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# Limitations of Restricted Open-Shell Self-Consistent Field Calculations Applied to Molecules with Multiple Bonds. Electronic Structure and Geometry of the Ground State of HCCN

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**Abstract:** The restricted open-shell SCF theory predicts the ground state of HCCN to be a bent triplet carbene, with the nitrene isomer a local minimum on the ground-state surface approximately 8 kcal/mol above the bent carbene. A modest configuration interaction calculation predicts only one minimum on the ground-state surface and this is neither the carbene (H-C-C≡N) nor the nitrene (H-C≡C-N), but rather the "allene-like" structure, H-C=C=N. Reasons for the qualitatively different predictions of the SCF and CI theories are discussed.

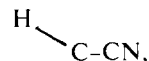
## Introduction

The first spectroscopic observation of the free radical HCCN was by Bernheim et al.,<sup>1</sup> who, on the basis of the ESR spectrum, concluded that the molecule was a ground-state linear triplet. Subsequent ESR studies by Wasserman et al.<sup>2</sup> reaffirmed this conclusion. These studies suggest that the structure is H-C-C≡N, i.e., linear cyanocarbene. Merer and Travis<sup>3</sup> attempted to study the UV spectrum of HCCN by generating it in the gas phase via flash photolysis of diazoacetonitrile. The presence of other radicals such as CNC and CCN, which were formed during the photolysis, prevented a successful analysis. Recently Dendramis and Leroi<sup>4</sup> published a detailed investigation of the infrared spectrum of HCCN and several isotopic modifications, isolated in an inert matrix. These authors were able to fit the observed frequencies with a valence force field characterized by force constants which suggest an allenic structure, H-C=C=N.

In addition, Dendramis and Leroi<sup>4</sup> observed a band system in the UV between 2400 and 3400 Å which is similar to that attributed to the isoelectronic radical N=C=N, again suggesting the allenic structure.

Previous theoretical work pertaining to the geometry and electronic structure is meager. In their classic paper on the carbene structure, Hoffman et al.<sup>5</sup> reported extended Hückel calculations for HCCN with assumed bond lengths corresponding to the carbene structure, and concluded that the molecule was a linear ground-state triplet. Recently Baird and Taylor<sup>6</sup> reported ab initio restricted open-shell SCF calculations<sup>7</sup> in which the geometry of the lowest triplet state was optimized. They predict that the molecule is a bent carbene with a H-C-CN angle of 126°. In a related paper Lucchese and Schaefer<sup>8</sup> have studied NC-C-CN using the restricted open-shell SCF theory and concluded that this molecule is a bent triplet carbene.

In summary, there are published suggestions that HCCN is best represented as a linear triplet carbene, H-C-CN, a bent triplet carbene,



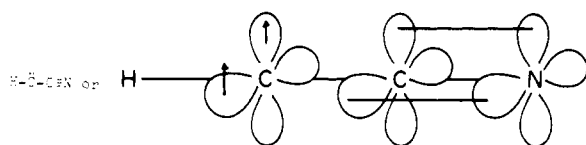
and a linear allene-like triplet, H-C=C=N. We have studied HCCN using the restricted open-shell SCF theory, augmented

by a modest configuration interaction (CI), and we conclude that the allenic structure is the best representation of the ground state.<sup>9</sup>

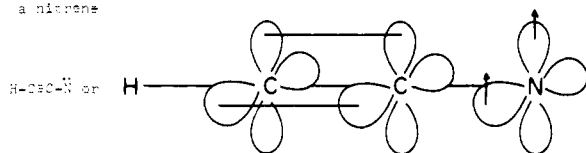
### Preliminary Considerations

The HCCN molecule contains 20 electrons which, in the linear symmetry, may be partitioned as  $14\sigma$  and  $6\pi$ . The  $\sigma$  electrons are the two in the  $1s$  orbitals on N and each C, the two in essentially the  $2s$  orbital on N, and the two in each of the three  $\sigma$  bonds. The six  $\pi$  electrons may be distributed in the molecule so as to be consistent with at least three classical triplet structures.

