

An ab Initio Study of the Electronic Structure of the Ground Triplet and Low-Lying Singlet States of Formylnitrene, HCON, and Formylphosphinidene, HCOP

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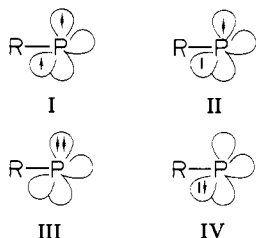
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Abstract: We have studied the electronic structure of the nitrene HCON and phosphinidene HCOP by using SCF and GVB wave functions. In both cases the ground state is ³A'' while the first two excited states are ¹A' and ¹A''. These excited states are calculated to be 36.8 and 39.0 kcal/mol above the triplet in HCON and 26.8 and 27.9 kcal/mol above the triplet in HCOP. In each of the states studied we find very little conjugation between the formyl group and the N or P atom.

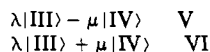
Introduction

Phosphinidenes^{2a} are compounds of the form R-P where the phosphorous atom is, at least formally, monovalent. They are the second-row analogues of the nitrenes,^{2b,3} R-N, and one expects that for every nitrene there should be an isovalent phosphinidene. Unlike the nitrenes, however, virtually nothing is known about the phosphinidenes with the exception of the parent compound,^{2c} P-H. This paper contrasts the electronic structure of the parent carbonylnitrene, HCON, and the as yet uncharacterized carbonylphosphinidene, HCOP. Previous work^{4,5} has shown that the electronic structure of the carbonylnitrenes R-C(=O)-N is insensitive to the substituent R and therefore the simplest carbonylnitrene, H-C(=O)-N, serves well as a model for the entire class. We assume this situation obtains with the carbonylphosphinidenes and that formylphosphinidene will be representative of the entire class of carbonyl compounds, R-C(=O)-P.

If we form R-P from R-PH₂ by removing two H atoms, we expect to have two nonbonding electrons left on P and we may allocate them in four different ways to the available phosphorous 3p orbitals. Schematically we have structures I-IV. We expect



I (the triplet) to be the ground state and II, III, and IV to be excited singlets. Further, structures III and IV will interact very strongly, and they are more realistically taken as the linear combinations V and VI.



In P-H, for example, structure I corresponds to the ground ³Σ⁻ state, II and V (with λ = μ = (1/2)^{1/2}) to the ¹Δ state, and VI to the ¹Σ⁺ state. The extent to which R is not cylindrically symmetric is measured by the deviation of λ and μ from (1/2)^{1/2}. Identical arguments⁴ may be made for R-N.

Computational Details

The fundamental expansion basis was Huzinagas⁶ 9s, 5p for O, N, and C, his 11s, 6p for P, and his 4s for H. These were contracted, according to Raffanetti,⁷ to 3s, 2p for O, N, and C, 4s, 3p for P, and 2s for H. The hydrogen functions were scaled by 1.2. This procedure results in an expansion basis of 29 and 33 orbitals for HCON and HCOP, respectively. When this double-ζ (DZ) level basis was augmented by a single component p orbital (exponent = 1.0) on the H and a single component d orbital on all other atoms (with exponents of 0.85 (O), 0.80 (N), 0.75 (C), and 0.55 (P)), the expansion basis contains 50 and 54 functions for HCON and HCOP, respectively, and will be referred to as the DZP basis.

The integrals were evaluated with the BIGGMOLI⁸ system, and all triplet SCF wave functions were constructed with POLYATOM.⁹ The various singlet wave functions were constructed with the GVB TWO¹⁰ code.

The Triplet State

The ³A'' state of HCON corresponds to the electronic configuration in which 19 electrons are in molecular orbitals of a' symmetry (symmetric with respect to the molecular plane) and 3 electrons are in a'' orbitals (these have a node in the molecular plane). In the corresponding ³A'' state of HCOP there are 25 electrons in a' orbitals and 5 in a'' orbitals. In both cases we will represent the highest a' orbital as σ and the highest a'' as π. Suppressing all but these two orbitals, we may represent the ³A'' state (structure I) as in eq 1.

$$|^3A''\rangle = |\sigma\pi\alpha\alpha\rangle \quad (1)$$

We constrained both molecules to be planar, fixed the C-H distance at 1.09 Å, and optimized the remaining geometry at the restricted open-shell level by using the double-ζ basis. The resulting geometries for the ³A'' ground state are shown in Figure 1 where we also display several relevant formamide structures from a previous ab initio study by Christensen¹¹ et al. These authors fixed the various angles and C-H and N-H bond lengths in formamide at the experimental values of Costain and Dowling (Figure 1c)^{12a} and optimized the CO and CN bond lengths at the

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(8) Richard C. Raffanetti, BIGGMOLI, Program 328, Quantum Chemistry Program Exchange, Indiana University.

