its lower symmetry, is also relatively easy to predict. Again, the PA model is nearly as good as the LP model. The LP model alone has the correct ordering of the energies of the two crystal forms, as contrasted to the other three models, but the predicted heat of transition is too low. Rae[16] calculated the energy of transition as 1.0 kJ mol^{-1} at absolute zero.

The crystal structure of *s*-tetrazine is the most difficult to predict and provides the most stringent test of the model for the molecular charge distribution. The PA and NLP models are poor; even the LP model is not as good as we would like. Surprisingly, the NC model is about as good as the LP model in its prediction. However, the NC model has a negative eigenvalue of the Hessian at the observed structure, and also the calculated energy appears to be too small.

Overall the LP model is the best of the four tested. Since in this work no attempt to optimize this model was made, it is likely that further improvement is possible. Since an important overall goal is to obtain transferability of the model parameters, a wider range of nitrogen-containing molecules should be considered in such an optimization. Another important overall goal is to allow the model to be applied to large molecules, even as large as proteins. The site-charge model has an advantage of computational simplicity to allow treatment of such larger molecules.

Acknowledgment. This work was supported by research grant GM16260 from the National Institutes of Health.

Registry No. Pyridine, 110-86-1; pyridazine, 289-80-5; pyrimidine, 289-95-2; pyrazine, 290-37-9; *s*-triazine, 290-87-9; *s*-tetrazine, 290-96-0.

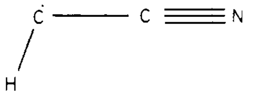
Vibrational Frequencies of the HCCN Molecule. A Near Degeneracy between Bent Cyanocarbene and Linear Allene-Related Geometries

Kwang S. Kim,[†] Henry F. Schaefer III,*[†] Leo Radom,[‡] John A. Pople,[§] and J. Stephen Binkley[∥]

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600 Australia, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and Theoretical Division, Sandia Laboratory, Livermore, California 94550. *Received July 19, 1982*

Abstract: The geometrical structure and vibrational frequencies of the ground triplet electronic state of HCCN have been examined at a wide range of levels of ab initio electronic structure theory. The potential energy surface of HCC bending is very flat for HCCN owing to a competition between linear allene $H\dot{C}{=}C{=}\dot{N}$ and bent carbene $H\ddot{C}C{\equiv}N$ valence structures. Evidence is presented that both the restricted Hartree–Fock (RHF) and unrestricted Hartree–Fock (UHF) methods treat this potential surface in a somewhat uneven manner. When the effects of electron correlation are included, however, RHF- and UHF-based methods converge to a similar set of structural and energetic predictions. The most reliable levels of theory suggest that HCCN is a quasi-linear molecule, with $\theta_e(HCC) \approx 138°$ and a barrier to linearity of only about 2 kcal/mol.

The first experimental studies of the HCCN triplet ground state were made via electron paramagnetic resonance (EPR) technique.[7-9] These results were interpreted in terms of a linear carbene model, as was considered natural[1,2] during the 1960s. However, in their landmark 1970 EPR study of CH_2 (declaring a substantially bent triplet ground state), Wasserman, Yager, and Kuck[5] comment briefly on HCCN. They note first that the nonlinearity of CH_2 might well be expected to carry over to cyanocarbene.



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This introduction notwithstanding, Wasserman states[5] that "the attempts we have made to examine $H\dot{C}CN$ in a variety of matrices at 4 K have only given spectra corresponding to *E* (zero field splitting parameter) = 0 thus supporting the linear form." In assessing these EPR data, Dendramis and Leroi[6] note that matrices may impose barriers to rotation, and the inability to detect rotation does not necessarily mean that the molecule must be linear. Hyperfine structural data, not yet available for HCCN, are necessary before a definitive pronouncement about the geometry can be made.

The most detailed experimental data available for HCCN come from the matrix isolation infrared study of Dendramis and Leroi.[6] They assigned five fundamental frequencies for DCCN and four each for HCCN, $HC^{13}CN$, and $HCC^{15}N$. Dendramis and Leroi (DL) state specifically that their failure to observe more than five vibrational fundamentals does not prove the linearity of HCCN. However, they do eventually conclude that the molecule is linear (with the allene-like structure **2**) on the basis of their normal-coordinate analysis. For example, the observed frequency at 1735

[†] University of California.

[‡] Australian National University.

[§] Carnegie-Mellon University.

[∥] Sandia Laboratory.

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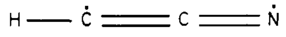
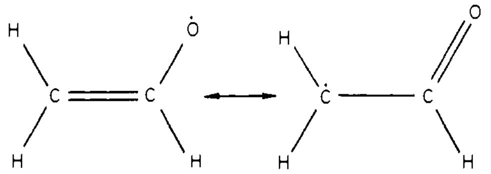

$H-\dot{C}=C=\dot{N}$

2

cm^{-1} is far from the C≡N stretching frequency[10] of 2129 cm^{-1} in the prototype HCN, and no other observed fundamental comes close to the anticipated C≡N stretch. In addition DL state that the low value (458 cm^{-1}) of the frequency assigned as a CCH bend is far below the values ($\geq$750 cm^{-1}) normally associated with the CCH bend in nonlinear molecules.