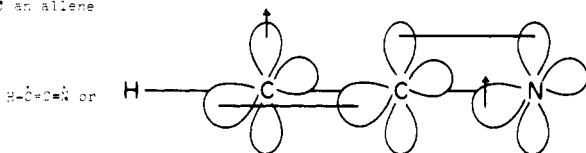
i) a carbene



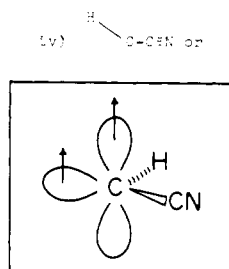
ii) a nitrene



iii) an allene



Of these three structures it is reasonable to expect that the carbene might be more stable in the bent configuration.<sup>6,8</sup>



### Self-Consistent Field Study

The basis functions on carbon and nitrogen were the  $9s$ ,  $5p$  set of Huzinaga<sup>10</sup> contracted to  $4s$ ,  $2p$ , while the H basis was his  $4s$  set contracted to  $2s$  with the exponents on the H functions scaled by 1.2. All contractions were as recommended by Dunning.<sup>11</sup> The required integrals were calculated with a modified version of IBMOLII and the restricted open-shell SCF functions were constructed with the POLYATOM codes.<sup>12</sup>

Our strategy for finding the geometry corresponding to the minimum energy was to fix the C-H distance at a reasonable value ( $1.08 \text{ \AA}$ ), find the optimal C-C and C-N bond lengths, and then move the H off the C-C-N line holding the C-C and C-N bonds fixed at their optimal (linear molecule) values. The energy of the molecule in the linear geometry as a function of C-C and C-N distances is shown in Figure 1. The assumptions made in labeling this figure are that when the C-C distance is small and the C-N distance large, the molecule is best described as a nitrene, i.e., structure ii. Conversely, when the C-C distance is large and the C-N distance small a carbene structure (i) is appropriate. When the CN and CC distances are "comparable" we assume that the molecule is allenic, structure

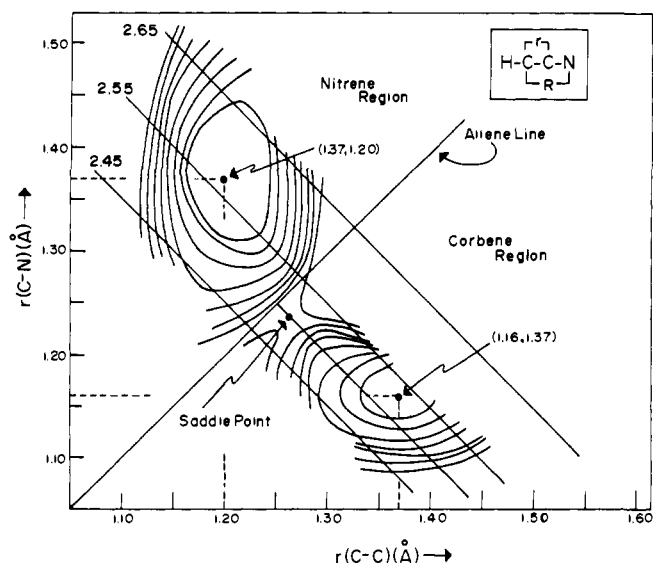


Figure 1. SCF energy contours of the linear molecule HCCN as a function of the C-C and C-N bond lengths. The innermost contour corresponds to  $-130.5940 \text{ au}$  and they increase by  $0.002 \text{ au}$  per contour.

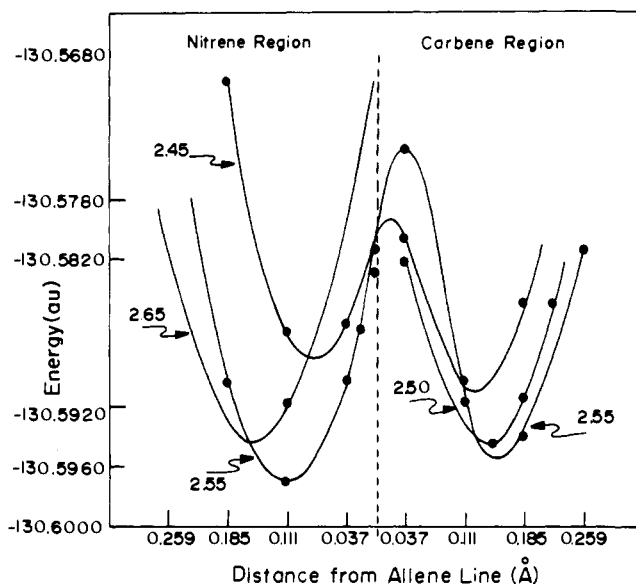


Figure 2. SCF energy variation along lines of constant  $R = r(\text{C-C}) + r(\text{C-N})$ .

