Journal of the American Chemical Society / 101:5 / February 28, 1979

Effects of Electron Correlation on the Geometrical Structure of HCCN

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Received August 15, 1978

Abstract: The effects of electron correlation on the geometrical structure of ground-state triplet HCCN have been investigated by means of ab initio SCF and CI calculations. At both the double ζ SCF and CI levels of theory HCCN is predicted to be bent ($\theta_{\mathrm{HCC}} \sim 135°$), with linear geometries ~8.5 (SCF) or ~4.4 (CI) kcal/mol higher in energy. The present research indicates that ground-state triplet HCCN is best described as a bent cyanocarbene at both the SCF and CI levels of theory.

Introduction

Very recently, Harrison, Dendramis, and Leroi (HDL) have reported[2] quantum mechanical calculations that indicate a substantial difference in character between the SCF and CI potential energy surfaces of HCCN. Their results indicate that the ground-state triplet surface has a double minimum at the SCF level corresponding to *linear* nitrene ($\mathrm{H{-}C{\equiv}C{-}N{:}}$) and *bent* carbene ($\mathrm{H{-}\dot{C}{-}C{\equiv}N{:}}$) structures. Upon the inclusion of a modest amount of configuration interaction a *single* global minimum corresponding to a *linear* allene structure ($\mathrm{H{-}\dot{C}{=}\dot{C}{=}N{:}}$) was found. A difference of this magnitude between SCF and CI surfaces is almost unprecedented in quantum mechanical calculations. Here a search of the ab initio triplet SCF and CI surfaces for HCCN is reported with the conclusion that the unperturbed HCCN radical is probably nonlinear.

There is considerable uncertainty concerning the structure of the unstable free radical HCCN. Although there is general agreement that the electronic ground state is of triplet multiplicity, the weight of experimental evidence suggests a linear geometry, while theoretical work is divided between linear and bent geometries. Early observations of the ESR spectrum of HCCN by Bernheim[3] and Wasserman[4] led them to conclude that HCCN is a linear cyanocarbene. However, it is known[5] that free rotation of a bent radical about its long axis in a matrix may result in ESR zero-field splitting parameters normally characteristic of a linear molecule. Recently, Dendramis and Leroi[5] have reported the infrared spectra of various isotopically substituted forms of HCCN in an argon matrix. Frequency trends in the spectra and results of a normal-coordinate analysis using bent and linear geometries led them to conclude that HCCN is best described as a linear allene. They also report[5] the UV spectra of HCCN, in which a band system is found similar to that of the isoelectronic and linear $\mathrm{N{=}C{=}N}$ radical and thus supports a linear, allenic structure for HCCN.

The earliest theoretical study of HCCN was that of Hoffmann, Zeiss, and Van Dine,[6] using the extended Hückel method. The properties of numerous carbenes were computed in their study and many of their qualitative predictions concerning the various carbenes have been supported by recent ab initio work.[7,8] However, their conclusion that the ground states of $C(CN)_2$ and HC(CN) are *linear* triplets has not been supported by recent ab initio SCF studies. In a recent optimization of the double ζ (DZ) triplet SCF potential energy surface of $C(CN)_2$, Lucchese and Schaefer[9] conclude that dicyanocarbene is distinctly bent (CCC angle of ~134°). The energy-optimized SCF linear geometry is about 9 kcal higher than the bent form, and this difference increases to ~10 kcal upon inclusion of central carbon d functions. Baird and Taylor[8] have recently reported ab initio SCF calculations on some 18 carbenes, including HCCN and $C(CN)_2$, using a minimal STO-3G basis set with polarization functions at the divalent carbon and including 2×2 CI for the singlet states. Although they were most interested in the singlet-triplet energy separation, they also carried out geometry optimizations yielding bent structures for all triplets and all singlets except the molecular ion $HC(CH_2)^+$. As mentioned above, HDL[2b] have very recently studied the double ζ (DZ) SCF energy surface of HCCN. They found that the minimum corresponding to a linear nitrene structure is actually lower in energy than the linear carbene form. However, the bent carbene is the global SCF minimum. When they carried out a modest configuration interaction (CI) calculation for the linear molecule, including all single and double excitations within the π electron space, they obtained the remarkable result that the two SCF minima disappear and are replaced by a single allenic minimum. Our studies using more extensive CI support this aspect of the linear surface, but, as will be seen, our calculations show a smaller shift from a carbene-like geometry toward an allene-like geometry. When HDL[2b] proceeded to bend the H atom 20° off the CCN line, they calculated an energy increase of ~15 kcal on the CI surface. In contrast our calculations show an energy decrease upon bending of ~4 kcal on the CI surface, thereby yielding as a global minimum the bent form of HCCN.

