The Electronic Structure of Reactive Intermediates. Carbonylnitrenes

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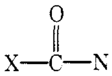
Abstract: An a priori theoretical study of the electronic structure of the carbonylnitrenes XC(O)N (X = H, F, CH_3, and OCH_3) has been carried out. The ground state for all substituents is a triplet with the next two states being closely spaced singlets. In our best calculation on HCON these singlets are approximately 35 kcal above the triplet.

This study is concerned with the electronic structure of a class of carbonylnitrenes[2]

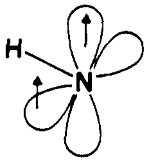


$$X-\overset{\overset{\displaystyle O}{\|}}{C}-N$$

where X is H, F, CH_3, and OCH_3. We are interested in the ground state multiplicity and charge distribution as well as the relative energies of the low lying excited states as a function of the substituent X.

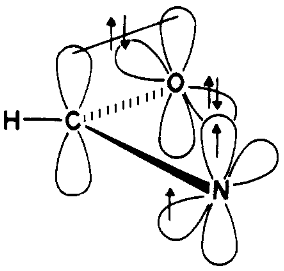
A. Formylnitrene

The parent nitrene, imidogen, is a ground state triplet[3] ($^3\Sigma^-$) with the schematic representation



(1)

where we suppress displaying the "lone pair" on the N. We expect the formylnitrene ground state to resemble



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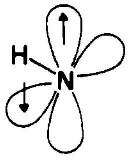
where we display the carbonyl π orbital (π_{co}), the oxygen lone pair orbital (σ_o), as well as the nitrogen orbitals σ_N (in plane orbital) and p_N (perpendicular to the molecular plane). In C_s symmetry this is a $^3A''$ state, i.e., odd upon reflection in the molecular plane. Since the first excited state[3] of imidogen is $^1\Delta$ with the two degenerate components



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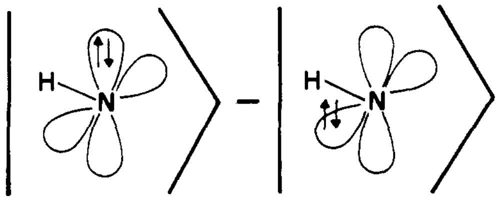

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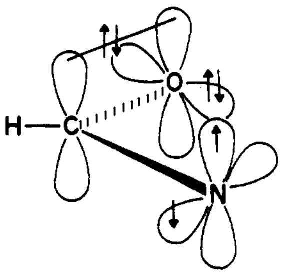
we anticipate a pair of formylnitrene states with the structures



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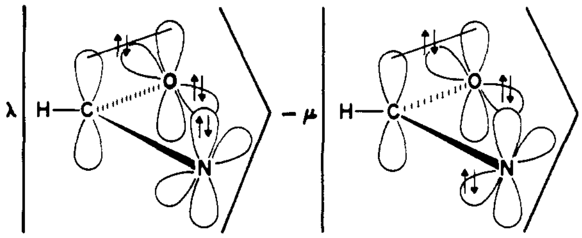

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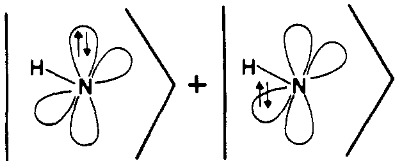
The former structure corresponds to a $^1A''$ state while the latter is a $^1A'$ (does not change sign upon reflection in the molecular plane). The deviation of the ratio λ/μ from unity (λ, $\mu > 0$) is, of course, a measure of the spatial bias introduced by the noncylindrically symmetric formyl group.