(9) D. B. Neumann, H. Basch, R. L. Kornegoy, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann, POLYATOM (Version 2), Program 199, Quantum Chemistry Program Exchange, Indiana University.

(10) The GVB TWO code was written by F. W. Bobrowicz and modified by S. P. Walch to make use of BIGGMOLI Integral files and was used at the Argonne National Laboratory.

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(12) (a) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960); (b) E. Hirota, R. Sugisaki, C. J. Nielsen, and G. O. Sorensen, *J. Mol. Spectrosc.*, **49**, 251 (1974).

(1) On leave from the Chemistry Department, University of Athens, Athens, Greece.

(2) (a) U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **14**, 523 (1975); (b) P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 649 (1967); (c) P. E. Cade, *Can. J. Phys.*, **46**, 1989 (1968).

(3) W. Luowski, Ed., "Nitrenes", Wiley-Interscience, New York 1970.

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(5) P. F. Alewood, P. M. Kazmaier, and A. Rauk, *J. Am. Chem. Soc.*, **95**, 5466 (1973).

Table I. Energies (hartrees) and Equilibrium Structural Parameters (Bond Lengths in Angstroms and Angles in Degrees) of HCON and HCOP Molecules

state and level of calculatn	HCON					HCOP				
	$-E$	R_{C-N}	R_{C-O}	$\angle HCO$	$\angle HCN$	$-E$	R_{C-P}	R_{C-O}	$\angle HCO$	$\angle HCP$
$ ^3A''\rangle$ DZ	167.633811	1.447	1.214	122.0	116.4	453.922407	1.889	1.222	119.0	119.3
$ ^3A''\rangle$ DZP	167.716445	1.447	1.214	122.0	116.4	453.999732	1.889	1.222	119.0	119.3
$ ^1A'\rangle$ DZP	167.654352	1.447	1.214	122.0	116.4	453.955322	1.889	1.222	119.0	119.3
$ ^1A'\rangle$ DZ-GVB ^a	167.571198	1.405	1.222 ^b	120.0 ^c	120.0 ^c	453.878543	1.864	1.228 ^b	120.0 ^c	120.0 ^c
$ ^1A'\rangle$ DZP-GVB ^a	167.657847	1.405	1.222 ^b	120.0 ^c	120.0 ^c	453.957002	1.864	1.228 ^b	120.0 ^c	120.0 ^c

^a $|^1A'\rangle$ DZ-GVB = $0.49|^1A', \sigma^2\rangle - 0.87|^1A', \pi^2\rangle$ and $|^1A'\rangle$ DZP-GVB = $0.45|^1A', \sigma^2\rangle - 0.89|^1A', \pi^2\rangle$ for HCON and $|^1A'\rangle$ DZ-GVB = $0.54|^1A', \sigma^2\rangle - 0.84|^1A', \pi^2\rangle$ and $|^1A'\rangle$ DZP-GVB = $0.51|^1A', \sigma^2\rangle - 0.85|^1A', \pi^2\rangle$ for HCOP. ^b These values were obtained by weighting the equilibrium R_{C-O} values of SCF $|^1A', \sigma^2\rangle$ and $|^1A', \pi^2\rangle$ states with the squares of the corresponding DZ-GVB coefficients cited in *a*. ^c Assumed.

