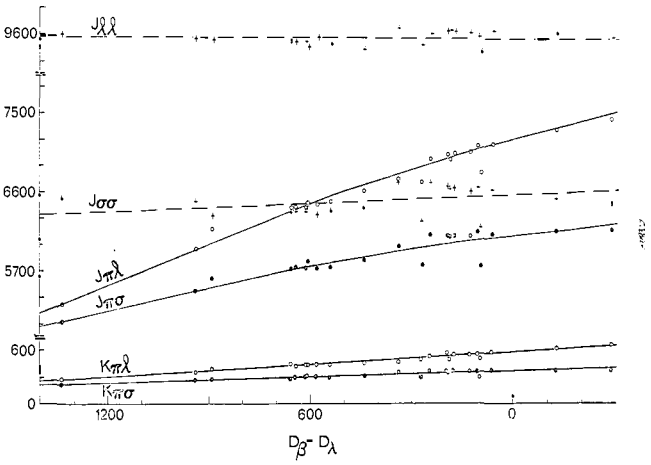


Figure 3. The gross correlations of J's and K's with structure preference. Both axes with scales of 10^{-4} au. Read from left to right the sequence of points here corresponds to the numerical sequence in Table II.

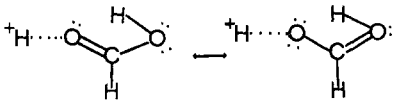
to reveal the conditions for β or λ structure preference. Given the greater localization of l than σ at oxygen, all three terms in brackets of eq 4 are negative. Because J_{ll} will not change greatly with carbon substituent, the variation in $D_\beta - D_\lambda$ will depend primarily on changes in the CO_σ and CO_π amplitudes at oxygen. That is,

$$\delta(D_\beta - D_\lambda) \sim 2[\delta K_{\sigma\pi} - \delta K_{l\pi}] + [\delta J_{\sigma\pi} - \delta J_{l\pi}] - \frac{1}{2}\delta J_{\sigma\sigma} \quad (5)$$

In terms of eq 5, CO_π polarization favors the λ structure through the first two terms.[10] CO_σ polarization *toward* oxygen tends to favor the β structure through these same terms, but *disfavors* this structure through $\delta J_{\sigma\sigma}$. The π,σ synergism mentioned above acts through all three σ terms, while $\delta J_{\sigma\sigma}$ suppresses the effect of increased $\delta K_{\sigma\pi}$ and $\delta J_{\sigma\pi}$.

Looking first at the noco results, the third term in eq 4 is seen to dominate (because l is much better localized than σ) and, in terms of eq 5, changing the substituent at carbon does not upset this balance. Note that changing the substituent will primarily affect the CO_σ LMO and only secondarily affect the CO_π LMO. Protonation induces greater localization of both σ and π MOs at oxygen, but again the offsetting natures of the first two and third terms prevent a sign reversal of eq 4.

Rather markedly different results can be obtained when π conjugation of the substituent with the CO group is permitted. Among the unprotonated species, F and OH are "poor" π donors and strong σ acceptors and so inhibit polarization of CO_σ and CO_π toward oxygen and the β structure preference is maintained. Methyl as a substituent is much like F and OH in this regard. This is interesting because CH_3 is a much poorer σ acceptor and might have led to a λ structure through σ polarization.[13] That such is not the case emphasizes the importance of substituent π conjugation to the form of the final MOs. Dramatically, even protonation fails to undermine the β structure preference for CH_3,[14] while this is not unexpected for F. That OH π conjugation in formic acid drastically increases on protonation is clearly evident in Figure 2 and thus provides an example of λ preference. The localized MO topography implied by Figure 2 is also reflected in the oxygen atom electron densities in Table III. Both criteria underscore the considerable lone pair characteristics of both π pairs in the classical resonance structures:[15]



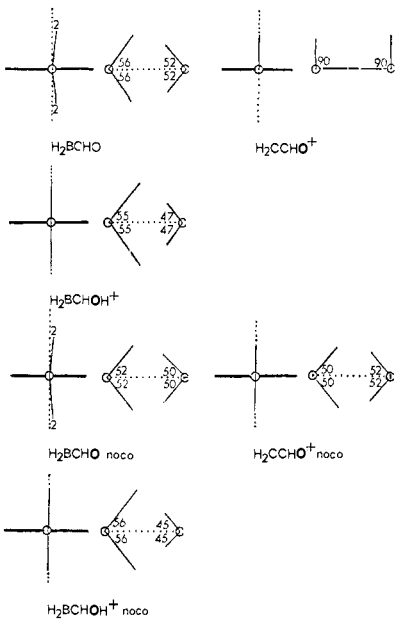


Figure 4. Views from the $+z$ and $-y$ directions of the fully localized CO MOs (π acceptor substituents).