We have previously noted[11] that the most reliable existing theoretical results suggest the bent cyanocarbene **1** lies ~4 kcal below the linear structure, which has considerable resemblence to the allene-like structure **2**. Here, we move on to make a much more direct comparison with the experiments of Dendramis and Leroi,[6] by presenting ab initio predictions of the harmonic vibrational frequencies. Moreover, the level of theory used here is significantly higher than in previous work.[11-14] This seems particularly appropriate in light of the recent study by Dupuis, Wendoloski, and Lester[15] of the CH_2CHO radical. The problem pointed out by Dupuis is the near degeneracy of two bond-shifted isomers, the vinoxy radical **3** and the formylmethyl radical **4**. The relation between **3** and **4** is clearly related to that between cyanocarbene **1** and its allene-like isomer **2**, and Dupuis shows that the former energy difference is very sensitive to the level of theory employed. Borden and Davidson[16] have discussed this case and others in which radical and diradical bond-switched isomers are nearly degenerate and likewise conclude that a high level of theory is required to resolve such issues. In this theoretical context (even without considering the very rich experimental background for HCCN), it seems highly worthwhile to have at least one very detailed study of such a bond-switching isomerism.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The Restricted Hartree-Fock Approximation as a Starting Point

A. Theoretical Approach. Our previous research[11] on HCCN was carried out almost exclusively with a double-ζ (DZ) basis set of contracted Gaussian functions.[17] Specifically the Huzinaga-Dunning[18,19] C,N(9s 5p/4s 2p), H(4s/2s) basis was chosen. Both spin-restricted self-consistent field (SCF) and configuration interaction (CI) treatments were carried out, the latter involving all Hartree-Fock interacting[20] valence electron single and double excitations. In the CI treatment the three occupied 1s-like core molecular orbitals were constrained to be doubly occupied in all configurations, and the three highest SCF orbitals (also of 1s-like character for a DZ basis set) were deleted from the CI. Thus a total of 6338 $^3A''$ configurations were included in point group C_s. The results of this earlier study[11] are summarized in Table I.

Table I shows first of all that a number of structural assumptions were made at different stages of the previous work. In the present study, however, *all* geometrical parameters have been optimized simultaneously, and, even more important, each stationary point has been subjected to a harmonic vibrational analysis to determine its character.[21] Two structural results of the previous study stand out: (a) the linear HCCN structure has C-C and C-N bonds more allene-like (see **2**) than the bent structure; (b) correlation effects push both the linear and bent geometries toward the allene structure. The above results notwithstanding, even the linear DZ CI structure is not entirely allene-like. For example, the C-N distance, 1.208 Å, is still closer to the triple bond in $CH_3C\equiv N$ (1.157 Å)[22] than to the double bond in $H_2C=NH$ (1.273 Å).[23] Also, although the linear CI C-C bond distance (1.353 Å) is just that expected for a C=C double bond, it must be recognized that C-C single bonds adjacent to multiple bonds can be quite short. For example, the undisputed single C-C bond in cyanoacetylene[22] (**5**) is very short, 1.382 Å. Comparable C-C single bond distances are observed[24] for cyanogen, N≡CC≡N, and diacetylene, HC≡CC≡CH. In summary, the previous theoretical study[11] described the linear HCCN as allene-like but with a strong carbene contribution and the bent HCCN as carbene-like with a strong allene contribution. In both cases it is clear that counterbalancing forces are at work and the final conclusion might be significantly changed at a higher level of theory.

$HC\equiv C-C\equiv N$

5

A full double-ζ plus polarization (DZ+P) basis set was used primarily in the present study. This means that to the above described DZ basis were added d functions on the carbon and nitrogen nuclei and a set of p functions on the hydrogen atom. The Gaussian orbital exponents took on the standard values[17] $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_p(H) = 1.0$. Thus the complete basis set includes 50 contracted Gaussian functions and may be designated C,N(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p). The CI including all single and double excitations (CISD) with this basis involves 22 519 $^3A''$ configurations in point group C_s (planar) and 43 390 ^3A configurations in point group C_1 (no elements of symmetry other than the identity).

In this research we have also systematically used the Davidson correction[25] for higher than double excitations, namely, unlinked clusters. This simple formula

$$\Delta E = (1 - c_0^2)\Delta E_{SD} \qquad (1)$$

gives an approximation to the contribution ΔE to the correlation energy due to unlinked quadruple excitations. In eq 1, c_0 is the coefficient of the Hartee-Fock configuration in the CISD and ΔE_{SD} is just the correlation energy due to single and double excitations. This ΔE has been appended to the CISD variational energies to predict both geometrical structures and harmonic vibrational frequencies for the linear and bent forms of HCCN.

In conclusion, the improvements in the scope and the level of theory presented here relative to that of ref 11 are (a) the consistent determination of *all* geometrical parameters for the linear and bent HCCN at each of three distinct levels of theory, (b) the use of the larger DZ+P basis set throughout, (c) systematic application of Davidson's correction[25] to the CISD energies, and

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Table I. Predicted Linear and Bent HCCN Structures of Zandler, Goddard, and Schaefer[11] [a]

	r_e(CC)	r_e(CN)	r_e(CH)	θ_e(HCC)	θ_e(CCN)	rel energy, kcal
linear RHF	1.370	1.162	(1.080)[b]	(180.0)[b]	(180.0)[b]	10.2
bent RHF	1.407	1.157	(1.080)[b]	(135.0)[b]	(180.0)[b]	0.0
linear CI	1.353	1.208	(1.080)[b]	(180.0)[b]	(180.0)[b]	4.3
bent CI	1.400	1.194	1.085	135.3	176.8	0.0

[a] These results were obtained with a DZ basis set. Bond distances in anstroms and bond angles in degrees. [b] Assumed geometrical parameter.