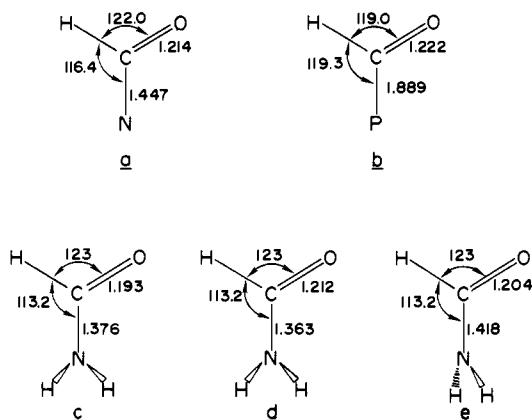


Figure 1. (a) Calculated geometry of the triplet nitrene. (b) Calculated geometry of the triplet phosphinidene. (c) Experimental geometry of formamide from ref 12. (d) Optimal CO and CN bond lengths in SCF theory (other experimental parameters held at experimental values) from ref 11. (e) Optimal CO and CN bond lengths in SCF theory when the plane of the formyl group bisects the NH_2 group, from ref 11. (All distances are in angstroms and angles in degrees.)

single determinant SCF level with an extended basis set. The results are shown in Figure 1d and suggest that within the SCF approximation the CO bond length is slightly larger than the experimental one while the converse is true for the CN linkage. Interestingly, these SCF determined bond lengths agree more closely with the most recent experimental determination^{12b} (CO = 1.21 Å, CN = 1.35 Å) than with the experimental values^{12a} in use at the time of Christensen's¹¹ calculation. More important for our purposes is the result obtained by Christensen et al. when they rotated the NH_2 group around the CN bond until the formyl group bisected the NH_2 angle. The optimal CO and CN bond lengths are shown in Figure 1e. We interpret the decrease in the CO bond length (0.008 Å) and the increase in the CN bond length (0.055 Å) in going from d to e as a slight strengthening of the CO and a more significant weakening of the CN bond, due to the loss of the CN π -bonding component. Comparing our calculated formylnitrene structure 1a-d and -e suggests that the CN bond is essentially a single bond and that the formyl group is little changed from formamide. These results are in overall agreement with Rauk and Alewood,¹³ who found a CN distance of 1.481 Å and a CO distance of 1.263 Å. Although there are few data with which we may compare, our calculated phosphinidene structure seems intuitively sensible. In particular the calculated value of 1.89 Å for the CP bond length is comparable to the average experimental value¹⁴ of 1.84 ± 0.006 Å.

We assumed that the double- ζ geometry reported in Figure 1 was sufficiently accurate for our purposes and recomputed the $^3A''$ energy of both molecules at this geometry with the DZP basis. As can be seen from Table I, the polarization function results in a significant but similar energy lowering for both molecules (51.9

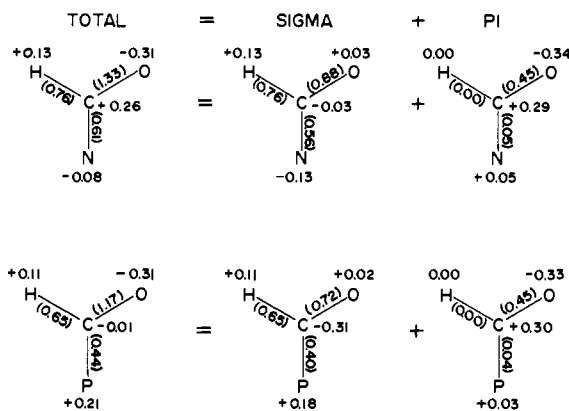


Figure 2. Mulliken population analysis of $^3A''$ states of HCON and HCOP. Numbers in parentheses are overlap populations.