Theoretical Aspects

The standard Dunning-Huzinaga double ζ (DZ) contracted Gaussian basis set,[10] carbon and nitrogen (9s 5p/4s 2p) and hydrogen (4s/2s), was used for the SCF energy calculations. For two geometries, a larger double ζ plus polarization (DZ + P) basis set was used, which includes hydrogen p functions with exponent 1.0 and carbon and nitrogen d functions with exponents 0.75 and 0.80, respectively. The calculations were performed on the Harris Slash Four minicomputer[11] using modified POLYATOM[12,13] codes for integral and SCF calculations (restricted Hartree-Fock) and the BERKELEY system[14] of programs for the CI calculations.

The standard CI calculations include all Hartree-Fock interacting configurations, i.e., those constructed from all Slater determinants different by one or two spin orbitals from the triplet SCF reference configuration. Core-core and core-valence correlation effects are effectively excluded by doubly occupying the lowest three orbitals in all determinants, and not allowing excitation into the highest three virtual orbitals. Since the 14 valence electrons are correlated, this level of theory will be referred to as CI14. For the DZ + P CI calculations, the lowest six and highest three orbitals were frozen. At this level of theory, labeled CI8, correlation effects involving the eight outermost electrons are considered.

For nonlinear geometries, the computations were performed in C_2 symmetry, in which the orbital occupancy for triplet

0002-7863/79/1501-1072$01.00/0

Table I. SCF and CI14 Results.[a] Calculated Energies (mhartrees below 130.0 hartrees)[b] for Various Geometries[c] of HCCN

			linear (θ = 180°)		bent (θ = 135°)	
point	R_{CC}, Å	R_{CN}, Å	SCF	CI	SCF	CI
1	1.200	1.370	−596.872	−831.936	−571.548	−811.876
2	1.290	1.280	−579.293	−836.178	−572.479	(−833.44)[d]
3	1.280	1.250	−578.374	−837.546	−580.427	−838.333
4	1.340	1.230	−584.668	−844.833	−596.052	−848.206
5	1.325	1.205	−589.144	−845.131	−599.946	−848.116
6	1.300	1.180	−589.565	−841.536	−598.960	−843.342
7	1.370	1.200	−590.907	−845.287	−605.303	−851.790
8	1.350	1.180	−593.213	−844.367	(−606.55)[d]	(−849.79)[d]
9	1.390	1.180	−592.867	−843.736	−608.972	−851.967
10	1.370	1.160	−594.180	−841.763	−609.278	−849.138
11	1.430	1.180	(−589.7)[d]		−608.738	−851.584
12	1.410	1.150	−592.578		−610.346	(−848.98)
13	1.380	1.130	−591.741		−607.928	(−844.0)[d]
14	1.440	1.130	−588.234		−607.963	(−844.7)[d]
15	1.410	1.200	−589.079	−843.234	−606.204	−852.331
		θ = 145°			−603.124	−851.022
		θ = 125°			−605.970	−850.872
		ϕ = 175° (trans)			−605.215	−852.422
		ϕ = 170° (trans)			−605.453	−851.843
		R_{CH} = 1.09	−588.654	−843.069	−605.978	−852.328
		R_{CH} = 1.07			−606.290	−852.181

[a] CI14—lowest three occupied and highest three virtual orbitals frozen. [b] That is, the first tabulated energy of −596.872 is meant to imply a total energy of −130.596 872 hartrees. [c] Unless otherwise stated R_{CH} = 1.080 Å, ϕ = 180°, δ = 0°. [d] Energies in parentheses from least-squares quadratic, where point is close enough to expect error smaller than ~0.2 mhartree.