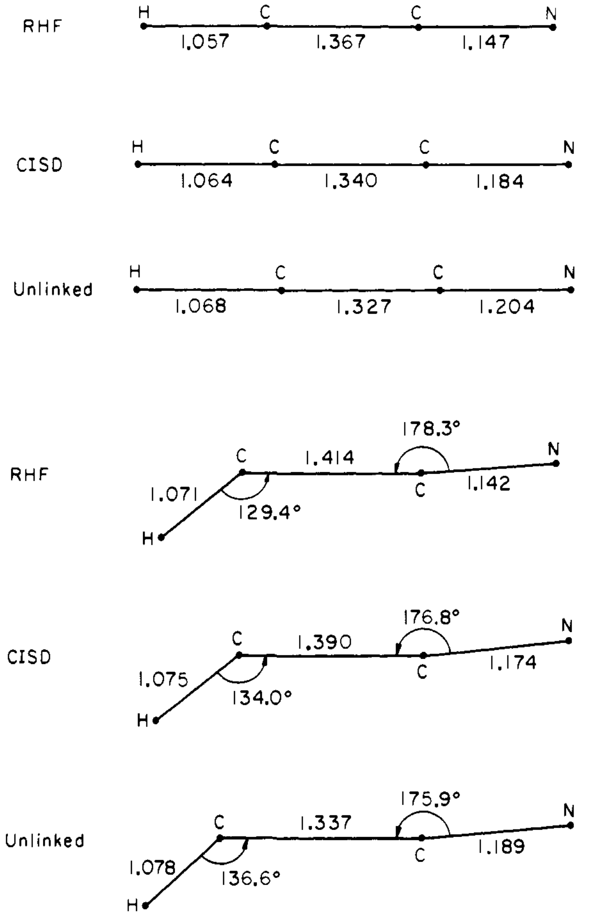

Figure 1. Stationary point geometries predicted for linear and bent HCCN. Bond distances are given in angstroms. RHF refers to the spin-restricted self-consistent field method, CISD to configuration interaction including single and double excitations, and Unlinked to the results obtained by appending the Davidson correction for quadruple excitations to the CISD variational energies. All results were obtained using a double zeta plus polarization (DZ+P) basis set.

(d) determination of harmonic vibrational frequencies for each stationary point at each level of theory.

B. Geometrical Structures. Although not the most significant aspect of the present research, the predicted molecular structures are in principle more reliable than those reported in earlier theoretical studies[11-14] and are accordingly summarized in Figure 1. At every level of theory, the linear stationary point geometries are more allene-like and the bent structures more carbene-like. That is, the linear structures have shorter C–C distances, by 0.047, 0.050, and 0.010 Å, respectively, at the RHF, CISD, and Davidson corrected CISD levels of theory. Similarly the linear C–N distances are longer than the bent C–N distances by 0.005, 0.010, and 0.015 Å for the three levels of theory. This is of course consistent with the qualitative idea of Harrison and Leroi[6,12,14] that the linear structure is allene-like and the bent structure carbene-like. It should be noted, however, that the difference in the C–C bond distance nearly disappears at the highest level of theory. By the criteria discussed in the previous section, *both* linear and bent structures are intermediate between allene and carbene.

Table II. Total and Relative Energies of HCCN Linear and Bent Structures at Three Levels of Theory[a]

	total energy, hartrees	rel energy, kcal/mol
linear RHF	−130.657 04	10.9
bent RHF	−130.674 34	0.0
linear CI	−131.008 25	5.1
bent CI	−131.016 39	0.0
linear Davidson	−131.052 14	3.2
bent Davidson	−131.057 27	0.0

[a] A DZ+P basis set was used throughout.

From a theoretical persepctive, the most surprising result in Figure 1 is the enormous change in the predicted C–C bond distance of the bent structure brought about by the appendage of the Davidson correction[25] to the CISD variational energies. This decrease of 0.053 Å was certainly unexpected[26] and indicates that the CISD description of the electronic structure is not entirely satisfactory. Even the increase of 0.015 Å in the C–N distance is somewhat greater in this regard than one feels comfortable with. The changes in bond angle from 129.4° (RHF) to 134.0° (CISD) to 136.6° (Davidson corrected) show the same trend toward allene-like structures as the level of theory is improved. Although the final C–N distance of 1.189 Å might be considered a long triple bond, the C–C distance of 1.337 Å for the bent structure clearly reflects an element of C=C double-bond character. This is true even when one takes into account the fact (mentioned earlier) that the C–C single bond distance in cyanoacetylene is only 1.382 Å. Note also that the very short carbon–carbon distance in bent HCCN could not be anticipated from the previous CI studies[11] using a DZ basis set, with which (see Table I) r_e(C–C) = 1.400 Å at the CISD level.

The structural predictions of Figure 1 may be compared with the structure used by Dendramis and Leroi in their normal-coordinate calculations,[6] namely, r(CH) = 1.07 Å, r(CC) = 1.30 Å, and r(CN) = 1.23 Å. The most reliable theoretical linear structure has a CH distance 0.002 Å shorter, a CC distance 0.027 Å longer, and a CN distance 0.026 Å shorter. Thus one finds qualitative accord, although the Dendramis–Leroi structure is significantly more allene-like. It should be noted that the DL structure is not deduced from experiment but is a hypothetical structure with bond lengths transferred from allene and NCN.

C. Relative Energies. The total and relative energies obtained in this research are summarized in Table II. There it is seen that at each of the three levels of theory, the bent structure of HCCN is predicted to lie lower in energy than the linear form. However, this energy difference decreases from 10.9 (RHF) to 5.1 (CISD) to 3.2 kcal (Davidson corrected CISD) as the level of theory is improved. This energetic approach of the bent and linear structures parallels the approach of the bent and linear geometrical parameters as the theory moves toward completeness. Comparison of Tables I and II shows that the trend of electron correlation to reduce the RHF value of the bent–linear energy difference is

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(26) For example, the structure of the water molecule is only changed marginally [CISD r_e(OH) = 0.953 Å, θ_e(HOH) = 104.9°; Davidson corrected r_e(OH) = 0.957 Å, θ_e(HOH) = 104.6°] with a larger Slater basis set. See: B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.*, **65**, 4072 (1976).