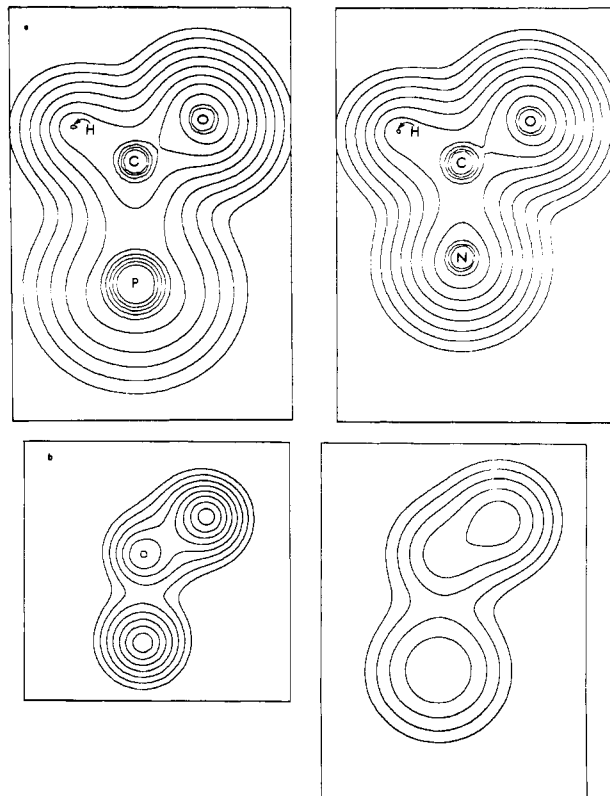


Figure 3. (a) Total electron density in molecular plane contours displayed are 3.2, 1.6, 0.8, 0.4, 0.2, 0.1, 0.05, 0.025, 0.0125, 0.00625 electron/au³. The frame is 8×12 au. (b) Total π -electron density for HCON (0.4 au above the molecular plane) and HCOP (1.4 au above the molecular plane). The HCON frame on the left is 8×8 au, while the HCOP frame is 8×10.5 au. All contours are in electrons/au³ and include 0.003125, 0.00625, 0.0125, 0.025, 0.05, 0.10, 0.20 and 0.40.

kcal/mol for HCON and 48.5 kcal/mol for HCOP). d polarization functions seem as equally important for the HCON

(13) A. Rauk and P. F. Alewood, *Can. J. Chem.*, **55**, 1498, (1977).

(14) Exp. P-C bond lengths from D. E. C. Corbridge in "Topics in Phosphorus Chemistry", Vol. III, M. Grayson and E. J. Griffith, Eds., Interscience, New York, 1966, p 57.

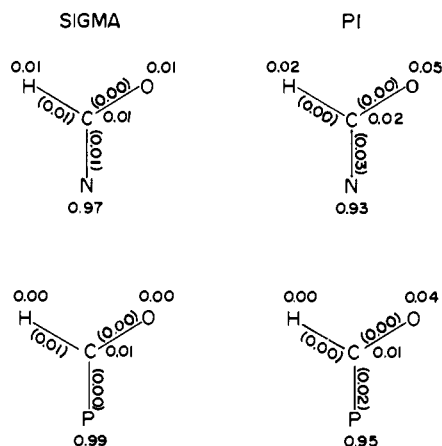


Figure 4. Mulliken population analysis of σ and π orbitals of $^3A''$ states of HCON and HCOP.

molecule (containing all first row atoms) as for the phosphinidene HCOP. Bear in mind, however, that the d exponents have not been optimized in the molecular environment. A Mulliken population analysis¹⁵ for both molecules in the DZP basis results in the charge distribution shown in Figure 2 and contoured in Figure 3. Several features of this distribution warrant comment. The first and perhaps most striking is the opposite polarity of the CN and CP bonds and the apparent conversion of the strongly electrophilic carbon in HCON to a neutral or even slightly nucleophilic carbon in HCOP. Insight into the origin of this change in polarity is readily acquired by partitioning the total charge hosted by the various atoms into their σ and π contributions. From Figure 2 we see that the charge distribution within the π system of both molecules is remarkably similar and the difference between the CN and CP bond polarities arises from charge transferred through the σ system. Not only are the π systems of these molecules similar in so far as the atomic charges are concerned but also the π overlap populations are identical and indicate that in both molecules there is little π bonding in either the CN or CP bonds. Indeed, if we take our computed CO π overlap population of 0.45 as being representative of a heteronuclear π bond, then our calculations suggest that the CN and CP bonds have approximately 10% " π character". This small π character is consistent with the long (relative to formamide) CN bond length found for this molecule. The similarity of the π orbitals in the CO region of both molecules and the lack of a significant π interaction in CP and CN is also apparent in the contours of the π -electron density presented in Figure 3b.

Finally, the spatial distribution of the two unpaired electrons in each molecule shown in Figure 4 indicates that these electrons are essentially localized on the N and P atoms in spite of the large difference in the polarity of the host atom. This localization is confirmed in the contour plots shown in Figure 5.