Then, corresponding to the second excited level of imidogen, the $^1\Sigma^+$ state



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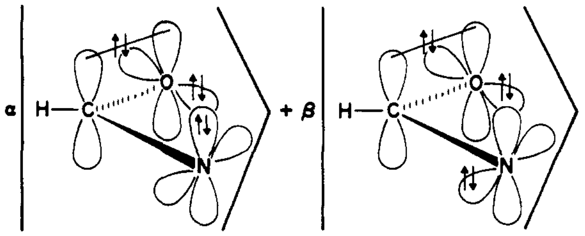
we expect



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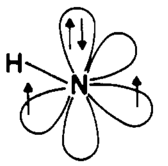
i.e., the second state of $^1A'$ symmetry which we will designate as $^1A'^*$. As in the companion $^1A'$ state, α and β measure the spatial bias of the formyl group. In imidogen the lowest excited triplet[3] state is $^3\pi$ and results when a nitrogen lone pair electron (mostly 2s) is excited into one of the π orbitals



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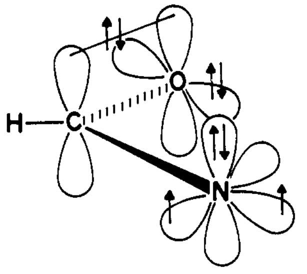
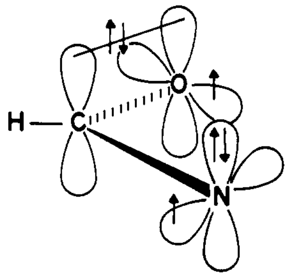
The corresponding state in formylnitrene is



(10)

However, an additional triplet corresponding to



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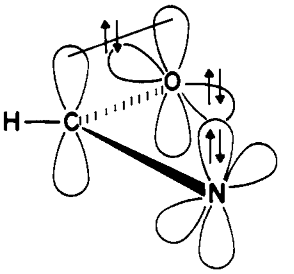
also seems possible and the lowest $^3A'$ state is expected to be a linear combination of these two structures.

Wave Function Construction. We used the STO-3G basis of Hehre, Stewart, and Pople[4] with their recommended exponents and solved the Hartree-Fock-Roothaan equations for the configuration



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This resulted in 16 molecular orbitals (13σ and 3π) of which nine σ and two π are doubly occupied. The three π orbitals are easily identified as π_{CO}, p_N and $\pi_{CO}{}^*$. Within the σ orbitals, σ_O is the highest occupied while σ_N is the lowest empty. That the σ_N orbital is empty is a manifestation of the shortcoming of a single determinant representation of the wave function and will be modified in the configuration interaction phase of our study. We then assume that an adequate representation of the low lying states of formylnitrene can be obtained by maintaining the lowest 8σ orbitals doubly occupied and alloting the remaining six electrons in all possible ways among the π_{CO}, p_N, $\pi_{CO}{}^*$, σ_O, and σ_N orbitals. This results in 52 structures of A′ symmetry and 48 of A″.

Some Results. The bond lengths and angles of formylnitrene in several low lying electronic states are presented in Figure 1 and the corresponding energy differences in Figure 2. The geometry was optimized by minimizing the total energy using the 52 structure representation of the A′ state and the 48 structure representation of the A″ states. The geometries of the $^3A'$ and $^1A'{}^*$ states were not optimized and the reported energy for these two states corresponds to the geometry of the $^1A'$ state.

