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Ab Initio Heat of Formation and Singlet−Triplet Splitting for Cyanocarbene (HCCN) and Isocyanocarbene (HCNC)

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The heat of formation and singlet−triplet splitting for cyanocarbene (HCCN) and isocyanocarbene (HCNC) have been determined in large-scale ab initio calculations, using the coupled-cluster method and basis sets of double- through quintuple-zeta quality. The heats of formation at 0 K for X^3A'' HCCN and X^1A' HCNC are predicted to be 116.8 and 140.5 kcal/mol, respectively, with the uncertainty estimated to be ±2 kcal/mol or less. These values are substantially larger than those derived recently from experimental data, suggesting that the true values of the heats of formation must be at the upper end of their (large) experimental ranges. The singlet−triplet splittings are calculated to be 10.8 and 1.3 kcal/mol for HCCN and HCNC, respectively, with both values being in good agreement with the experimental data. The biradical nature of both molecules is discussed, on the basis of the results of calculations using the multireference methods.

1. Introduction

The experimental values of the heat of formation for cyanocarbene (HCCN) and isocyanocarbene (HCNC) have not been known until recently.[1,2] On the basis of the collision-induced dissociation experiment for the $ClCHCN^-$ anion, Poutsama et al.[1] determined the heat of formation at 298 K for HCCN to be 115.6 ± 5 kcal/mol. Using negative-ion photoelectron spectroscopy, Nimlos et al.[2] determined the heat of formation at 0 K to be 110 ± 4 kcal/mol for HCCN and 133 ± 5 kcal/mol for HCNC. The ground electronic state of HCCN is a triplet A'' state, whereas that of HCNC is a singlet A' state (in the C_s symmetry point group). For HCCN, the singlet−triplet splitting has been found experimentally to be 11.1 ± 5.8 kcal/mol[1] and 11.9 ± 0.3 kcal/mol.[2] For HCNC, the singlet−triplet splitting was determined to be an order of magnitude smaller, being only 1.4 ± 0.6 kcal/mol.[2]

The theoretical studies on cyanocarbene[3−12] focused on the problem of a ground-state equilibrium structure of the HCCN molecule, and those on HCNC are rather sparse.[9,11,13] The energetics of HCCN were investigated by Francisco.[10] At the highest level of theory applied in that study, QCISD(T)/6-311G-(3df,3pd)//QCISD(T)/6-311G(2d,2p),[14,15] the heat of formation at 0 K for X^3A'' HCCN was calculated to be 114.8 kcal/mol, and the singlet−triplet splitting was found to be 11.6 kcal/mol. Both calculated values are in reasonable agreement with the recent experimental data.[1,2] However, Francisco[10] noted that the theoretical values depend substantially on the calculated equilibrium geometries, the one-particle basis set applied, and the extent of electron correlation that is accounted for, with differences between the calculated values being as large as 10 kcal/mol. Using the G2 approach,[16] the heat of formation and singlet−triplet splitting were determined[10] to be 117.4 and 8.2 kcal/mol, respectively. In a recent study, Nimlos et al.[2] calculated the heat of formation at 0 K for X^3A'' HCCN to be 107.3 and 108.4 kcal/mol at the CBS-APNO[17] and CBS-QB3[18] levels of theory, respectively. The corresponding values of the singlet−triplet splitting were determined to be 13.2 and 12.9 kcal/mol, respectively. Results of similar calculations were reported by Poutsma et al.[1] (these authors quoted only the values derived at 298 K). For X^1A' HCNC, Nimlos et al.[2] calculated the heat of formation at 0 K to be 130.6 and 131.1 kcal/mol at the CBS-APNO and CBS-QB3 levels of theory, respectively. The corresponding values of the singlet−triplet splitting were determined to be 1.8 and 3.3 kcal/mol, respectively.