iii. Along the straight lines perpendicular to the allene line the sum of the C-C and C-N distances is constant, Motion along this coordinate (in passing from the nitrene to the carbene region) corresponds to the breaking of the  $\pi$  component of the C-C triple bond and the formation of the  $\pi$  component of the C-N triple bond, with the halfway point corresponding to the allenic structure.

Cross sections through this surface along the 2.45, 2.50, 2.55, and 2.65 lines are shown in Figure 2. The restricted open-shell SCF theory predicts two minima in the linear geometry corresponding to the nitrene and carbene structures, with the nitrene being less than  $2 \text{ kcal/mol}$  lower in energy. In addition, it predicts that the allenic structure is a local maximum on the energy surface, some  $13 \text{ kcal/mol}$  above the nitrene minimum through the allenic maximum to the carbene minimum is shown in Figure 3.

We then fixed the C-C and C-N bond lengths at the linear carbene values ( $1.37$  and  $1.16 \text{ \AA}$ , respectively) and moved the H atom off the C-C-N line. As shown in Figure 4a, the energy

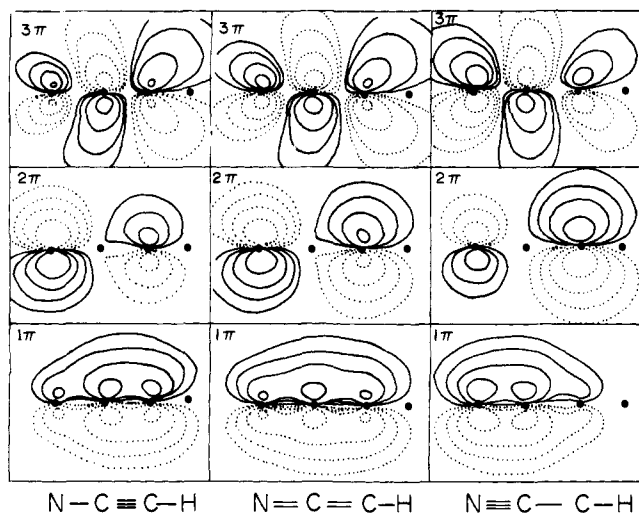


Figure 3. Contours of the  $\pi$  molecular orbitals of the  $^3\Sigma^-$  SCF function for the nitrene, allenic, and carbene geometries of linear HCCN.

was minimized at a H-C-CN angle of  $132^\circ$ , approximately 9.5 kcal/mol below the linear form. When we moved the H off line at the allenic maximum the energy increased. We did not bend HCCN in the region of the nitrene minimum.

In summary, for the ground triplet electronic state of HCCN, the restricted open-shell SCF theory predicts a bent carbene as the global minimum, with a linear nitrene as a local minimum and an allenic structure as a local maximum.

### Configuration Interaction Studies

In order to allow for possible correlation energy differences among the different geometries, we constructed a modest configuration interaction wave function for several nuclear configurations. For the linear symmetry the SCF configuration is  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 1\pi^4 2\pi^2$  and all configurations included in the CI have the first seven  $\sigma$  molecular orbitals doubly occupied. We then constructed the 48 functions of  $^3\Sigma^-$  symmetry which one can form from the first three spatial  $\pi$  orbitals and the six  $\pi$  electrons. The CI results for the linear symmetry are shown in Figure 5. Most remarkable, the two SCF minima have vanished and the allenic maximum has become the only minimum on the CI (linear molecule) surface!

The minimum geometry in the linear symmetry is predicted to be  $r(\text{CN}) = 1.25 \pm 0.01 \text{ \AA}$  and  $r(\text{CC}) = 1.28 \pm 0.01 \text{ \AA}$  (recall that we fixed the C-H distance at 1.08  $\text{\AA}$ ) with an energy of  $-130.6755 \text{ au}$ . Holding  $r(\text{CN})$  at 1.16 and  $r(\text{CC})$  at 1.37  $\text{\AA}$ , i.e., the linear carbene SCF geometry, we moved the H atom  $20^\circ$  off the CCN line. As shown in Figure 4b, the energy increased by 15 kcal/mol, suggesting, very strongly, that the linear allenic structure is the global minimum on the HCCN surface. Cuts through the CI and SCF surfaces along the 2.55- $\text{\AA}$  line (linear geometry) are shown at the top and bottom in Figure 6.