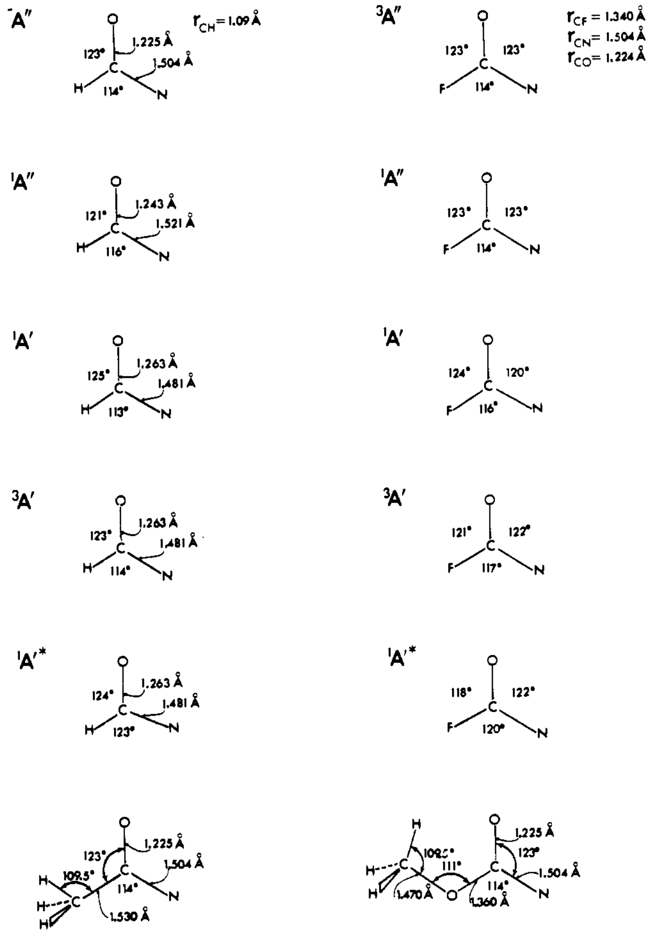


Figure 1. Structural data on the carbonylnitrenes studied.

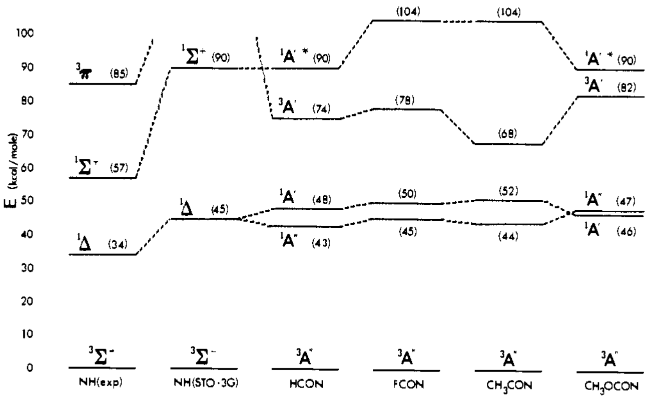


Figure 2. Comparison of the computed energy level patterns (STO-3G level) of various carbonylnitrenes.

Figure 2 compares the formylnitrene energy level patterns with that computed for NH in the same basis. In the virtual orbital approximation $E(^1\Delta) = E(^3\Sigma^-) + 2K_{XY}$ and $E(^1\Sigma^+) = E(^3\Sigma^-) + 4K_{XY}$ where K_{XY}, the exchange integral between the π_X and π_Y orbitals on N, was computed to be 22 kcal/mol. The experimental separations[3a] are also plotted. Note that while the $^3\Sigma^- \leftarrow {}^1\Delta$ separation is not known experimentally, a recent estimate[3b] which reproduces the experimental $^1\Delta \leftarrow {}^1\Sigma^+$ separation of 24 kcal/mol suggests a singlet-triplet separation of 34 kcal/mol. This comparison indicates that our estimates of the $^1\Delta \leftarrow {}^3\Sigma^-$ and $^1\Sigma^+ \leftarrow {}^3\Sigma^-$ separations are too high by 25% and at least 35%, respectively. This is not unexpected in an STO-3G basis and emphasizes the caution which should be brought to the interpretation of minimal basis set studies.

Table I. Natural Orbital Occupations in the Three Lowest States of XCON

	$^3A''$				$^1A''$				$^1A'$			
	H	F	CH_3	OCH_3	H	F	CH_3	OCH_3	H	F	CH_3	CH_3O
σ_N	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.746	0.509	0.467	0.673
p_N	1.000	1.003	1.001	1.002	1.001	1.005	1.004	1.002	1.256	1.492	1.527	1.334
σ_O	1.999	2.000	2.000	2.000	2.000	2.000	2.000	2.000	1.993	1.973	1.999	1.988
π_{CO}	1.867	1.881	1.878	1.902	1.836	1.871	1.867	1.905	1.867	1.923	1.916	1.914
π_{CO}^*	0.131	0.117	0.121	0.098	0.164	0.125	0.130	0.096	0.139	0.104	0.095	0.096