The present work was undertaken as an extension of the author's previous study,[12] with the aim of gaining a deeper insight into the energetics of HCCN and related species. In this paper, we report the results of calculations performed by the single-reference coupled-cluster method and systematically expandable correlation-consistent polarized basis sets, up to spdfgh quality. This approach, in conjunction with various extrapolation techniques, was shown[19] to be a remarkably powerful ab initio technique for computing molecular properties—especially the structure and energetics—to high accuracy.

2. Method of Calculation

The molecular parameters of cyanocarbene and related species were calculated using the coupled-cluster method, including single and double excitations, and a perturbational correction that was due to connected triple excitations (CCSD(T)).[20−24] For open-shell species, the spin-restricted method (RCCSD(T)) was applied,[25−27] with the spin-restricted Hartree−Fock (RHF) molecular orbitals being used as a reference wave function. The one-particle basis sets were the correlation-consistent polarized valence basis sets (cc-pV*n*Z).[28] The quality of the basis sets ranged from double zeta (*n* = D) to quintuple zeta (*n* = 5). The largest basis set employed, cc-pV5Z, consists of a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for carbon and nitrogen, and a (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen. Only the spherical harmonic components of the d through h polarization functions were used. In the correlation treatment, the 1s-like core orbitals of the C and N atoms were excluded from the active space. The accuracy of the results obtained with increasing quality of the one-particle basis set can be conveniently estimated, assuming monotonic convergence of the calculated

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properties toward the limit of an infinite basis set. The complete-basis-set (CBS) limits can be determined using various extrapolation techniques.[29−33] The best estimate of a molecular parameter was obtained in this study by averaging the CBS limit values calculated with the exponential,[29] exponential/Gaussian,[30] and two Schwartz-type[31−33] extrapolation formulas. The root-mean-square deviation of the average was used as an estimate for extrapolation accuracy.

The core−electron correlation effects were investigated using the correlation-consistent polarized core-valence basis set of quadruple-zeta quality (cc-pCVQZ).[34] In the correlation treatment involving the core and valence electrons, all the molecular orbitals were included in the active space.

The scalar relativistic corrections to the molecular and atomic total energies were determined as expectation values of the mass−velocity and one-electron Darwin contact term integrals.[35] The calculations were performed using the single-reference configuration interaction method including single and double excitations (CISD), with the cc-pCVQZ basis set. The computed atomization energies were also corrected for atomic zero-field spin−orbit splittings. The corrections[36] amounted to −0.08 kcal/mol per C atom and 0.00 kcal/mol per N atom. The molecular spin−orbit matrix elements between pairs of interacting singlet and triplet states were calculated using the full Breit-Pauli operator.[37]

The calculations were performed using the MOLPRO-2000 package of ab initio programs.[38] Some calculations were also performed using the Gaussian 98[39] and MOLCAS-4[40] packages.

3. Results and Discussion

It is instructive to consider first the parent species: methylene (CH_2). The CH_2 molecule has been the subject of considerable experimental and theoretical interest (see the works of Peterson and Dunning,[41] Sherrill et al.,[42] and Gu et al.,[43] and references therein). A comparison of the results of these high-level studies should provide a realistic assessment of the accuracy of the theoretical methods applied in this work for HCCN and HCNC.