The Singlet States

The singlet states corresponding to II, V, and VI are

$$|^1A''\rangle = |\sigma\pi(\alpha\beta - \beta\alpha)/\sqrt{2}\rangle \quad (2)$$

$$|^1A'\rangle = \lambda|\sigma^2\rangle - \mu|\pi^2\rangle \quad (3)$$

$$|^1A'\rangle^* = \lambda|\sigma^2\rangle + \mu|\pi^2\rangle \quad (4)$$

The localized nature of the σ and π orbitals in the $^3A''$ states and previous studies⁴ suggest that

$$E(^1A'') \approx E(^1A')$$

and

$$E(^1A')^* > E(^1A')$$

Consequently, in the following we will consider only the structure of the $^1A''$ and $^1A'$ states, leaving the higher energy $^1A'^*$ for another study.

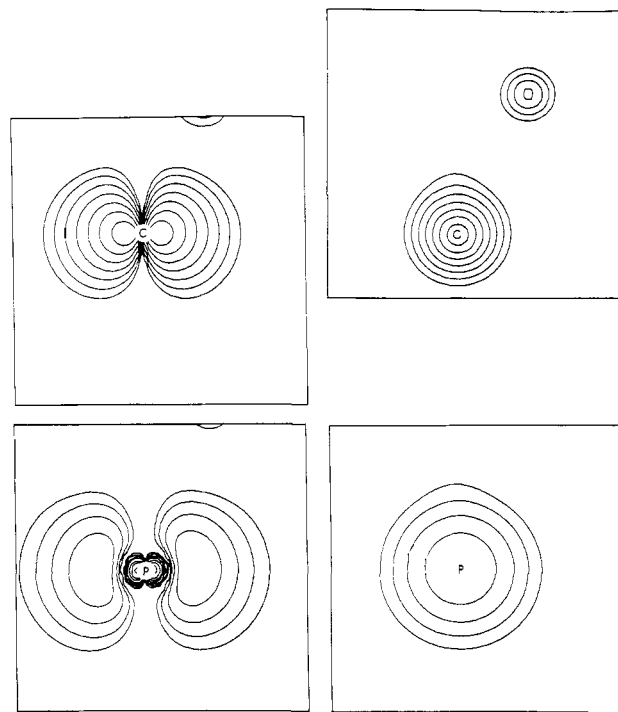


Figure 5. Electron density for the σ and π orbitals of HCON (top) and HCOP. Frames are 8×8 au. Contours are as in Figure 3b. The σ density is in the molecular plane, the HCON π is 0.4 au, while the HCOP π is 1.4 au above the molecular plane.

The open-shell singlet $^1A''$ was assumed to have a geometry similar to its companion, the $^3A''$ state, and no geometrical optimization was attempted. The energy of the $^1A''$ state of both HCON and HCOP was computed with the DZP basis and is reported in Table I. The charge distribution and molecular orbitals in this state are essentially identical with those of the previously discussed $^3A''$ state and will not be presented.

In constructing the wave functions for the closed-shell singlet, $^1A'$, we slightly idealized the molecular geometry by constraining the molecule to be planar and taking all angles as 120° . As before the CH bond length was fixed at 1.09 Å while the CO bond lengths were determined by taking the average of the optimum values obtained from singlet determinant restricted SCF calculations in a DZ basis for the two $^1A'$ states for each molecule; these are 2.310 and 2.320 au for HCON and HCOP, respectively. Although these selections are not optimal, we feel that they are more than adequate for calculations at this level. We then determined the optimal values for the CN and CP bond lengths by using a DZ basis and (3) as the wave function ansatz. Keep in mind that all of the orbitals and both mixing coefficients λ and μ were simultaneously optimized. The CN and CP bond lengths are reported in Table I and in each case are slightly smaller than their optimal values in the corresponding $^3A''$ state. In addition our calculated CN bond length is also smaller than the optimized STO-3G result of Poppinger et al.¹⁶ Adding polarization functions to both molecules and recomputing the energy at the double- ζ geometry lowers the energy of HCON by 53.9 and 49.2 kcal/mol for HCOP. This is essentially the same as the energy lowering observed in the $^3A''$ state under the same circumstances and means that the singlet-triplet separation in both the DZ and DZP basis will be very similar.

Figure 6 displays the results of a population analysis on the DZP wave function for the $^1A'$ state and indicates that the charge distribution is remarkably similar to that of the $^3A''$ state reported in Figure 2. The largest difference between this singlet and the triplet seems to be in the CN and CP overlap populations which we interpret as indicating slightly stronger CN and CP bonds in

(15) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(16) D. Poppinger, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 7806 (1977).