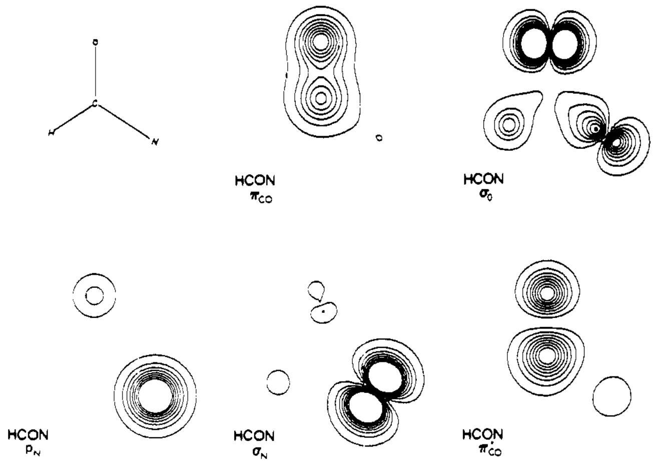


Figure 3. Contour maps of the electron density associated with selected natural orbitals of HCON.

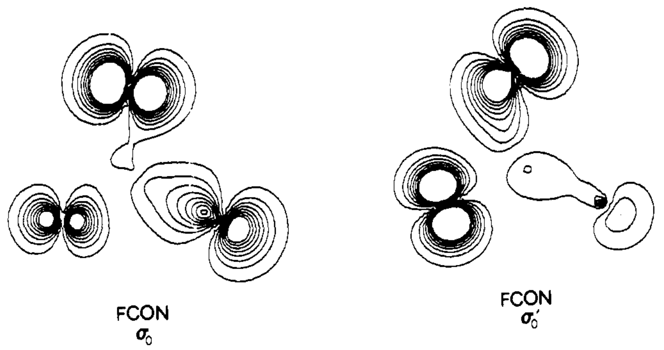
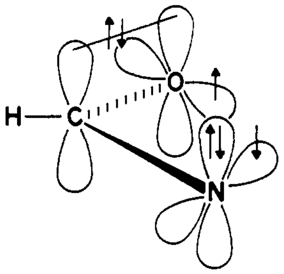


Figure 4. Contour maps of the electron density associated with the two choices for the σ_O orbital in FCON.

With this qualification we note the remarkable coincidence of the computed energy level pattern of NH and HCON and the small splitting between the two states of HCON which trace their lineage to the $^1\Delta$ state of NH.

Since in N-H the $^3\pi$ state is higher than the $^1\Sigma^+$ it is noteworthy that in formylnitrene the $^3A'$ is below the $^1A'^*$. This is most likely a consequence of the increased stability of the HCNO π system. The singlet state associated with this $^3A'$ state would correspond to



(13)

and exhibits the potential for an N-O single bond. The geometry of this state would be quite different from the $^3A''$, $^1A''$, and $^1A'$ states, which we have optimized, and we did not pursue it.

In order to discuss the charge distribution in the various states we diagonalized the first-order density matrix[5] for each CI function and obtained the natural orbitals, ϕ_i, and their occupation number, n_i. Recall that in the natural orbital representation the electron density at a point $\mathbf{R}$ is given by

$$\rho(\mathbf{R}) = \Sigma n_i \phi_i^2(\mathbf{R})$$

Since we keep the first 8σ MO's doubly occupied they are not modified when we diagonalize the density matrix and may be regarded as natural orbitals with an occupation number of 2. In Table I we present the occupation numbers of the remaining natural orbitals and display in Figure 3 the corresponding contour plots for several of the ground $^3A''$ natural orbitals. On the scale plotted, the NO's for the states $^1A''$ and $^1A'$ are essentially indistinguishable from these. Most striking is the extent of the localization of σ_N and p_N on N and π_{CO} and π_{CO}^* in the carbonyl region. Interestingly Figure 3 shows the major nonoxygen contribution to the σ_O orbital is the nitrogen lone pair.