HCCN (in the *yz* plane) is

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 1a''^2\ 9a'\ 2a''$$

For linear geometries, the computations were performed in C_{2v} symmetry, in which the orbital occupancy for HCCN (internuclear axis = C_2 axis) is

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ 7a_1^2\ 1b_1^2\ 1b_2^2\ 2b_1\ 2b_2$$

A check was made to verify that results were identical when a linear geometry was run using C_s or C_{2v} symmetry input.

There are 76 primitive Gaussians contracted to 32 basis functions in the DZ basis set while in the DZ + P basis set these numbers increase to 97 and 53, respectively. For the DZ basis set there are 20 a_1, 6 b_1, 6 b_2, and no a_2 orbitals in C_{2v} symmetry, while there are 26 a′ and 6 a″ molecular orbitals in C_s symmetry. Average times on the Slash Four (which is about 27 times slower than the CDC 7600)[11] for the DZ SCF calculations were 35 min for C_{2v} and 50 min for C_s symmetry. For the DZ + P basis, there are 27 a_1, 10 b_2, 10 b_1, and 3 a_2 orbitals in C_{2v}, which become 37 a′ and 13 a″ in C_s symmetry. Here the "s"-like linear combinations of the six d-like Gaussians on carbon and nitrogen were eliminated from the SCF calculation. Times for the DZ + P SCF calculations were 190 min for C_{2v} and 245 min for C_s symmetry. The DZ CI calculations (CI14) involved 3390 triplet configurations in C_{2v} and 6338 triplet configurations in C_s symmetry, requiring an average of 40 and 95 min, respectively, for the integral transformation plus CI. The DZ + P CI (CI8) involves 3947 triplet configurations in C_{2v} and 7825 triplet configurations in C_s symmetry, requiring 110 and 255 min, respectively. The simplest calculations by far involved only the first few π orbitals, and were carried out using the double ζ basis. These π CI calculations, in which all orbitals were frozen except the lowest three b_1 and lowest three b_2 orbitals, involved 39 configurations.

Table II. SCF and π CI Results.[a] Calculated Energies (mhartrees below 130.0 hartrees)[b] for Various Linear Geometries[c] of HCCN

			linear (θ = 180°)	
point	R_{CC}, Å	R_{CN}, Å	SCF	π CI
1	1.200	1.370	−596.872	−643.378
2	1.290	1.280	−579.293	−651.929
3	1.280	1.250	−578.374	−652.834
10	1.370	1.160	−594.180	−654.128
15	1.410	1.200	−588.654	−654.890

[a] π CI. All orbitals frozen except (in C_{2v}) lowest three b_1 and lowest three b_2. [b] The first tabulated energy implies a total energy of −130.596 872 hartrees. [c] R_{CH} = 1.080 Å, ϕ = 180°, and δ = 0° except for point 15, where R_{CH} = 1.09 Å.

Energy Surfaces

A complete potential surface for HCCN would involve 3(4) − 6 = 6 independent geometrical parameters. The six internal coordinates selected were the CH bond length R_{CH}, the carbon-carbon bond length R_{CC}, the carbon-nitrogen bond length R_{CN}, the HCC bond angle θ, the CCN bond angle ϕ, and the HCCN dihedral angle δ. Our initial strategy was to set R_{CH} = 1.08 Å, ϕ = 180°, θ = 180 (linear) or 135° (bent) and vary R_{CC} and R_{CN}. Starting with the optimized linear geometries of Harrison et al.[2] for the nitrene and carbene on the SCF surface and for allene on the CI surface (designated points 1, 2, 9) we computed at each point (R_{CC}, R_{CN}) the DZ SCF and DZ CI[14] energies for both linear and bent geometries (see Table I). Other points in the R_{CC}, R_{CN} plane were then selected until the general shape of the electronic energy surfaces became clear at about seven points. Additional points were selected and the two-dimensional minima on each surface determined by the procedure discussed below, which may be described as stationary point determination by iteration with a Gaussian weighted least squares quadratic function[15] (program SPLSQUAD).[16] Near the global minimum on the CI surface (point 15) the HCC and CCN bond angles and CH bond length were changed, with the molecule assumed to be trans planar (δ = 180°) and final optimum values of each parameter determined.