The ground electronic state of CH_2 is a triplet B_1 state (in the C_{2v} symmetry point group). From analysis of the photoelectron spectrum of the CH_2^- anion,[44] the heat of formation at 0 K for X^3B_1 CH_2 was determined to be $\Delta H_f^\circ = 92.8 \pm 0.6$ kcal/mol. This value was derived using the heat of formation at 0 K for a^1A_1 CH_2, 101.8 ± 0.5 kcal/mol.[45,46] The vibrationless singlet−triplet splitting (T_e) was derived from experimental spectroscopic data to be 3159 cm^{-1}.[43] In the present work, the equilibrium molecular parameters for the X^3B_1 and a^1A_1 states of CH_2 were calculated at the RCCSD(T)/cc-pV*n*Z level of theory, and the results were found to be identical with those of previous theoretical studies.[34,41,42] For X^3B_1 CH_2, the vibrationless total atomization energy ($\sum D_e$) was determined to be 186.63, 188.79, and 189.39 kcal/mol for n = T, Q, and 5, respectively. The CBS limit for the total atomization energy was then estimated to be $\sum D_e = 189.8 \pm 0.2$ kcal/mol. The singlet−triplet energy difference (ΔE_{ST}) was calculated to be 3556, 3322, and 3237 cm^{-1} for n = T, Q, and 5, respectively, and its CBS limit was estimated to be $\Delta E_{ST} = 3169 \pm 20$ cm^{-1}. The estimated values can be compared with those calculated at various levels of theory (see Table VI of ref 42). In particular, Comeau et al.[47] calculated the total atomization energy and singlet−triplet energy difference by the multireference configuration interaction method, in conjunction with an atomic-natural-orbital basis set (MRCI/ANO).[48,49] The total atomization energy was predicted there to be 189.7 and 190.6 kcal/mol by the MRCI and MRCI+Q approaches, respectively. The corresponding singlet−triplet energy differences were found to be 3243 and 3199 cm^{-1}. Very similar results were also reported by Bauschlicher et al.[50] For both X^3B_1 and a^1A_1 states, Sherrill et al.[42] found that the equilibrium structural parameters of methylene were essentially identical, using the coupled-cluster and full configuration interaction (FCI) approaches. With the basis set of triple-zeta quality (TZ2P), the singlet−triplet energy difference was determined[42] to be 3990 and 3897 cm^{-1} by the CCSD(T) and FCI methods, respectively.

Inclusion of the core−electron correlation effects at the RCCSD(T)/cc-pCVQZ level of theory increases the total atomization energy of X^3B_1 CH_2 by 0.76 kcal/mol and the singlet−triplet energy difference by 135 cm^{-1}. Concerning the singlet−triplet energy difference, similar corrections due to the core-related effects were predicted using the MRCI and MRCI+Q methods; these values were +145 cm^{-1},[34] +158 cm^{-1},[47] and +122 cm^{-1}.[50] Employing a sequence of the cc-pCV*n*Z basis sets, Woon and Dunning[34] determined this correction to be +153 cm^{-1} at the RCCSD(T)/CBS level of theory.

The calculated scalar relativistic corrections to total energies appeared to be quite insensitive to the extent of electron correlation that was accounted for. For the total atomization energy of X^3B_1 CH_2, the correction was determined by the RHF, CISD, and icMRCI[51,52] approaches to be −0.17, −0.15, and −0.15 kcal/mol, respectively. The spin−orbit constant for the X^3B_1 and a^1A_1 pair of states of CH_2 was predicted in this study to be 7.2 and 7.7 cm^{-1}, using the CISD and icMRCI methods, respectively, both in conjunction with the uncontracted cc-pVTZ basis set. Therefore, the molecular zero-field spin−orbit splitting is negligible and only the atomic corrections to the total energies must be applied. Inclusion of the scalar relativistic corrections decreased the singlet−triplet energy difference by 24, 22, and 21 cm^{-1}, using the RHF, CISD, and icMRCI approaches, respectively. Very similar corrections were determined in previous theoretical studies.[50,53]