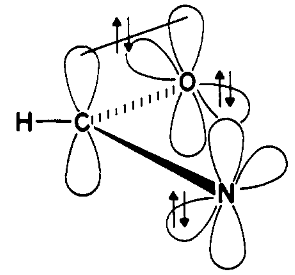
From Table I we note that

$$\eta(\pi_{CO}) + \eta(\pi_{CO}^*) = 2.00$$

and

$$\eta(\sigma_N) + \eta(p_N) = 2.00$$

in the $^3A''$, $^1A''$, and $^1A'$ states indicating little charge transfer between the N atom and formyl groups. Also, while the electron distribution around N in $^3A''$ and $^1A''$ is cylindrically symmetric there is an asymmetry approaching 2 to 1 in the p_N, σ_N occupancy of the $^1A'$ state, reflecting the lower energy of the 4π electron component, eq 11, relative to the two π electron contributor.



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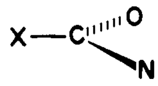
Interestingly, this intimate mixture results in the lowest $^1A'$ state hosting a resultant π system containing 3.26 electrons.

B. Other Carbonylnitrenes

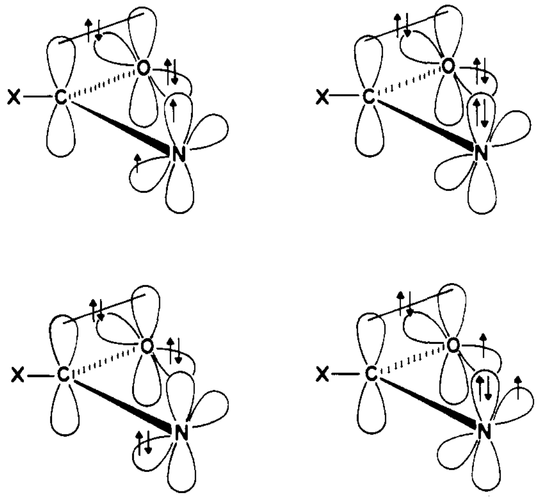
To determine the effect of substituents on the energy levels and orbital occupancies we generalized our study to the systems



where X is F, CH_3, and OCH_3.

As with formylnitrene we used an STO-3G atomic basis, constructed the Hartree-Fock-Roothaan solution for the $\pi_{co}{}^2\sigma_o{}^2p_N{}^2$ configuration, and used the resulting MO's in a subsequent configuration interaction study. The structure selection for the CI entailed much experimentation before the following compromise between expediency and accuracy was adopted.

We define four reference configurations



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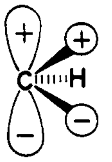
and consider all single and double excitations from each of these structures into orbitals of the set π_{co}, p_N, $\pi_{co}{}^*$, π_x, σ_o, and σ_N. For F, π_x is simply the fluorine p_π orbital. For OCH_3, it is the oxygen p_π orbital, while for CH_3 it is the orbital represented by



σ_N is easily identified in all three molecules but σ_o is localized (to the extent that it was in HCNO) only in $CH_3C(O)N$. In the F and OCH_3 substituted cases, two orbitals qualify as σ_o: the in-phase and out-of-phase combinations of the carbonyl oxygen lone pair with the F and methoxy oxygen plane lone pair, respectively. Figure 4 displays these orbitals for the F case. In these cases we used both orbitals in constructing the various structures.

The geometry of FCON was fixed at the computed geometry of the $^3A''$ state of HCON and the C-F bond length was optimized in the $^3A''$ state. These bond lengths were then fixed and the angles in the lowest three states, $^3A''$, $^1A''$, and $^1A'$, were determined. The results are displayed in Figure 1 and are quite similar to those for HCNO. The geometries used for CH_3CNO and CH_3OCNO (Figure 1) are composites from our optimized HCNO and standard methyl and methoxy structures.