### Discussion

In an attempt to gain some insight into the striking differences between the SCF and CI results we determined the natural orbitals (NOs) for the CI function. Interestingly, the form of the  $\pi$  NOs is very similar to the corresponding MOs, the effect of the CI being in the occupation numbers. These are collected in Table 1 (for the points along the 2.55- $\text{\AA}$  line), from which we note that as we approach the allenic geometry the CI significantly increases the occupancy of the  $3\pi$  NO. Since the  $\pi$  orbitals (MOs or NOs) in this molecule have the approximate nodal structures shown, an increased occupancy of

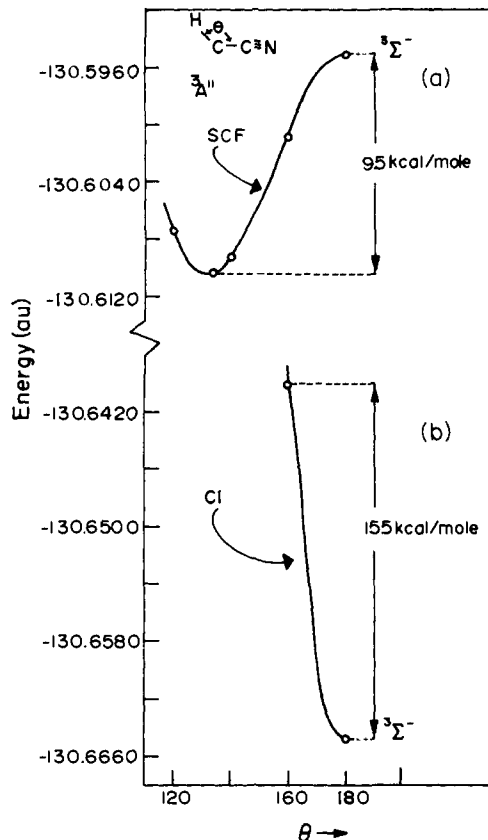
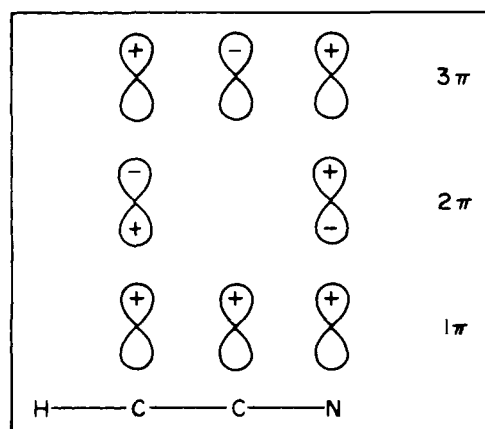


Figure 4. The energy of HCCN as a function of the H-C-CN angle as predicted by the (a) SCF and (b) CI theories. The bond lengths are  $r(\text{H-C}) = 1.08 \text{ \AA}$ ,  $r(\text{C-C}) = 1.37 \text{ \AA}$ , and  $r(\text{C-N}) = 1.16 \text{ \AA}$ .

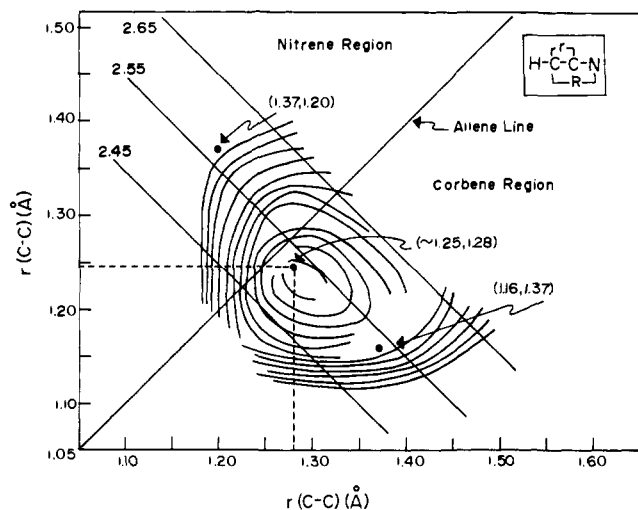
the  $3\pi$  NO provides a mechanism for decreasing the amount of  $\pi$  bonding between the central carbon atom and both the nitrogen and terminal carbon. This ability is necessary if one