Table III. Theoretical and Experimentally Inferred Values of the Quadratic Force Constants for the HCCN Triplet Ground State

	bent HCCN			linear HCCN			
force const	RHF	CI	Davidson	RHF	CI	Davidson	Dendramis and Leroi[6]
K_{CH}	6.49	6.37	6.20	7.08	6.79	6.55	5.57
K_{CC}	6.48	6.29	6.18	7.38	6.69	6.61	7.53
K_{CN}	22.90	18.43	16.27	21.89	16.53	13.42	12.24
$F_{CC,CN}$	0.69	1.25	1.66	1.46	2.76	3.32	2.84
$F_{CH,CC}$	−0.06	−0.12	−0.14	−0.06	−0.09	−0.06	−0.46
H_{CCH}	0.57	0.41	0.35	−0.47	−0.22	−0.15	0.11
H_{CCN}	0.44	0.37	0.34	0.46	0.40	0.35	0.31
$F''_{CCH,CCN}$	0.07	0.05	0.04	−0.11	−0.09	−0.08	−0.05
CH,CCH	0.11	0.12	0.11				
CC,CCH	0.35	0.40	0.45				
CC,CCN	0.02	0.02	0.02				
CN,CCN	0.02	0.07	0.07				
out-of-plane	0.45	0.38	0.36				

[a] Stretching force constants *K* and *F* are given in mdyn/Å; bending force constants H and F″ are presented in mdyn·Å.

Table IV. Theoretical and Experimental Vibrational Frequencies (in cm^{-1}) for HCCN and Three Isotopic Variations[a]

	Σ^+	Σ^+	Σ^+	Π	Π		A′	A′	A′	A′	A′	A″
						HCCN						
linear DZ+P SCF	3613	2444	1167	987i	483	bent DZ+P SCF	3447	2530	1086	1041	428	484
DZ+P CI	3535	2021	1134	684i	429	DZ+P CI	3418	2243	1080	885	394	
unlinked	3475	1758	1132	577i	402	unlinked	3372	2079	1080	793	377	
expt	3229	1735	1179	458	(370)[b]							
						DCCN						
linear DZ+P SCF	2688	2435	1128	779i	464	bent DZ+P SCF	2569	2501	1073	834	395	484
DZ+P CI	2623	2020	1096	541i	411	DZ+P CI	2528	2237	1054	723	361	
unlinked	2577	1758	1094	456i	386	unlinked	2495	2075	1046	656	343	
expt	2424	1730	1127	405	318							
						$HC^{13}CN$						
linear DZ+P SCF	3613	2386	1163	985i	471	bent DZ+P SCF	3447	2470	1082	1037	418	471
DZ+P CI	3550	1976	1129	683i	419	DZ+P CI	3418	2191	1077	881	385	
unlinked	3475	1721	1126	576i	392	unlinked	3372	2031	1076	789	368	
expt	3229	1698	1177	458	(365)[b]							
						$HCC^{15}N$						
linear DZ+P SCF	3613	2412	1157	986i	479	bent DZ+P SCF	3447	2497	1077	1040	425	481
DZ+P CI	3535	1993	1226	684i	427	DZ+P CI	3418	2215	1071	885	392	
unlinked	3475	1732	1125	577i	399	unlinked	3372	2052	1071	793	374	
expt	3229	1718	1168	458								

[a] All experimental frequencies are from Dendramis and Leroi.[6] Note that all theoretical predictions are restricted to the harmonic approximation, while the experimental results are the observed (anharmonic) fundamentals. [b] Uncertain experimental band.

independent of basis set, in that the DZ basis results[11] give the same qualitative prediction. The addition of polarization functions (DZ→DZ+P) actually increases the energy difference a bit, by 0.7 kcal at the RHF level and 0.8 kcal at the CISD level. One hopes that this bent–linear energy difference is stable (to within ~1 kcal) with respect to further extensions of the basis set. The simplest argument[27] would suggest that basis functions of higher angular momentum (additional d functions, f functions, etc. on the C and N atoms) would be slightly more important for the anisotropic bent HCN than for the linear structure.

D. Vibrational Frequencies. Beginning with each of the six predicted stationary points, enough additinal energies were calculated to determine all of the quadratic force constants. These results are compared with each other and with those deduced from experiment by Dendramis and Leroi[6] in Table III. It is to be emphasized that the theoretical and experimental force constants are *not* directly comparable. This is because the experimentally based force constants represent a truncated fit to the HCCN potential energy hypersurface. That is, Dendramis and Leroi neglected all cubic, quartic, etc. force constants and then fit the quadratic force constants to give best agreement with the observed fundamentals. So, in a certain sense the force constants of Dendramis and Leroi are "effective" quadratic force constants. The theoretical force constants are of course imperfect as well, due to the incompleteness of the three levels of theory employed. However, the reported results are the precise quadratic force constants for the three theoretical potential surfaces in question.