Figure 2 compares the computed energy level patterns for the carbonylnitrenes with one another. The various carbonylnitrenes studied all have triplet ground states and small energy separation (~10 kcal/mol) between the first two singlet states, and they should exhibit a triplet-triplet transition ($^3A' \leftarrow {}^3A''$) at a lower energy than the $^3\pi \leftarrow {}^3\Sigma^-$ transition of NH.

Detailed analysis of the electron distribution as reflected in the natural orbital occupation reveals an insensitivity to the nature of the substituent in the $^3A''$ and $^1A''$ states. As in formylnitrene the σ_N and p_N each host 1 electron, the σ_o hosts 2, and the π_{co} and $\pi_{co}{}^*$, collectively, contain 2. Again, as in formylnitrene, the $^1A'$ state seems to be the most interesting. The natural orbital occupations for this state (Table I) reflect the enhanced p/σ bias as H is replaced by substituents with more structure. Once again, however, these numbers indicate that little charge transfer has taken place between N and XC(O)-. Our calculations suggest that discrete alkyl- or alkoxylnitrenes in either the ground triplet or first two singlet states would not have an empty orbital on nitrogen and would not easily rearrange to the corresponding isocyanate.

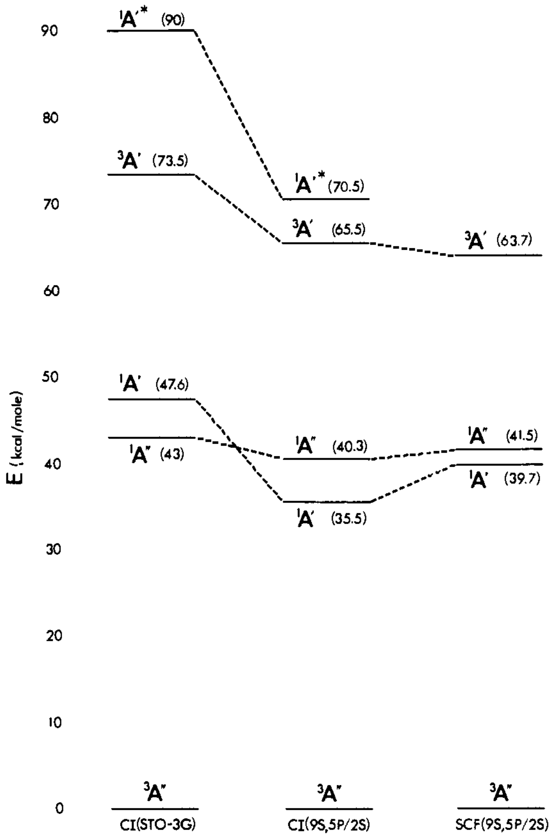


Figure 5. Effect of basis set size and configuration selection on the energy level pattern in HCON.

C. Formylnitrene. In a More Flexible Basis

The similarity of the energy level patterns and electron distribution among the various carbonylnitrenes suggests that the electronic structure of formylnitrene might be representative of the class of alkanoyl- and alkoxynitrenes. With this motivation we undertook a more elaborate ab initio study of formylnitrene.

We selected the Dunning[6] [3s,2p/2s] contraction of Huzinaga's[7] (9s,5p/4s) basis, and constructed the solution to the restricted open shell SCF[8,9] equations for the $^3A''$ and $^3A'$ states and the closed shell equations for the $^1A'$ state, all at the equilibrium geometry of the $^3A''$ state of HCNO (determined previously with the STO-3G basis).

The molecular orbitals of the $^1A'$ state, obtained with the closed shell SCF technique, did not seem especially suitable for a small CI study of this state. Specifically, not having the σ_N occupied resulted in a set of virtual σ orbitals which were much too diffuse. To correct this we wrote

$$\psi(^1A') = c_0|p_N{}^2\rangle + c_1|\sigma_N{}^2\rangle + \sum_{i=2} c_i|\sigma_N\sigma_i\rangle$$

where $|p_N{}^2\rangle = \mathfrak{a}(\text{core})^2 p_N\alpha p_N\beta$, etc. We determined the c_i's variationally, constructed the natural orbitals, and used the resulting NO's as input for another cycle (the iterative natural orbital technique[5,10]). The natural orbitals of this second iteration were taken as appropriate starting orbitals for a more extensive CI.