After seven points were computed in the vicinity of the minima, each of the four surfaces was least squares fitted to the quadratic form $c_1x^2 + c_2xy + c_3y^2 + c_4x + c_5y + c_6$. The points were weighted by means of an elliptical Gaussian function centered at an estimate of the stationary point (initially the minimum obtained with weights equal to unity) and of extent determined by setting the weight of the sixth closest

Table III. SCF and CI8[a] Results. Calculated Energies (mhartrees below 130.0 hartrees)[b] for Various Geometries of HCCN

point	R_{CC}, Å	R_{CN}, Å	linear (θ = 180°) SCF	linear (θ = 180°) CI8	bent (θ = 135°) SCF	bent (θ = 135°) CI8
7	1.370	1.200	−590.907	−739.352	−605.303	−750.138
15 DZ R_{CH} = 1.09	1.410	1.200	−588.654	−735.132	−605.978	−749.217
15 DZ + P R_{CH} = 1.07	1.410	1.200	−648.206	−836.057	−655.900	−850.073

[a] CI8. Lowest six occupied and highest three virtuals frozen. [b] The first tabulated energy implies a total energy of −130.590 907 hartrees.

Table IV. Predicted Geometrical Structures[a] for HCCN (Bond Lengths in Ångstrom, Angles in Degrees)

surface	R_{CC}	R_{CN}	R_{CH}	θ_{HCC}	ϕ_{CCN}	E, au
linear SCF						
carbene	1.370	1.162	(1.080)	(180.0)	(180.0)	−130.594 15
nitrene	1.21	1.37	(1.080)	(180.0)	(180.0)	−130.596 86
bent SCF	1.407	1.157	(1.080)	(135.0)	(180.0)	−130.610 46
global SCF	1.407	1.157	1.069	130.7	177.4	−130.610 96[b]
linear CI	1.353	1.208	(1.080)	(180.0)	(180.0)	−130.845 71
bent CI	1.400	1.194	(1.080)	(135.0)	(180.0)	−130.852 49
global CI	1.400	1.194	1.085	135.3	176.8	−130.852 62[b]

[a] Parameters in parentheses were not optimized—only planar geometries considered, i.e., δ = 180°, trans. [b] The fitted surface predicted energies of −130.610 96 (global SCF) and −130.852 62 au (global CI).

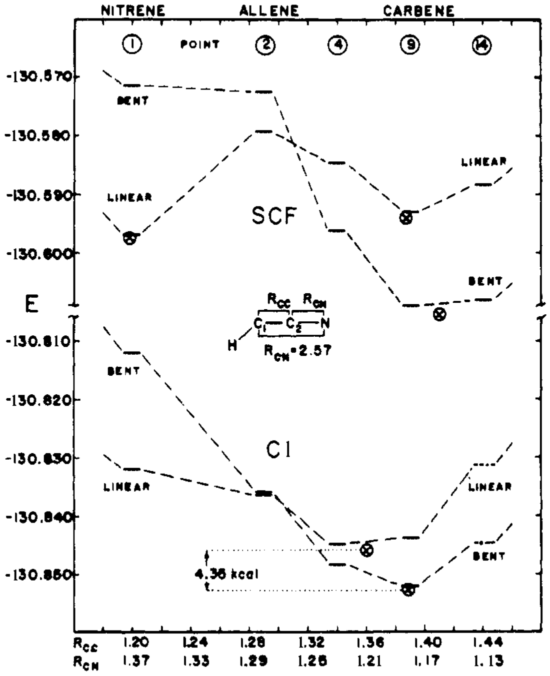

Figure 1. Energy variation at five points along the line of constant $R_{C,N}$ = 2.57 for bent (θ = 135°) and linear geometries of HCCN using SCF and CI14 calculations. At all points ϕ_{CCN} = 180° and R_{CH} = 1.080 Å. Energy minima are indicated by ⊗.