Table III shows a similar contrast between theory and "experiment" as that found for the HCCN geometrical structure. The C–N stretching force constant (16.3 mdyn/Å) is much larger than the experimentally deduced value (12.2 mdyn/Å), indicating as before a stronger CN bond from theory. The linear HCCN structure, although not the theoretical equilibrium geometry, shows a CN stretching force constant (13.4 mdyn/Å) in much better agreement with Dendramis and Leroi.[6] In an analogous fashion, the CC stretching force constant from theory (6.2 mdyn/Å) is less than that of Dendramis and Leroi (7.5 mdyn/Å); as before the linear structure gives an "improved" (relative to DL[6]) CC force constant, 6.6 mdyn/Å. These results confirm the view that the structure deduced by DL from experiment is significantly more allene-like (and less carbene-like) than the best theoretical picture to date for HCCN.

Predicted harmonic vibrational frequencies are compared with the observed fundamentals in Table IV. Since Dendramis and Leroi report vibrational frequencies for four isotopic HCCN molecules, theoretical predictions have been made for the same four nuclear mass variations. Perhaps the first observation to be made is that the theoretical and observed frequencies fall in the same general pattern for all four isotopic molecules. This provides

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solid evidence that the differences between theory and experiment are genuine and not the product of clerical error (in the case of theory) or misassignment (in the case of experiment). Since a systematic study of the reliability of harmonic vibrational frequencies at the DZ+P SCF and DZ+P CISD levels of theory has recently appeared,[28] one has a good idea what sort of agreement to expect between theory and experiment. For the closed-shell molecules HCN, H_2O, H_2CO, and CH_4 and DZ+P SCF and CI harmonic frequencies were an average 8.0% and 3.5% higher than the experimental harmonic frequencies. For HCCN of course the experimental harmonic frequencies are not known. However, harmonic vibrational frequencies tend to be of the order of 4% greater than the observed (anharmonic) frequencies.

The major discrepancy between theory and experiment occurs for the CN stretching frequency. The RHF, CI, and Davidson values for bent HCCN are 46%, 29%, and 20% larger than the observed fundamental at 1735 cm^{-1}. Similar comparisons are found for the other isotopic molecules. Since the CI stretching frequency is in error by more than 3 times the expected deviation from experiment, something extraordinary seems to be indicated. For the parent cyanide HCN, for example, the DZ+P CI harmonic CN stretching frequency[28] is 2224 cm^{-1} while the observed fundamental is at 2097 cm^{-1}. Possible explanations include the idea that anharmonicity effects (cubic and quartic force constants) may be much more important for HCCN than for more normal molecules. Should this be the case, of course, then DL's use of a quadratic force field to deduce the structure (and force constants) of HCCN is quite inappropriate. Another possibility is the idea that the argon matrix itself could result in large ($\sim$100 cm^{-1}) shifts in the vibrational frequencies relative to those expected for the gas-phase HCCN molecule. A final possibility, of course, is that the level of theory used to approach the problem was inadequate.

A less serious problem may appear in the comparison between theory and experiment for the C–C stretching frequencies. This frequency is remarkably invariant to the level of theory applied (assuming the DZ+P basis is used) and is always $\sim$100 cm^{-1} *less than* the observed fundamental at 1179 cm^{-1}. This of course is contrary to the usual finding that SCF and CISD frequencies are higher than the observed fundamentals. However, such a comparison is consistent with the hypothesis that our wave functions incorporate too little allene-like character.

The HCC harmonic bending frequencies are much larger than the observed fundamental at 458 cm^{-1}. However, the HCC bending is precisely the degree of freedom expected to be the most anharmonic, and thus the harmonic bending frequency should be much greater than the observed fundamental. As an example of a similar, very well-characterized gas-phase example, consider the lowest triplet state of formaldehyde. There the DZ+P RHF harmonic pyramidalization frequency[29] is 924 cm^{-1}, as compared to the observed fundamental[30] at 453 cm^{-1}.

Some idea of how extreme is the bending anharmonicity may be garnered by comparing the predicted barrier to linearity, 3.2 kcal, with the observed fundamental. In common units the barrier is 1120 cm^{-1}, while the $v = 2$ vibrational level of this normal mode is predicted to lie at 1145 cm^{-1}, assuming harmonic spacing. Since we show in the next section that the true barrier to linearity may be as low as 1.6 kcal, it is possible that only a single bending vibrational level lies below the energy of linear HCCN.

The primary point to be observed in the linear HCCN vibrational frequencies is that one of the degenerate (π) frequencies is imaginary. This confirms the fact that the linear structure is not a candidate for the equilibrium geometry at any of these three levels of theory. Instead the linear stationary point is a maximum with respect to CCH bending. Given this fact, it must also be noted that the theoretical linear CN stretching frequency (1758 cm^{-1}) is in close agreement with the observed fundamental at 1735 cm^{-1}! Furthermore, the CC stretching frequency for the linear structure is in better agreement (than the bent prediction for CC stretching) with the observed fundamental at 1179 cm^{-1}. The only way we can imagine this agreement (between linear and observed frequencies) having any basis in reality would involve the barrier to linearity being so small that the thermal motions of the molecule would be such as to yield a nearly linear vibrationally averaged structure.

Before closing this discussion it is worth noting that the DZ+P SCF vibrational frequencies have been predicted[31] earlier for the related (two more valence electrons)[32] quasi-linear molecule HCNO. HCNO is known from experiment[33] to have an equilibrium geometry that is linear to within $\pm 1°$, but the potential energy hypersurface is extremely flat with respect to HCN bending. HCNO, unlike HCCN, is predicted to be linear at the DZ+P SCF level of theory. Moreover the predicted harmonic vibrational frequencies[31] 3674, 2508, and 1294 cm^{-1} (Σ^+) and 612 and 591 cm^{-1} (Π) are all greater than the observed fundamentals[34] 3336, 2196, and 1254 cm^{-1} (Σ^+) and 538 and 224 cm^{-1} (Π). As expected, the predicted harmonic HCN bending frequency at 591 cm^{-1} is much greater than the observed anharmonic frequency at 224 cm^{-1}. Thus there is nothing in the comparison between theory and experiment for HCNO comparable to the differences reported here for HCCN.