Assuming additivity of all the previously mentioned corrections, the vibrationless total atomization energy of X^3B_1 CH_2 is predicted in this study to be $\sum D_e = 190.3 \pm 0.2$ kcal/mol at the RCCSD(T) level of theory. Similarly, the vibrationless singlet−triplet splitting is predicted to be $T_e = 3280 \pm 20$ cm^{-1}. The latter value can be compared with the best CBS estimates by Woon and Dunning:[34] 3315, 3218, and 3137 cm^{-1}, as determined at the RCCSD(T), icMRCI, and icMRCI+Q levels, respectively. To account for the zero-point vibrational energy contributions, the harmonic force field and frequencies for both the X^3B_1 and a^1A_1 states of CH_2 were calculated in this study at the RCCSD(T)/cc-pVTZ level of theory. The harmonic zero-point energy (ZPE) was predicted to be 3807 and 3651 cm^{-1} for the X^3B_1 and a^1A_1 states, respectively. Enlarging the one-particle basis set to cc-pVQZ leads to the corresponding ZPE values of 3808 and 3661 cm^{-1}. The anharmonic zero-point energies were derived from experimental data to be 3689 cm^{-1} for the X^3B_1 state[54] and 3701 cm^{-1} for the a^1A_1 state.[43] Therefore, neglecting vibrational anharmonicity introduces an additional error of ~0.3 kcal/mol to the total atomization energy. Including the calculated zero-point vibrational energy, the total atomization energy of X^3B_1 CH_2 is predicted to be $\sum D_0 = 179.4 \pm 0.5$ kcal/mol. This value can be combined with the experimental heats of formation at 0 K for gaseous atoms,[55] leading to the heat of formation for CH_2, which is calculated, in this way, to be $\Delta H_f^\circ = 93.8 \pm 0.5$ kcal/mol and 102.8 ± 0.5 kcal/mol for the X^3B_1 and a^1A_1 states, respectively. The theoretical predictions agree favorably with the corresponding experimental

TABLE 1: Equilibrium Molecular Parameters of HCCN, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets[a]

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
		X^3A'' [b]		
r(HC) (Å)	1.0895	1.0718	1.0709	1.0706
r(CC) (Å)	1.3607	1.3356	1.3317	1.3309
r(CN) (Å)	1.2036	1.1918	1.1886	1.1879
$\angle$(HCC) (deg)	140.49	144.08	144.55	144.56
$\angle$(CCN) (deg)	175.06	175.21	175.32	175.33
energy + 131 (hartree)	−0.072987	−0.187281	−0.221910	−0.232458
		a^1A'		
r(HC) (Å)	1.1179	1.0999	1.0985	1.0981
r(CC) (Å)	1.4172	1.3959	1.3918	1.3908
r(CN) (Å)	1.1956	1.1821	1.1786	1.1780
$\angle$(HCC) (deg)	107.47	108.92	109.24	109.34
$\angle$(CCN) (deg)	171.76	172.20	172.29	172.33
ΔE_{ST}[c] (cm^{-1})	4186	3836	3699	3641

[a] The equilibrium structure is planar, with the trans conformation of the HCCN chain. [b] From ref 12. [c] ΔE_{ST} is the energy difference between the equilibrium configurations of a^1A' and X^3A'' HCCN.

heats of formation at 0 K of 92.8 ± 0.6 kcal/mol (from ref 44) and 101.8 ± 0.5 kcal/mol (from refs 45 and 46). The remaining discrepancy is predominately due to neglect of vibrational anharmonicity and, as shown by Bak et al.,[56] the incomplete treatment of connected triple excitations and neglect of higher connected excitations in the CCSD(T) approach. The singlet−triplet splitting of the zero-point energy levels (T_0) is predicted to be 3130 ± 20 cm^{-1}, compared to the experimental value[54] of 3147 cm^{-1}.

Turning to the main subject of this study, Table 1 lists the equilibrium molecular parameters calculated for the first excited singlet state (a^1A') of HCCN. The molecular parameters determined for the ground $^3A''$ state[12] are also given for comparison. Using these data, the singlet−triplet energy difference for HCCN is predicted to be slightly larger than that for the parent CH_2 molecule. As expected from the results for the parent species, the HCCN molecule is well bent in the first excited singlet state.