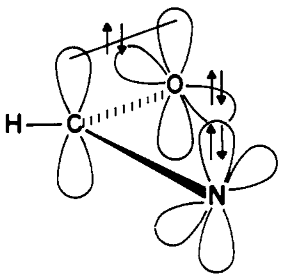
The "SCF" energies are indicated in Figure 5. We list as the SCF energy of the $^1A''$ state the energy of $^3A''$ plus twice the appropriate exchange integral (computed with $^3A''$ orbitals). For the $^1A'$ state we take the two by two CI result using the configurations $|p_N{}^2)$ and $|\sigma_N{}^2>$ with the orbitals as determined by the INO technique described previously.

To construct the final CI function for each of the four states we reduced the number of orbitals from 29 to 22 by eliminating highly antibonding functions localized on a single center while maintaining the first three orbitals doubly occupied. We then generated all configurations for the first order wave function,[5,11] ordered them on the basis of a two by two CI with the "SCF" structure, and selected the best 100 (spin and symmetry adapted) structures. The resulting energies are displayed in Figure 5 along with the corresponding STO-3G results.

Note that although the total energy in the more elaborate basis is more than two atomic units (~1250 kcal/mol) lower that that computed in the STO-3G basis the relative separations are only slightly affected. In going from the SCF to the CI the energy level pattern remains the same, the relative separation changing very little. Further a detailed analysis of the natural orbitals substantiates our minimal basis set conclusions presented previously, the main exception being the occupancies of the σ_N and p_N orbitals in the $^1A'$ state. In this calculation these orbitals host 0.61 and 1.38 electrons, respectively, while our previous result was 0.74 and 1.26. Although it increased the asymmetry in the N charge distribution this result concurs with the minimal basis in predicting a significant σ_N occupancy in this state.

Previous Work

The only previous study which we are aware of is by Alewood, Kazmaier and Rauk[12] who studied HCNO, CH_3CNO, and OHCNO using a minimal basis of Slater orbitals and assuming the geometry of the nitrene was that of the corresponding amide. They constructed the molecular orbitals for the configuration corresponding to



and estimated the energies of various excited states within the virtual orbital approximation.

Although we prefer a larger S-T separation we concur with their conclusion that HCON and CH_3CON have triplet ground states (they estimate by 15 and 12 kcal/mol, respectively). While we have not studied HOCON, which they predict to have a singlet ground state, some 23 kcal/mol below the triplet, our prediction that CH_3OCON should possess a triplet ground state would seem to be at variance with their result.

We believe the differences in the predictions of the two calculations are a result of Alewood, Kazmaier, Rauk's use of the virtual orbital approximation which leads to less than an optimal description of the various electronic states.

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Linear Dichroic Spectra and Fluorescence Polarization of Biliverdin

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Abstract: The ratio of the oscillator strengths of the near uv (Soret) and visible band of biliverdin is 3.2. The angle between the transition moments of these two bands, which are assigned to $S_4 \leftarrow S_0$ (analog of $B_x \leftarrow A$ in porphyrins) and $S_1 \leftarrow S_0$ (analog of $Q_y \leftarrow A$ in porphyrins) transitions, respectively, is estimated to be 68° from PVA linear dichroism and approximately 55-60° from fluorescence polarization measurements. These values are consistent with the theoretically predicted angle of 56° (SCF-MO-CI PPP data). Analysis of these data suggests that the likely conformation of the π-electron system is neither fully linear nor circular as in the case of porphyrin.

The bile pigment, biliverdin, is spectroscopically interesting because its structure and absorption spectra are similar to the P_{fr} form of the plant photoreceptor pigment, phytochrome. Furthermore, analysis of the electronic spectrum of biliverdin is of theoretical interest in ascertaining the effect of opening of the cyclic polyene ring on porphyrin spectra. In order to analyze the absorption spectrum of biliverdin we have utilized linear dichroism and fluorescence po-