Multiconfiguration SCF Studies

The comparison between theoretical and observed vibrational frequencies was sufficiently unsettling to press us to further theoretical explorations. Further stimulus was provided by the fact that the bent–linear energy difference decreases from 10.9 kcal at the DZ+P RHF level to only 3.2 kcal with the best treatment of electron correlation. This suggests that the restricted Hartree–Fock approximation[35] may be incapable of providing even a qualitatively reasonable description of the linear, allene-like HCCN. If the linear RHF HCCN orbitals are fundamentally flawed, then an exceptionally high level of theory might be required for an equivalent treatment of the bent and linear structures. Specifically, it might be necessary to include essentially all triply and quadruply excited configurations in a variational treatment.

With this background, it was decided to obtain multiconfiguration (MC) SCF wave functions[36] for two representative linear HCCN structures. Since the addition of polarization functions was found to have relatively little effect on the bent–linear energy difference, the MCSCF wave functions employed the smaller DZ basis. All single and double excitations (no frozen core or deleted virtual orbitals) relative to the SCF configuration

$$ {}^3\Sigma^- \quad 1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 5\sigma^2\, 6\sigma^2\, 7\sigma^2\, 1\pi^4\, 2\pi^2 \qquad (2) $$

were included. The actual calculations were carried out in the subgroup C_{2v}, in which there are 9759 ${}^3A_2$ configurations. The first structure is just the linear stationary point geometry of Figure 1 obtained with the Davidson corrected DZ+P CI method. The second linear structure was more truly allene-like, with $r(CH) = 1.070$ Å, $r(CC) = 1.290$ Å, and $r(CN) = 1.230$ Å.

For the first linear structure the SCF, straight CI (using canonical RHF orbitals), and MCSCF energies were −130.58969, −130.88149, and −130.88294 hartrees, respectively. The absolute energy lowering due to the optimization of orbitals via the MCSCF procedure is only 0.00145 hartrees or 0.91 kcal/mol. For the second linear structure the analogous energies were −130.58200, −130.87957, and −130.88137 hartrees. As expected, the energy lowering due to orbital optimization is greater here but still only 0.00183 hartrees or 1.13 kcal. Thus it seems likely that a complete

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Table V. Comparison of Unrestricted Hartree-Fock (UHF) and Experimental[6] Vibrational Frequencies (in cm^{-1}) for HCCN[a]

	Σ^+	Σ^+	Σ^+	Π	Π		A'	A'	A'	A'	A'	A''
linear 6-31G	3579	1658	1214	364	290i	bent 6-31G	3534	1685	1197	527	365	376
6-31G*	3587	1605	1264	409	433i	6-31G*	3522	1683	1213	656	380	409
UMP2/6-31G*	3509	1715	1215	514	556i	UMP2/6-31G*	3385	2284	1088	852	453	525
expt	3229	1735	1179	458	(370)[b]							

[a] The stationary point total energies are given in Table VI. [b] Uncertain experimental band; see ref 6.

Table VI. Total and Relative Energies of HCCN Linear and Bent Structures Using Spin-Unrestricted Wave Functions

		total energy, hartrees	rel energy, kcal/mol
linear	UHF/6-31G	-130.631 07	0.6
bent	UHF/6-31G	-130.632 06	0.0
linear	UHF/6-31G*	-130.678 17	1.5
bent	UHF/6-31G*	-130.680 64	0.0
linear	UMP4SDQ/6-31G*	-131.030 76[a]	1.6
bent	UMP4SDQ/6-31G*	-131.033 48[a]	0.0
linear	UMP4SDTQ/6-31G*	-131.042 95[a]	1.8
bent	UMP4SDTQ/6-31G*	-131.045 88[a]	0.0
linear	UMP4SDQ/6-31G**	-131.038 22[a]	1.9
bent	UMP4SDQ/6-31G**	-131.041 20[a]	0.0
linear	UMP4SDTQ/6-31G**	-131.050 58[a]	2.0
bent	UMP4SDTQ/6-31G**	-131.053 75[a]	0.0
linear	UMP2/6-31G*	-130.676 52[b]	0.3
bent	UMP2/6-31G*	-130.677 03[b]	0.0
linear	UMP4SDQ/6-31G**	-131.038 04[b]	1.9
bent	UMP4SDQ/6-31G**	-131.041 13[b]	0.0
linear	UMP4SDTQ/6-31G**	-131.050 48[b]	2.3
bent	UMP4SDTQ/6-31G**	-131.054 14[b]	0.0
linear	UMP4SDTQ/6-31G**	-131.050 98[c]	2.5
bent	UMP4SDTQ/6-31G**	-131.055 01[c]	0.0

[a] Uses UHF/6-31G* geometries. [b] Uses UMP2/6-31G* geometries. [c] Uses UMP4SDTQ/6-31G** geometries.

reoptimization of the structures in Figure 1 with the MCSCF method would provide some shift toward allene-like structures. However the energy lowering due to the complete optimization of orbitals is so small that it would probably not lower the final prediction of 3.2 kcal for the linear–bent energy difference by more than 0.5 kcal.