Table V. Energy Difference between Linear [θ(HCC) = 180°] and Bent (135°) HCCN for R(CH) = 1.08 Å, R(CC) = 1.41 Å, and R(CN) = 1.20 Å[b]

method	ΔE, kcal/mol	method	ΔE, kcal/mol
DZ SCF	10.9	DZ CI14	5.8
DZ + P SCF	11.1	DZ + P π CI	
DZ π CI		DZ + P CI8	8.8
DZ CI8	8.8	DZ + P CI14	~5.8[a]

[a] Estimated by subtracting 8.8 − 5.8 = 3.0 from 8.8. [b] Note that these geometrical parameters are nearly optimum for the bent CI14 minimum, and that the true *equilibrium* separations between linear and bent forms are ~1.5 kcal less.

point to the center (in an elliptical sense) to 1/e. Since all nonpathological functions become quadratic at points sufficiently close to the stationary point, this weighted least-squares procedure serves to accurately determine minima or transition states by focusing on points near the stationary point yet retaining information from points far away. Problems associated with the direct fitting of a quadratic function to six points in two dimensions, such as shifting of stationary point location, or appearance and disappearance of negative eigenvalues of the matrix of quadratic coefficients when points are poorly situated near a minimum or transition state, are substantially reduced. For HCCN the method was very stable as additional points were added, leading to high confidence in the positions and energy of the minima (~0.001 Å and ~0.05 kcal) with a small number of computed points (15).

Results and Discussion

As shown in Figures 1 and 2 and Table IV, there are two minima on the linear SCF surface, the nitrene being some 1.7 kcal/mol lower than the carbene, with a relative maximum at the allenic geometry. Bending the hydrogen causes the nitrene energy to rise considerably. Bending the carbene causes the energy to be lowered by about the same amount, yielding a single minimum at somewhat longer CC bond length and only slightly shorter CN bond length. Curiously, the allene energy hardly changes at all. On the linear CI surface, note that the nitrene energy is lowered much less by correlation effects than are the carbene or allene structures, with the result that a single energy minimum occurs at relatively short CC bond length but surprisingly long CN bond length, corresponding to a fairly small shift toward allenic character.

HDL compute a large CI shift toward the geometry of point 3, which corresponds to the linear allene. In order to understand this shift in their calculations, π CI calculations were performed at selected points and are reported in Table II. As noted above, these calculations involve only the lowest three π orbitals, analogous to the calculation of HDL. However, there are only small geometry effects on the difference between

Table VI. Force Constants from Quadratic Fits to Computed Energy Surface

	c_1 K_{CC}[a]	$c_{2/2}$ $F_{CC,CN}$[a]	c_3 K_{CN}[a]	K_{CH}[a]	H_{HCC}[b]	H_{CCN}[b]
linear SCF	7.8	1.8	19.9			
linear CI	7.0	1.2	15.1			
bent SCF	7.8	0.8	20.2	6.1	0.47	0.44
bent CI	7.0	1.9	16.1	6.7	0.40	0.38
ref 1	7.53	2.84	12.24	5.57	0.11	0.31

[a] mdyn/Å. [b] mdyn Å.

Table VII. INO-CI Results for Linear Geometries of HCCN[a]

	point iteration	2	3 carbene	3 nitrene	4	5	7
E_{SCF}	0	−579.293	−576.445	−578.374	−584.668	−589.144	−590.907
$E_{INO\text{-}CI}$	1	−836.138	−842.956	−837.617	−844.836	−845.122	−845.294
	2	−837.745	−843.161	−841.059	−839.690	−836.214	−831.722
	3	−841.573	−843.137	−842.244			
	4	−841.829		−842.736			
	5	−841.846		−842.949			
	6	−841.843		−843.043			

[a] See Table I for a description of the points. Energies in millihartrees relative to 130.0 hartrees.

CI14 and the π CI, i.e., although picking up only ~25% of the correlation energy of CI14 (compare Tables I and II), the π CI surface essentially mimics the large CI surface.