The vibrationless total atomization energy for the ground $^3A''$ state of HCCN was determined to be 384.06, 392.16, and 394.68 kcal/mol for n = T, Q, and 5, respectively. The CBS limit for the total atomization energy was then estimated to be $\sum D_e$ = 396.5 ± 0.6 kcal/mol. It is worth noting that the CBS limit value differs from the best directly computed value ($n = 5$) by only 1.8 kcal/mol. Inclusion of the core−electron correlation effects was found to increase the total atomization energy by 2.37 kcal/mol. The correction for the scalar relativistic effects, including the atomic spin−orbit splittings, was calculated to be −0.56 kcal/mol. As for CH_2, the molecular zero-field spin−orbit splitting appeared to be negligible, because the spin−orbit constant for the X^3A'' and a^1A' pair of states was predicted to be only 7.2 cm^{-1}. Thus, the best estimate of the vibrationless total atomization energy for X^3A'' HCCN is $\sum D_e$ = 398.3 ± 0.6 kcal/mol. The harmonic zero-point vibrational energy for the ground $^3A''$ state was determined by the RCCSD(T) method to be 3868 and 3864 cm^{-1} with the cc-pVTZ and cc-pVQZ basis sets, respectively. Comparing the calculated harmonic vibrational frequencies (see Table 10 of ref 12) with the experimental fundamentals,[57,58] a maximum error of 0.3 kcal/mol can be assigned to the calculated zero-point energy. Therefore, the total atomization energy for X^3A'' HCCN is predicted to be $\sum D_0$ = 387.3 ± 0.9 kcal/mol. Combining this value with the experimental heats of formation for gaseous atoms,[55] the heat of formation at 0 K is calculated in this study to be ΔH_f° = 116.8 ± 0.9 kcal/mol. The predicted heat of formation for X^3A'' HCCN is substantially larger than the experimental values of 110 ± 4 kcal/mol (from ref 2) and 112.6 ± 5 kcal/mol (from ref 1) (the reported 298 K value is converted to 0 K by us, using the calculated molecular parameters). Compared with the previous ab initio calculated values, the heat of formation for X^3A'' HCCN predicted here is consistent with the best estimates of Francisco:[10] 114.8 kcal/mol (QCISD(T)/6-311G(3df,3pd)) and 117.4 kcal/mol (G2). However, it is much larger than the best values of Nimlos et al.:[2] 107.3 kcal/mol (CBS-APNO) and 108.4 kcal/mol (CBS-QB3). Such large differences are quite disappointing, because the CBS-APNO and CBS-QB3 methods of Petersson and co-workers[17,18] and the theoretical approach applied in this study all are expected to be accurate to within approximately ±1 kcal/mol, on average. It must be noted that both the experimental and theoretical value of the heat of formation derived by Nimlos et al.[2] are based on the acidity/electron-affinity (EA) thermodynamic cycle involving the molecules CH_3CN, CH_2CN, and HCCN, as well as the corresponding anions. The approach based on the total atomization energy results in somewhat different thermodynamic information. Using the CBS-APNO method,[17] the total atomization energy for X^3A'' HCCN is predicted here to be $\sum D_0$ = 389.6 kcal/mol, leading to the heat of formation at 0 K of ΔH_f° = 114.5 kcal/mol. The latter value is 7.2 kcal/mol larger than that calculated from the acidity/EA thermodynamic cycle,[2] and it is nicely consistent with our best estimate.

The CBS limit for the energy difference between the X^3A'' and a^1A' states of HCCN is estimated in this study to be ΔE_{ST} = 3587 ± 17 cm^{-1}, compared to that for CH_2 of 3169 ± 20 cm^{-1}. The correction for the core−electron correlation effects was calculated to be +140 cm^{-1}, whereas that for the scalar relativistic effects was calculated to be −25 cm^{-1}. Thus, the best estimate of the vibrationless singlet−triplet splitting is T_e = 3702 ± 20 cm^{-1}. The harmonic zero-point vibrational energy for the excited $^1A'$ state was calculated at the CCSD(T)/cc-pVTZ level of theory to be 3929 cm^{-1}, leading to singlet−triplet splitting of the zero-point energy levels of T_0 = 3763 ± 20 cm^{-1} (10.8 ± 0.1 kcal/mol). The predicted T_0 splitting for HCCN is somewhat lower than the experimental values of 11.1 ± 5.8 kcal/mol (from ref 1) and 11.9 ± 0.3 kcal/mol (from ref 2). It is midway between the previous theoretical estimates of 7.6 and 9.9 kcal/mol (G2),[1] 8.2 kcal/mol (G2),[10] 11.0 and 11.9 kcal/mol (CBS-Q),[1] 11.6 kcal/mol (QCISD(T)/6-311G-(3df,3pd)),[10] 12.9 kcal/mol (CBS-QB3),[2] and 13.2 kcal/mol (CBS-APNO).[2]