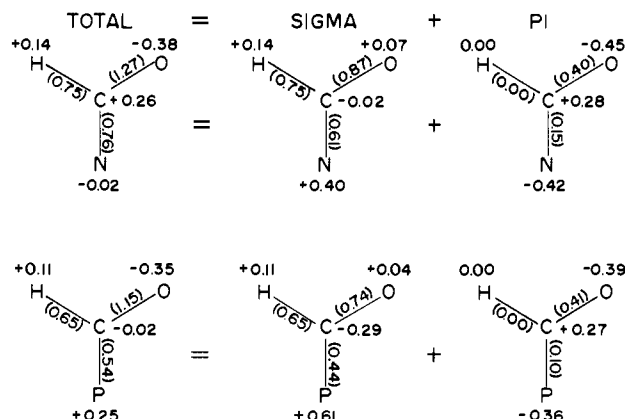


Figure 6. Mulliken population analysis of $^1A'$ states of HCON and HCOP. Numbers in parentheses are overlap populations.

the singlet state. Partitioning the charge and overlap populations into σ and π contributions shows that both increased by a comparable amount over their triplet values. Once again the similarity in the π system of both molecules is striking. Note however, that in order to partition the atomic charge between σ and π contributions, we had to assume a particular σ and π distribution in the noninteracting atoms. We chose to keep the distribution used in the $^3A''$ analysis, i.e., 1 electron each in the C, O, and N p_x orbitals and three in the P p_x orbitals. The large negative charge on the P and N in the π system then reflects the dominant contribution on the $|\pi^2\rangle$ configuration to the $^1A'$ function. Indeed, the strong mixing of $|\pi^2\rangle$ and $|\sigma^2\rangle$ in $^1A'$ results in the π system of HCON containing 3.60 electrons while HCOP hosts 5.48. This noninteger orbital occupancy is the price one pays for insisting on the most compact representation of this $^1A'$ state in terms of orthogonal orbitals. An alternate representation is possible. Since $|\sigma^2\rangle$ and $|\pi^2\rangle$ share the same core orbitals, we may write (3) as $^1A' = \lambda|\sigma^2\rangle - \mu|\pi^2\rangle = \text{Norm}|\chi\phi + \phi\chi\rangle$ where Norm is the normalization factor and the new orbitals

$$\chi = N(\sigma + (\mu/\lambda)^{1/2}\pi) \quad \phi = N(-\sigma + (\mu/\lambda)^{1/2}\pi) \\ N = (1 + \mu/\lambda)^{-1/2}$$

are nonorthogonal and have an overlap of

$$\langle\chi|\phi\rangle = (-1 + \mu/\lambda)/(1 + \mu/\lambda)$$

This corresponds to the cosine of the angle between these functions, and with use of the μ and λ values from Table I, we calculate the angle to be 70.9° for HCON and 75.3° for HCOP. These orbitals are contoured in Figure 7. This is of course the GVB form of the wave function as introduced by Goddard.¹⁷ The attractive feature of the GVB representation in this context is that the electronic configuration of this state for either molecule would be described as (core) $\chi^1\phi^1$ rather than (core) $\sigma^{0.40}\pi^{1.60}$ for HCON and (core) $\sigma^{0.52}\pi^{1.48}$ for HCOP.

Singlet-Triplet Separation

The calculated singlet-triplet separations are gathered in Figure 8 and compared with the calculations of Cade^{2c} on the parent monohydrides NH and PH. Cade's calculations are closer to the Hartree-Fock limit than ours, so it is most likely that the Hartree-Fock singlet-triplet separation in HCON and HCOP will be smaller than those in the parent hydride. Further since the σ and π orbitals in HCON and HCOP are localized on N and P, it is likely that the correlation energy difference between the $^3A''$ and $^1A''$ or $^1A'$ states will be adequately represented by the correlation energy difference between the $^3\Sigma^-$ and $^1\Delta$ states of NH and PH, respectively. Cade estimated this difference as 6.5

(17) W. A. Goddard, *Phys. Rev.*, **157**, 81 (1967); R. C. Ladner and W. A. Goddard, *J. Chem. Phys.*, **51**, 1073 (1969); *J. Am. Chem. Soc.*, **93**, 6750 (1971); W. J. Hunt, P. J. Hay, and W. A. Goddard, *J. Chem. Phys.*, **57**, 738 (1972). F. W. Bobrowicz and W. A. Goddard in "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum Press, New York, 1977.