On the bent DZ CI surface, the nitrene geometry is an extremely high energy form, being much higher than on the linear CI surface. However, the bent carbene is the global minimum lying about 4.4 kcal below the linear minimum. The HCC bond angle, the CCN bond angle, and the CH bond length were all varied at point 15 yielding values at the minima (Table IV) very close to those assumed for generating the surface. The HCC SCF and CI bond angles of 131 and 135° are somewhat larger than the 126° obtained by Baird and Taylor[8] using STO-3G. The global DZ CI minimum for HCCN is −130.852 62 au, for which HC and CN bond distances the linear DZ CI energy is ~5.8 kcal/mol higher. As might be expected the CI bond lengths are longer than the SCF values except for R_{CC}.

To check the effect of larger basis sets on the nonlinearity of HCCN, polarization functions were added at point 15. Since machine limitations did not allow the full CI14 the smaller CI8 was carried out using the DZ + P basis set. The results are reported in Table III. For comparison two points were also computed at the CI8 level using the DZ basis. The SCF energy difference between the linear and bent geometries changed very slightly, from 10.9 kcal/mol for the DZ basis to 11.1 kcal/mol for DZ + P. The DZ + P CI8 difference was 8.8 kcal/mol, about the same as the DZ CI8 difference of 8.8 kcal. Since the DZ CI8 energy difference is 3.0 kcal/mol larger than the comparable DZ CI14 result, it may be anticipated that the DZ + P CI14 difference between linear and bent geometry is about 5.8 kcal/mol at point 15 (very close to the minimum). Thus the DZ CI14 energy difference of 4.4 kcal between the global minimum and the constrained linear minimum is supported by the test calculations with polarization functions. These energy differences are collected in Table V.

The CC stretching, CN stretching, and CC–CN interaction force constants (Table VI) were determined from the three leading coefficients of the fitted two-dimensional quadratic. The CH stretching and the HCC and CCN bending force constants were determined from one-dimensional parabolic fits to the computed three points in each case at point 15. There is sure to be considerable uncertainty in these values, since many interaction terms were ignored. However, there also appears to be some uncertainty concerning the "experimental" values from the normal coordinate analysis by Dendramis and Leroi.[5] Using the bent global CI geometry of Table IV and starting with the six bent CI force constants of Table VI, order of magnitude estimates for four other force constants, and the experimentally observed frequencies of HCCN and its isotopically substituted forms the observed IR spectrum could be fit by a linear least-squares refinement of the force constants with a standard error of only 1.4 cm^{-1}.[17] The largest difference between a calculated and observed frequency for HCCN was 1.8 cm^{-1}. This normal coordinate analysis for a bent HCCN is thus of comparable accuracy to that obtained by HDL[2,5] for linear HCCN.

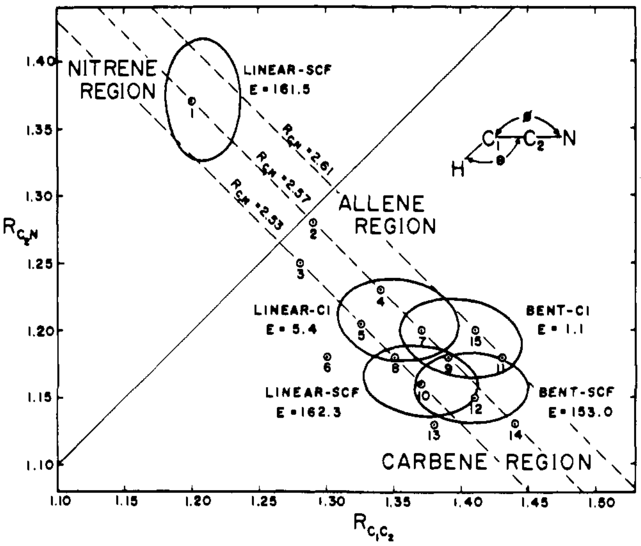

Figure 2. Energy contours, 1 kcal/mol above the minimum, as a function of the CC and CN bond lengths, for four surfaces of HCCN; the linear (L) molecule, $\theta = 180°$, for SCF and CI14 calculations, and the bent (B) molecule, $\theta = 135°$, for SCF and CI14 calculations. At all points, $\phi = 180°$, and $R_{CH} = 1.080$ Å. Energies are in kcal/mol above the global minimum $E = -130.852\ 62$ au.