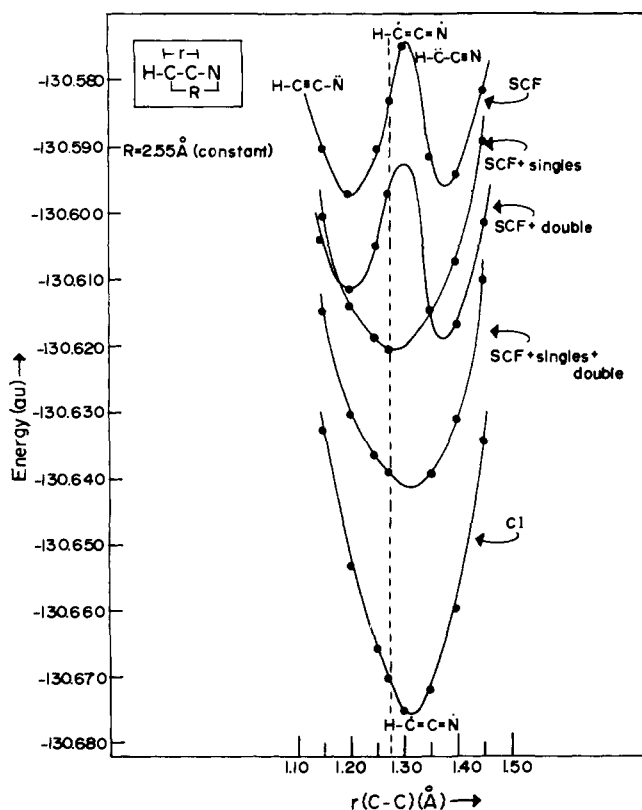
is to go smoothly from the carbene to the nitrene geometries.

One expects therefore that those configurations involving an excitation from the  $1\pi$  to the  $3\pi$  MOs will be most significant in an accurate description of the distance dependence of the total energy. There are two classes of such excitations, the single excitations  $1\pi^4 2\pi^2 \rightarrow 1\pi^3 2\pi^2 3\pi^1$ , which give rise to four functions of  $^3\Sigma^-$  symmetry, and the double excitation,  $1\pi^4 2\pi^2 \rightarrow 1\pi^2 2\pi^2 3\pi^2$ , from which we can form one function of  $^3\Sigma^-$  symmetry.

Figure 6 shows the results of CI calculations with each of these classes individually and together. Apparently the single excitations provide the flexibility lacking in the SCF and allow the continuous evolution of the  $\text{C}\equiv\text{N}$  and  $\text{C-C}$  linkages into the  $\text{C-N}$  and  $\text{C}\equiv\text{C}$  bonds, respectively.

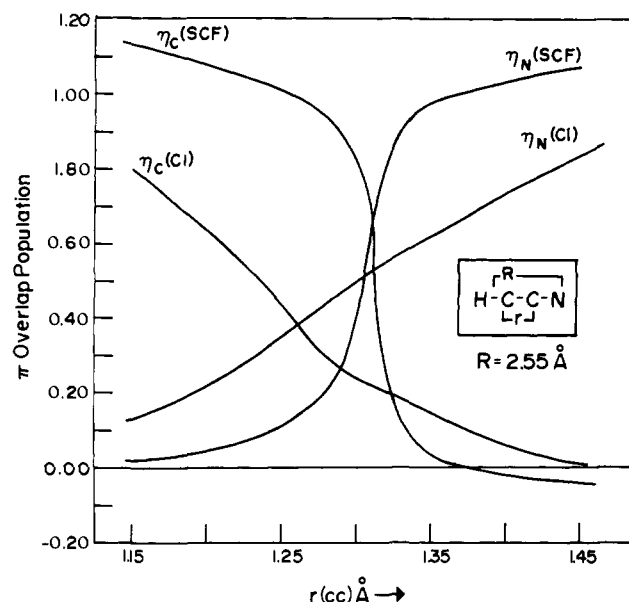


**Figure 5.** CI energy contours of the linear molecule HCCN as a function of the C-C and C-N bond lengths. The innermost contour corresponds to  $-130.6740$  au and they increase by  $0.002$  au per contour.