The Unrestricted Hartree–Fock Approximation as a Starting Point

Finally, it was decided to abandon the restricted Hartree–Fock (RHF) framework entirely and apply the unrestricted Hartree–Fock method of Pople and Nesbet.[37] For a system such as HCCN with six out of 12 possible π electrons occupied, differences between the RHF and UHF methods can be significant. Specifically, if we write the last six spin orbitals of configuration (2) as

$$\ldots 1\pi_x\alpha\, 1\pi_x\beta\, 1\pi_y\alpha\, 1\pi_y\beta\, 2\pi_x\alpha\, 2\pi_y\alpha \qquad (3)$$

then the RHF picture in principle requires all four 1π spin orbitals to be spatially equivalent. Similarly the two 2π spin orbitals are equivalent in a proper RHF wave function. In fact, the RHF wave functions reported here used only the subgroup C_{2v} (of the linear point group $C_{\infty v}$). That is, the actual RHF procedure involved the configuration

$$^3A_2 \quad 1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 6a_1^2 7a_1^2 1b_1^2 1b_2^2 2b_1\alpha\, 2b_2\alpha \qquad (4)$$

in which $1b_1$ is not required to be equivalent to $1b_2$, and $2b_1$ is not required to be equivalent to $2b_2$. In this sense one of the "restrictions" of the RHF method has been removed in the above-discussed research.

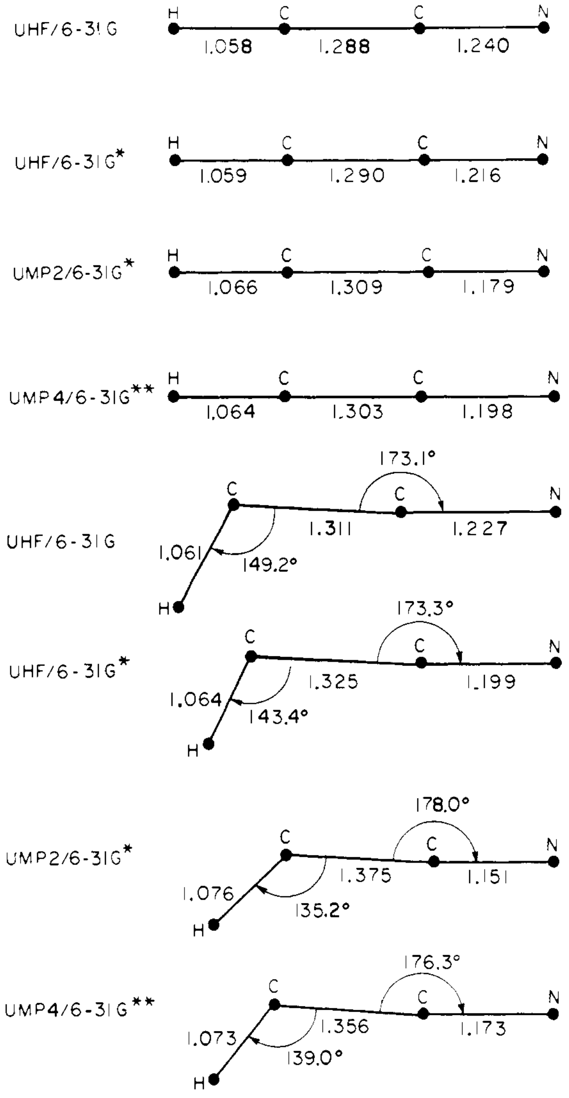

Figure 2. Unrestricted Hartree–Fock (UHF) based stationary point geometries for linear and bent HCCN. UMP4 designates full fourth-order perturbation theory with respect to a UHF starting point.

In the UHF wave functions obtained here, all four of the 1π spin orbitals ($1\pi_x\alpha$, $1\pi_x\beta$, $1\pi_y\alpha$, and $1\pi_y\beta$) may be spatially distinct. However, the $1\pi_x$ and $1\pi_y$ orbitals turn out to be spatially equivalent. In a certain sense this makes some allowance for the fact that the third π orbital, the 3π orbital, is unoccupied in the RHF picture. UHF stationary point structures and harmonic vibrational frequencies were obtained by using both 6-31G and 6-31G* basis sets, which are nearly comparable to the earlier discussed DZ and DZ+P basis sets. The predicted structures are seen in Figure 2, while the analogous vibrational frequencies for HCCN are given in Table V. Total energies are given in Table VI.

Turning first to the molecular structures, it is apparent that at the UHF/6-31G level of theory the bent structure is rather allene-like. The CC distance is 1.311 Å, certainly in the range of carbon–carbon double-bond character; the CN distance is 1.227 Å, about halfway between typical carbon–nitrogen double and

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(37) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

triple bonds. Note that this structure is significantly more allene-like than predicted by any of the six other levels of theory reported here. Even so, the bent structure lies below the corresponding linear geometry, although only by 0.6 kcal in this case.

With the larger polarized 6-31G* basis set, there is also a bent minimum point on the potential surface. The total UHF energies reported in Table VI show that this structure (Figure 2) lies 1.5 kcal/mol *below* the constrained linear structure. Further addition of correlation corrections to the UHF energies gives no evidence for any additional approach to linearity. Thus fourth-order Møller–Plesset calculations in the space of single, double, and quadruple substitutions (UMP4SDQ) at the UHF/6-31G* geometries give a very similar linear–bent difference of 1.6 kcal/mol (Table VI). The full fourth-order difference (including triple excitations as well) is slightly larger, 1.8 kcal. Therefore it appears that a major part of the correlation introduced for the RHF functions correct for the inadequate RHF treatment of spin polarization. At the UHF/6-31G* level of theory, the linear stationary point has two imaginary vibrational frequencies (a degenerate pair at 433i), consistent with the earlier presented RHF, CISD, and Davidson corrected CI predictions. Thus there is qualitative agreement concerning the equilibrium geometrical structure of HCCN at the four highest levels of theory discussed thus far.