The lone pair character of the CO_π pair has dramatically increased to the point that the sign of eq 4 is reversed and the LMOs clearly reveal the pronounced π polarization. A synergic σ polarization component is expected to moderate $\delta K_{\sigma\pi}$ and $\delta J_{\sigma\pi}$ as well.

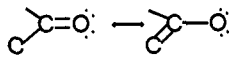
NH_2, of all the substituents, is most likely to exhibit this extreme polarization. This is clearly seen in Figure 2 for the protonated species but is even incipient for the unprotonated molecule. In this most unusual case, eq 4 has the value 93×10^{-4} (three to six times lower than the others) and eq 1 has the value 14×10^{-4} (six to ten times lower than the others); the distinction between λ, π, and β structures is definitely blurred and none of these three ideals is cleanly approached in the final LMO.

As a summary of these results, Figure 3 shows the variations in the terms of eq 4) in relation to $D_\beta - D_\lambda$. The assumption that J_{ll} is insensitive to substituent change and protonation is substantiated. As expected (because of synergism and low polarizability of σ MOs in general), $J_{\sigma\sigma}$ tends only to increase slightly as the β preference fades; more important are the variations in the $J_{l\pi}$ and $J_{\sigma\pi}$ terms. Note that, in eq 4, J_{ll} and $J_{\sigma\pi}$ favor the β structure while $J_{\sigma\sigma}$ and $J_{l\pi}$ favor the λ structure. Passing from the left side of Figure 3 (where $J_{ll} + J_{\sigma\pi}$ dominate eq 4) to the right, the marked increase in $J_{l\pi}$ overrides the smaller increase in $J_{\sigma\pi}$ and so is primarily responsible for the change in structure preference.

The π Acceptor Cases. As an extension of the preceding, we felt that study of the π-acceptor substituents BH_2 and CH_2^+ might turn up an example of σ,π preference through marked lowering of $J_{\sigma\pi}$ (eq 1) and $J_{l\pi}$ (eq 3). As indicated in Figure 4 and Table II, BH_2 is only moderately π withdrawing and equivalent banana orbitals arise in all four situations. The results fully fit Figure 3 and appear therein as the 2nd, 4th, 11th, and 15th columns of data.

The rather severely polarizing CH_2^+ substituent is prevented from its π withdrawal role in the noco set and banana orbitals result. When this constraint is removed, the strong reverse CO π polarization does lead to *σ,π MOs as the best localized set.* This is strikingly apparent in Table II where the ideal π structure corresponds to a surface maximum. These results also fit the trends in Figure 3 (columns 1 and 3). With regard to eq 1, $J_{\sigma\pi}$ in particular has dropped to such a low value (0.5129) that $\frac{1}{2}[J_{\sigma\sigma} + J_{\pi\pi}]$ (= 0.5763) now dominates the sign of D_β

$-D_\pi = -0.0181$ au (for comparison, the noco value is $+92 \times 10^{-4}$ au). In a sense, this result is the antithesis of the HO-CHOH$^+$ result cited earlier, where now the final LMO are a hybrid of the resonance forms[15]



Most certainly α-keto carbonium ions possess an unusual carbonyl group and serve as an illustration of the severe conditions needed to yield σ,π (rather than banana) LMOs.

Summary

As first suggested by Lipscomb[9] et al. for homonuclear frames with all bond pairs, conjugation of an X=Y pair can markedly flatten the repulsion surface in the direction of mixing of the X=Y bond pairs. In the heterosystems with oxygen lone pairs studied here, the polarization effects of π conjugation appear sufficient to extend this characteristic of "flattened" preference for β bonds through the range of β/λ hybrids, to a λ structure.

For substituents as strongly conjugating as NH_2, the localized orbital analysis reveals just how overly simplistic is the chemical valency model >C=O, particularly after coordination of the oxygen by a Lewis acid. In such cases, the carbonyl oxygen takes on the valence pair stereochemical attributes approaching those of an alcohol, with obvious implications to the electrophilicity of the CO group. Furthermore, any distinction between "σ" and "π" complexes as intermediates in 1,2 additions (hydro- and organometalations) becomes particularly obscure when strongly π-donating substituents are present.