**Figure 6.** Energy variation along the  $2.55$ -Å line for the SCF theory and various levels of CI, for the ground state of linear HCCN.

The  $\pi$  overlap populations<sup>13</sup> calculated with the SCF  $\pi$  MOs and the  $\pi$  NOs of the CI function are shown in Figure 7 (again along the  $2.55$ -Å line) as a function of the C-C distance. In this figure, we plot the  $\pi$  overlap population between the central carbon and both the end carbon ( $\eta_C$ ) and the nitrogen ( $\eta_N$ ). As the central carbon moves away from the terminal carbon and toward the nitrogen,  $\eta_C$  (SCF) first drops slowly until the allenic region is reached, where it drops precipitously to the low value appropriate to the  $\pi$  contribution to a C-C single bond. While  $\eta_C$  (CI) also drops, it does so much more gradually than  $\eta_C$  (SCF), reflecting the flexibility introduced by the single excitations.  $\eta_N$  behaves in a very similar manner, being small on the nitrene side (C-N bond) and large on the carbene side (C $\equiv$ N bond), with a precipitous change for the SCF function and a more gradual one for the CI.



**Figure 7.**  $\pi$  overlap populations as a function of the C-C bond length along the  $r(\text{C-C}) + r(\text{C-N}) = 2.55$  Å line;  $\eta_C$  is the carbon-carbon and  $\eta_N$  the carbon-nitrogen population.

**Table I.** Natural Orbital Occupation Numbers for HCCN ( $R = r(\text{C-C}) + r(\text{C-N}) = 2.55$  Å)

$r(\text{C-C}), \text{Å}$	$1\pi$	$2\pi$	$3\pi$
1.15	3.9186	2.0028	0.0788
1.20	3.8920	2.0042	0.1038
1.25	3.8656	2.0058	0.1288
1.275	3.8554	2.0064	0.1382
1.30	3.8490	2.0068	0.1442
1.35	3.8670	2.0068	0.1262
1.40	3.8910	2.0052	0.1038
1.45	3.9148	2.0036	0.0816

This inability of the restricted open-shell SCF theory to describe the simultaneous breaking of one bond and formation of an adjacent bond is similar to the inability of the closed-shell SCF theory to describe bond dissociations. Recall<sup>14</sup> that the MO function for  $\text{H}_2$  separates into  $\text{H}^+$ ,  $\text{H}^-$  as well as into H atoms; i.e., the ionic character of the bond being broken is exaggerated in the SCF theory.

In Figure 8 we plot the  $\pi$  charges (relative to  $2\pi$  electrons on each atom) as predicted by the SCF and CI theories.  $Q_E$ ,  $Q_M$ , and  $Q_N$  refer to the end carbon, middle carbon, and nitrogen atom  $\pi$  charges. The  $\pi$  charges are displayed on the molecular diagram at those points identified by the SCF theory as the carbene and nitrene minima and at the global minimum as predicted with the CI. As anticipated, the SCF function predicts a larger "ionic character" than the CI function.

## Conclusion

The restricted open-shell SCF theory is not able to describe reliably the energy variation when the central carbon in HCCN is moved from a position characteristic of a C $\equiv$ C bond to that appropriate for a C-C bond. This deficiency is similar to the inability of the closed-shell SCF theory to describe bond dissociation for closed-shell molecules. A small configuration interaction involving the four functions from the  $1\pi^3 2\pi^2 3\pi^1$  configuration corrects the SCF's deficiency and accounts for most of the geometry-sensitive correlation energy.