The UHF/6-31G* HCC bond angle of 143.5° is 6.9° larger than that seen in Figure 1 at the highest level of RHF theory. The bond distances are in better agreement, the differences being 0.013 Å for the CC distance and 0.010 Å for the CN distance. Thus, the UHF/6-31G* structure is generally somewhat more allene-like than the Davidson corrected DZ+P CISD structure. The fact that the UHF/6-31G* bond distances are closer to the latter than are the DZ+P CISD distances gives credence to the idea that UHF may indeed be a better starting point for problems of this type than is RHF.

The UHF/6-31G* vibrational frequencies seen in Table V are in some respects quite different from those predicted via methods based on RHF molecular orbitals. Specifically the CN stretching frequency is significantly lower and the CC stretching frequency significantly higher than those obtained by usng RHF orbitals. Moreover, the agreement with experiment is better for these two frequencies than for the RHF methods, suggesting possible weaknesses inherent in the latter approaches for a quasilinear molecule such as HCCN. In fact the agreement between the UHF/6-31G* vibrational frequencies and DL's experiments is now good enough, even within the harmonic approximation, to state that the remaining discrepancies are not untypical of those routinely reported for theoretically better behaved molecules.

The structures and vibrational frequencies of bent and linear HCCN were also predicted by using second-order Møller–Plesset perturbation theory based on a UHF starting point, e.g., UMP2. The results are included in Tables V and VI and Figure 2. As with every other theoretical technique used here, this method predicts HCCN to have a bent equilibrium geometry. Moreover, the UMP/6-31G* equilibrium structure has an HCC bong angle of 135.2°, very close to the CISD and Davidson corrected results based on an RHF starting point. Furthermore, the CC (1.375 Å) and CN (1.151 Å) distances from UMP2 are now much more carbene-like (i.e., HC̈—C≡H) than the UHF results with the same basis. In fact the UMP2 bent structure is even more carbene-like than the Davidson corrected structure seen in Figure 1. Thus the UHF and RHF methods do appear to eventually converge in terms of structural predictions and the result is an HCC equilibrium bond angle of ~135°.

The UMP2/6-31G* energy difference bent and linear HCCN is 0.3 kcal. The most complete UHF-based level of theory using these stationary point geometries is full UMP4/6-31G** and provides an energy difference of 2.3 kcal. The latter result is seen to approach the 3.2 kcal predicted by the Davidson corrected DZ+P CI method (see Table II).

The vibrational frequencies (Table V) from second-order perturbation theory based on a UHF starting point also agree with the final RHF-based predictions. The only difference greater than 100 cm^{-1} occurs for the CN stretching frequency, which is 2284 cm^{-1} for UMP2 and 2079 cm^{-1} for Davidson corrected DZ+P CISD. This agreement is encouraging in the sense that one expects different theoretical approaches to ultimately converge as each is pressed closer and closer to completeness. On the other hand, the "converged" theoretical vibrational frequency for the CN stretch is still not in satisfactory agreement with the observed value.[6]

Finally, the stationary point geometries of bent and linear HCCN were optimized (see Figure 2) by using complete fourth-order perturbation theory (UMP4) and the 6-31G** basis set. To our knowledge this is the largest system (four atoms, 20 electrons, 50 basis functions) for which complete UMP4 geometrical determinations have been reported. The HCC equilibrium angle for the bent structure is 139.0°, compared to the UMP2 value (135.2°) and the best CI-based result, 136.6°. The bent bond distances $r_e(CC) = 1.356$ Å and $r_e(CN) = 1.173$ Å show the UMP4 structure to be somewhat more allene-like than the UMP2 geometry but less so than the UHF structure.

The linear UMP4 6-31G** structure lies 2.5 kcal above the just reported bent equilibrium geometry. The agreement with the 3.2 kcal predicted at the DZ+P Davidson corrected CI level is excellent and may be taken as reasonably indicative that we are approaching the limiting results for this type of basis set.

Conclusions

For some time now, the structure of HCCN has been a matter of considerable interest.[4-9,11-14] Perhaps this "controversy" is something of a red herring, inasmuch as the structure of HCCN has not been determined experimentally. With this perspective we have made theoretical predictions of the vibrational frequencies of four isotopic variants of HCCN. The agreement with experiment is generally poorer than is the case for closed-shell singlet molecules for which comparable theory and reliable experiments are available. The highest levels of theory predict HCCN to be bent, with the linear allene-like structure lying only about 2 kcal higher in energy. This result does not appear to be consistent with the indirect inference from EPR and infrared studies that HCCN is linear.

What conclusions can we draw concerning the structure of HCCN? It would appear to us that at least three eventual outcomes are possible:

(1) The levels of theory used here, although approaching state-of-the-art 1982, are inadequate. Given the small bent–linear energy difference, this possiblity cannot be ruled out. However, CI and high-level perturbation theory agree for DZ+P-like basis sets that HCCN is bent. Therefore we feel that basis set incompleteness is the most significant potential source of error in the theoretical predictions reported here.

(2) The harmonic approximation is inadequate for describing the vibrational frequencies of a quasi-linear molecule such as HCCN, and thus our comparison with experiment is not valid. Should this be the case, then Dendramis and Leroi's use[6] of the harmonic approximation to deduce the structure of HCCN may not be completely satisfactory.

(3) For some reason not yet understood, the argon matrix used to isolate HCCN exerts an influence which gives the molecule a different equilibrium geometry than would be observed in the gas phase.

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