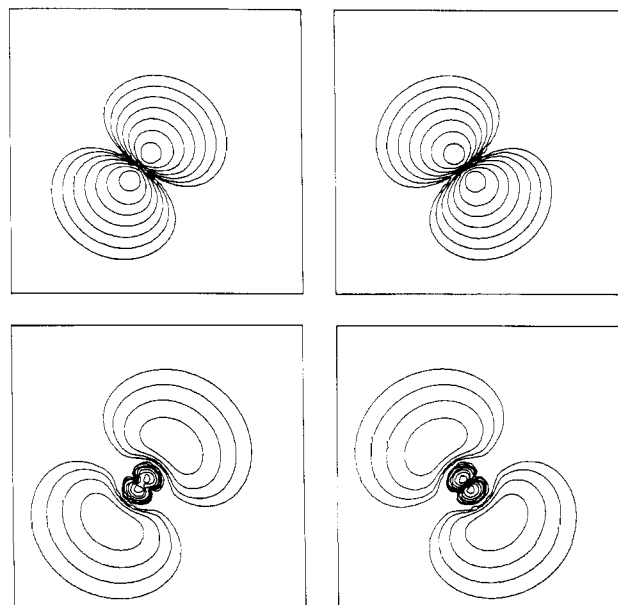


Figure 7. Electron density of GVB orbitals for HCON (top) and HCOP. Contours are as in Figure 3b. Frames are 8×8 au. Density is in the plane perpendicular to the CN or CP bonds and contains the N or P nucleus.

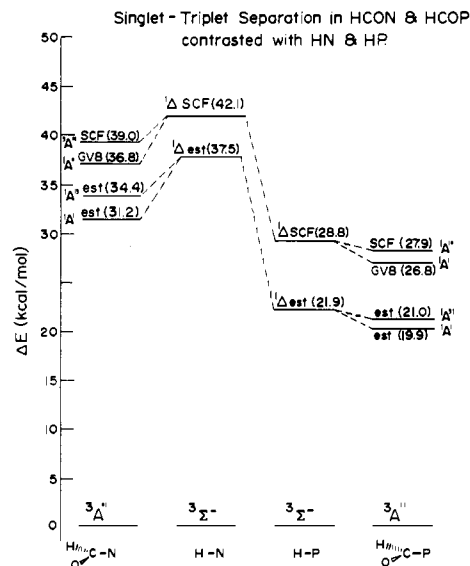


Figure 8. Singlet-triplet separation in HCON and HCOP contrasted with HN and HP.

kcal/mol for NH and 6.9 kcal/mol for PH. The energy levels predicted when this correction is applied to the $^1A''$ and $^1A'$ states are labeled as estimated in Figure 8.

Relative Stability of Various HCON Isomers

Out of many constitutional isomers which can be formed from the $4!/2 = 12$ "permutational" isomers obtained by permuting H, C, N, and O atoms, six are chemically important and can be rather well represented by classical valence bond graphs: H—O—C≡N (cyanic acid), H—N=C=O (isocyanic acid), H—C≡N→O (fulminic acid), H—O—N≡C (isofulminic acid), H—C(=O)—N (formyl nitrene), and H—C=N—O (oxazirene).

A comparison of the relative stabilities of the above six isomers is in order, and this is possible due to the recent work by Pople and co-workers¹⁶ as well as by McLean and co-workers.¹⁸ Although these two independent investigations show substantial

(18) A. D. McLean, G. H. Loew, and D. S. Berkowitz, *J. Mol. Spectrosc.*, **61**, 184 (1977).

Table II. Energies (hartrees) of Different Isomers Related to HCON

state	isomer	-E
$^1A'$	HNCO ^a	167.7003
$^1A'$	HOCN ^a	167.6701
$^3A''$	HCON ^b	167.6338
$^1A'$	HONC ^a	167.5833
$^1A'$	HCNO ^a	167.5814
$^1A'$	HCNO ^b	167.4995

^a Reference 17. ^b Present work.

agreement, we choose to make our comparison on the basis of the latter because our basis set and theirs are quite similar.