It seems reasonable to expect that a comparable situation would be found with electronically similar molecules. For example, in a recent restricted open-shell SCF study of NCCCN<sup>8</sup> the predicted ground state is a bent triplet carbene ( $\theta = 132.5^\circ$ ,  $R(\text{C-C}) = 1.407$  Å,  $R(\text{C-N}) = 1.154$  Å), corresponding to

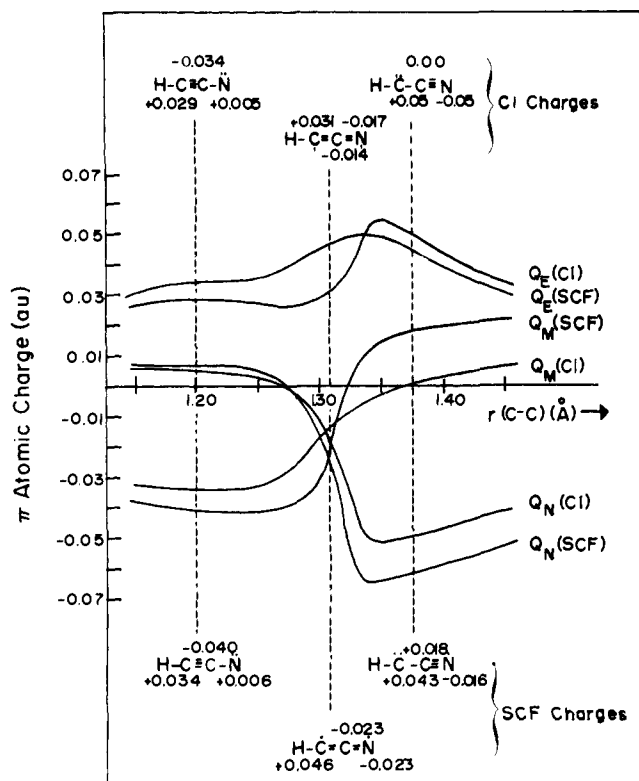
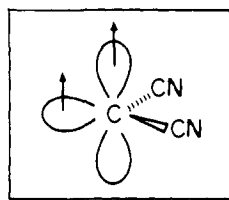


Figure 8.  $\pi$  charges (relative to two electrons on each atom) as a function of the C-C bond length along the  $r(\text{C-C}) + r(\text{C-N}) = 2.55 \text{ \AA}$  line.  $Q_E$ ,  $Q_M$ , and  $Q_N$  are the charges on the end carbon, middle carbon, and nitrogen atom, respectively.

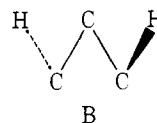
A. The minimum energy in the linear geometry is 8.6 kcal/mol higher and is characterized by  $r(\text{C-C}) = 1.358 \text{ \AA}$  and  $r(\text{C-N}) = 1.160 \text{ \AA}$ , corresponding to the linear carbene  $\text{N}\equiv\text{C}-\text{C}$ -



A

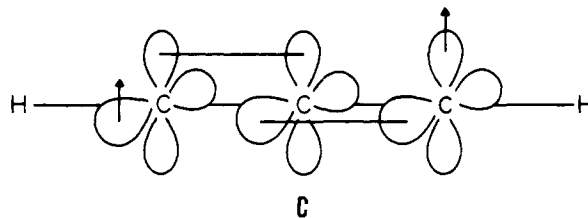
$\text{C}\equiv\text{N}$ . Note that these bond lengths are very close to those of our linear carbene,  $\text{N}\equiv\text{C}-\text{C}-\text{H}$  ( $r(\text{C-C}) = 1.37 \text{ \AA}$ ,  $r(\text{C}\equiv\text{N}) = 1.16 \text{ \AA}$ ). The factors which contribute to the differential lowering of  $\text{N}=\text{C}=\text{C}-\text{H}$  over  $\text{N}\equiv\text{C}-\text{C}-\text{H}$  in a CI calculation should also favor  $\text{N}=\text{C}=\text{C}=\text{C}=\text{N}$  rather than the linear, and perhaps the bent, carbene.

Also, a recent unrestricted Hartree-Fock study<sup>15</sup> of propargylene has predicted that the ground-state triplet has the interesting structure B rather than the more traditional linear structure C. This prediction should be tested at the CI level



B

$r(\text{C-C}) = 1.303 \text{ \AA}$ ,  $\angle(\text{CCC}) = 167.1^\circ$ ,  $\angle(\text{HCC}) = 145.7^\circ$ ,  $\angle(\text{HCCC}) = 144.5^\circ$



C

since the differential in the energy lowering which would result from a CI study on these two possibilities would favor the more traditional form.

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