Based on these results, the presence of lone pairs at, say, Y of X=Y is not sufficient to violate the generalization of banana bond preference. A necessary requirement is for there to be present a strongly conjugating group. NH_2 seems to be nearly capable of forcing a λ structure preference. In the other direction, strongly π-accepting groups such as carbonium ions α to >C=O lead to the π structure. To our knowledge, there is but one other report of such a structure for the minimum interorbital repulsion model, i.e., H_2BF.[17]

Finally, three critiques are necessary. While the results obtained here are chemically reasonable, and while INDO localized MOs faithfully reproduce the characteristics of ab initio localized MOs, such results can be basis set sensitive. Thus, the molecules with X = NH_2, OH, and CH_2^+ should be treated by *large basis*, ab initio techniques. Additionally, it will be interesting to learn whether the maximization-of-orbital-centroids criterion of Boys produces analogous results.[18] Finally, it should be noted that geometry optimization was not performed for the protonated species and that exact structures are not known for H_2BCHO and H_2CCHO^+ (the results obtained here arise for a C-C distance intermediate between single and double bond values and a normal C=O distance). For the protonated species, lengthening the CO bond should, in principle, favor the λ structure somewhat and, for H_2CCHO^+, shortening the CO distance should favor the π structure; uncertainties in structure are not expected to alter the qualitative aspects of the INDO results.

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(8) A reviewer comment prompts us to clarify the meaning of the idealized sketches of the λ set in Figure 1. This sketch does *not* imply that a p_π AO remains unoccupied at carbon. Both λ_1 and λ_2 make nonzero contributions to the density in this carbon AO, such that the contribution from λ_1, λ_2 = contribution from β_1, β_2 = contribution from π alone. The substituent X, in certain cases, also donates electron density to the carbon $p\pi$ AO and therefore is a key factor in the CO_π polarization toward oxygen and the degree to which the ideal λ_1, λ_2 set is approached by the CO LMO pairs. The limit of λ_1, λ_2 completely localized on oxygen would be accompanied by double bonding between carbon and X so as to maintain "tetravalence" of carbon.
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(10) Polarization of CO_σ and of CO_π toward oxygen has the effect of raising the J's and K's of the LMOs because the one-center AO repulsions are greater at oxygen than carbon. The effect on $(D_\lambda - D_\pi)$ and $(D_\beta - D_\pi)$ is less easy to predict; with reference to eq 1 and 2 to follow, the greater lone pair than CO_σ concentration at oxygen should render a greater + change in $(D_\lambda - D_\pi)$ than in $(D_\beta - D_\pi)$; in practice, the former does greatly increase while the latter may actually decrease.
(11) The total intraorbital repulsion energy for the π limit is given by $D_\pi = \Sigma\langle\sigma_i\sigma_i\|\sigma_i\sigma_i\rangle + \Sigma\langle\pi_j\pi_j\|\pi_j\pi_j\rangle$, where the σ's and π's are obtained by mutually exclusive localization. For the ideal β set, σ_{CO} is linearly combined in and out of phase with π_{CO} to give β_1 and β_2 and $D_\beta = \langle\beta_1\beta_1\|\beta_1\beta_1\rangle + \langle\beta_2\beta_2\|\beta_2\beta_2\rangle + \Sigma'\langle\sigma_i\sigma_i\|\sigma_i\sigma_i\rangle + \Sigma'\langle\pi_j\pi_j\|\pi_j\pi_j\rangle$, where the prime denotes summation over all but σ_{CO} and π_{CO}. In this way eq 1 represents a limiting-case mixture of σ and π MOs at CO. A full localization would result in π_{CO} being mixed with σ MOs in addition to σ_{CO}. Limiting-case mixing of π_{CO} with lp_O is represented by eq 2. Mixing of π_{CO} with σ_{CX} and σ_{CH} is ignored in eq 1 and 2 but these mixings are very small, as expected. Analogously, when X is a π donor or acceptor, mixing of π_{CX} with all σ MOs is ignored in eq 1 and 2. Clearly, π_{CX}-σ_{CX} mixing is of small consequence in the differences $D_\beta - D_\pi$ and $D_\lambda - D_\pi$. Mixing of π_{CX} with σ_{CO} is small, as expected from the strong polarizations of these MOs away from carbon, and leaves eq 1 and 2 as useful predictors of the full localization result.
(12) The omitted terms in eq 3 amount to less than 6% in all cases. All values of $D_\lambda - D_\pi$ and $D_\beta - D_\lambda$ quoted in this paper are, however, the full values.
(13) This argument is double edged; in eq 5, $\delta J_{\sigma\sigma} > 0$ and the electron release by CH_3 to the carbonyl carbon would facilitate CO_π polarization toward oxygen; both effects tend to favor the λ structure.
(14) This result is contrary to that reported earlier[3] for CH_3CHOH^+; we have found that an error in CH_3 hydrogen coordinates is responsible for the difference.
(15) This result is unlike those, e.g., of C_6H_6[9] and B_5H_9[16] for which the final LMO approximates one, rather than a hybrid, of the several symmetry-equivalent resonance structures. Here the resonance structures are nonequivalent and localization might have been expected to converge more cleanly on just one such structure, as was found to be the case for B_5H_{11}.[16]
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