In order to better assess the quality of McLean's basis set as compared to ours, an SCF calculation was carried out on cyanic acid by using our DZ basis and the structural parameters given.¹⁸ An energy value of -167.6698 hartrees was obtained as compared to -167.6702 hartrees of McLean et al., indicating that energy comparisons at that level can be made safely. In addition, the ground-state energy of the oxazirene molecule was calculated at a DZ-SCF level by using the partially optimized geometry of Rauk and Alewood.¹³ Table II shows where formylnitrene, HCON, fits with respect to the rest of the isomers at a DZ-SCF level. Although all isomers, but HCON, are closed-shell singlets and going beyond the Hartree-Fock model would rather change the relative position of HCON in Table II, we believe that the latter corresponds to the lowest triplet state of all triplets which can be formed from the other isomers. This in turn suggests that by forming a triplet from one of the singlets of Table II, it would probably end on the triplet energy surface of HCON. Certainly, any dynamical effects are excluded from the above considerations.

Conclusions

The principal conclusions of this study are as follows: (1) Both the formylnitrene and the formylphosphinidene are ground-state triplets. (2) Both molecules have two very closely spaced excited singlets. (3) The singlet-triplet splitting in the formylphosphinidene is smaller than in the formylnitrene. (4) The CN and CP bonds are oppositely polarized. (5) In the ground triplet and two low-lying singlet states the CN and CP linkages are essentially single bonds. (6) The carbonyl moiety remains essentially unaltered in going from HCON to HCOP.

Finally, we note that since the $^3A''$ and $^1A'$ states have been represented by single determinant SCF functions and the $^1A'$ state by a pair of determinants, the possibility exists that the $^1A'$ may be more correlated than the two SCF functions, resulting in an imbalance in the calculated separations. In this context it is worth repeating that for R-N or R-P molecules with cylindrically symmetric R groups this level of calculation would result in the $^1A''$ and $^1A'$ states being degenerate components of the $^1\Delta$ state; i.e., they could be treated differently but equivalently. In the calculations we report the formyl group is essentially unconjugated with the N and P atoms, and consequently the σ and π orbitals (Figure 5) are essentially pure p orbitals on N and P. We expect therefore that any imbalance this treatment introduces would result in slight shifts (a few kilocalories) in the relative position of the reported levels. While this might alter the relative positions of the two singlets, perhaps even interchanging them, it would not change the above conclusions.

Acknowledgment. We thank R. Raffanetti for his help in redimensioning the QCPE version of BIGGMOLI and B. Botch and T. Dunning for their assistance and advice in the use of the Argonne version of the GVB TWO codes.

An ab Initio Study on Ketene, Hydroxyacetylene, Formylmethylene, Oxirene, and Their Rearrangement Paths

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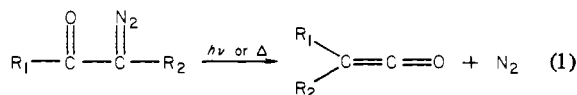
Contribution from the IBM Research Laboratory, San Jose, California 95193.

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Abstract: Ab initio quantum mechanical calculations on the singlet ground state of C_2H_2O have yielded geometries and rearrangement paths for ketene, hydroxyacetylene, formylmethylene, and oxirene. Geometries and rearrangement paths were determined by the single configuration self-consistent field method first by using the 4-31G basis set and then refined by using a double- ζ plus polarization basis set. Correlation energy corrections were calculated by using the configuration interaction method with a wave function which included all singly and doubly substituted configurations. The results show that hydroxyacetylene is 36 kcal/mol less stable than ketene, and there is a high barrier of 73 kcal/mol in the rearrangement path to ketene. Formylmethylene is unstable with respect to rearrangement to ketene, while oxirene is 82 kcal/mol above ketene with a small activation barrier of 2 kcal/mol for rearrangement to formylmethylene. These results together with preliminary results obtained for excited-state surfaces are used to elucidate the mechanism of the Wolff rearrangement. An analysis of the effects of polarization function and correlation energy on relative energy is also carried out to assess the accuracy of the results.

I. Introduction

The mechanism of the Wolff rearrangement of diazoketones (eq 1)^{1,2} has not been established unequivocally.^{3,5} Wolff ori-



ginally proposed that the rearrangement should proceed via ke-

tocarbene intermediates.¹ In recent years, however, experiments using isotope-labeled diazoketones have indicated that oxirene may also participate as short-lived intermediates in photochemical⁵ and thermal Wolff rearrangements.⁶ The participation of oxirene

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