Unusual Features of Electronic Structures Predicted for Allenic Geometries

HDL[2] reported severe convergence problems in obtaining the SCF solution as the allene geometry was approached. Slow convergence of the SCF procedure was also observed in this study at allenic geometries (e.g., 82 iterations at point 2 of Table I using a carbene-like initial guess for the wave function). The SCF results for linear geometries corresponding to points 2, 3, 4, 5, and 7 of Table I were examined further by requiring stricter convergence (difference of the square of the coefficients less than 1×10^{-8}) and by using three initial guess vectors (a carbene-like vector from point 3, a nitrene-like vector from point 3, and diagonalization of the one-electron Hamiltonian) for each point. The choice of orbitals with which to perform the CI was also examined by means of iterative natural orbital CI calculations on these points. All single and double valence excitations were allowed as described above as CI14.

For points 2, 4, 5, and 7 only one SCF energy (see Table I) was obtained with the various initial guesses at the MO. As noted, the convergence at point 2 was remarkably slow. For point 3, two distinct SCF solutions were obtained. The lower SCF energy (−130.578 374) was calculated using either the diagonalized one-electron Hamiltonian or the nitrene vector initial guesses. When a carbene initial guess was employed an SCF energy of −130.576 445 was obtained for what is almost certainly a fully converged iterative process (difference square coefficients 0.79×10^{-8}). A consideration of the highest two occupied MOs of the two SCF wave functions indicates that the final result for this allenic geometry retains the character of the initial guess. Thus the higher energy SCF wave function is of carbene and the lower energy result of nitrene character.

The INO-CI energy results are given in Table VII. For points 4, 5, and 7, the first iteration of the NO procedure yielded the lowest energy indicating that the SCF-MO provide a suitable set of correlating orbitals. However, for points 2 and 3, which most resemble allenic structures, several cycles of the INO procedure lead to lower energies. For point 3, the higher carbene SCF solution more rapidly reaches a minimum energy than does the lower SCF energy nitrene solution.

Thus, the electronic structure of HCCN is somewhat bizarre in the region of linear allenic geometries. This observation notwithstanding, it seems clear that at the level of theory reported here, no combination of alternate SCF solutions with natural orbital iterations leads to an energy lower than that of the conventional bent cyanocarbene. Therefore, it may be concluded that, although correlation effects significantly *flatten* the predicted Hartree–Fock potential energy surface, the qualitative SCF geometrical prediction of a bent cyanocarbene structure for HCCN remains valid.

Acknowledgments. M.E.Z. wishes to thank Morgan Conrad for many helpful discussions concerning quantum chemistry and computational methods. The collaboration leading to this paper was made possible through a sabbatical grant to M.E.Z. from Wichita State University. This work was supported by the National Science Foundation (Grant CHE-762261).

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(17) We thank Mr. D. Reuter for performing the normal coordinate analysis.

Determination and Analysis of the Formic Acid Conformational Hypersurface

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Received May 8, 1978

Abstract: An analytical conformational hypersurface was fitted to a total of 64 ab initio SCF energy points for formic acid. The geometries of the syn and anti minima, and the OH rotation and C–O–H in-plane inversion saddle points, were determined from the hypersurface. The syn and anti structures, as well as the saddle point for tautomerization (H transfer), were also found directly by complete geometry optimization.

A topic of considerable interest is the interdependence of isomerization or tautomerization and conformational change. Although it is traditional to discuss these processes as independent phenomena, in effect they represent different cross sections of the same energy hypersurface. Perhaps the justification for the separation of these processes lies in the difference in barrier heights, but sometimes certain conformational transition states may also have relatively high energies. This situation occurs for methanol, for which the barrier to OH rotation has been calculated[1] to be 1.44 kcal/mol, while the

0002-7863/79/1501-1076$01.00/0