Table 2 lists the equilibrium molecular parameters calculated for HCNC. Except for the smallest one-particle basis set (cc-pVDZ), the ground electronic state of the HCNC molecule was predicted to be a singlet A' state and the triplet A'' state was computed to lie ∼400 cm^{-1} above the ground state. For the cc-pVDZ basis set, the two states switch, being of essentially identical total energy. For both states, the HCNC molecule is well bent. At the RCCSD(T)/cc-pVnZ level of theory, the barrier to linearity for the $^3A''$ state was predicted to be 3450, 2977, 2876, and 2846 cm^{-1} for n = D, T, Q, and 5, respectively. Thus, the barrier to linearity for a^3A'' HCNC is ∼9 times higher than that for X^3A'' HCCN. In contrast to the quasi-linear X^3A'' HCCN molecule,[59] the a^3A'' HCNC molecule is predicted to be close to the limit of a semirigid bent molecule with a moderately anharmonic bending potential energy function. This is consistent with the results of previous ab initio studies on HCNC, in which the barrier to linearity for the $^3A''$ state was determined to be 2170 cm^{-1} (CISD+Q//QCISD(T)/D95(d,p)),[9]

TABLE 2: Equilibrium Molecular Parameters of HCNC, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets[a]

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
		X^1A'		
r(HC) (Å)	1.1242	1.1064	1.1050	1.1045
r(CN) (Å)	1.3454	1.3297	1.3254	1.3247
r(NC) (Å)	1.2198	1.2044	1.2008	1.2002
$\angle$(HCN) (deg)	105.31	106.18	106.42	106.46
$\angle$(CNC) (deg)	170.64	171.35	171.37	171.32
energy + 131 (hartree)	−0.034291	−0.149712	−0.184993	−0.195734
		a^3A''		
r(HC) (Å)	1.0955	1.0789	1.0780	1.0778
r(CN) (Å)	1.3158	1.2994	1.2952	1.2945
r(NC) (Å)	1.2194	1.2046	1.2013	1.2007
$\angle$(HCN) (deg)	129.41	130.40	130.53	130.51
$\angle$(CNC) (deg)	173.20	173.77	173.76	173.70
ΔE_{ST}[b] (cm^{-1})	−19	304	417	467

[a] The equilibrium structure is planar, with the trans conformation of the HCNC chain. [b] ΔE_{ST} is the energy difference between the equilibrium configurations of a^3A'' and X^1A' HCNC.

2410 cm^{-1} (CCSD(T)//CISD/TZ2P(f,d)),[13] and 2690 cm^{-1} (CBS-QB3).[2]

The vibrationless total atomization energy for the ground $^1A'$ state of HCNC was determined to be 360.49, 368.99, and 371.63 kcal/mol for n = T, Q, and 5, respectively. The CBS limit for the total atomization energy was then estimated to be $\sum D_e$ = 373.5 ± 0.6 kcal/mol. The correction for the core−electron correlation effects was calculated to be +1.69 kcal/mol. The correction for the scalar relativistic effects, including the spin−orbit splittings, was calculated to be −0.52 kcal/mol. Thus, the best estimate of the vibrationless total atomization energy for X^1A' HCNC is $\sum D_e = 374.7 \pm 0.6$ kcal/mol. The harmonic zero-point vibrational energy for the ground electronic state of HCNC was calculated at the CCSD(T)/cc-pVTZ level of theory to be 3897 cm^{-1}. Therefore, the total atomization energy for X^1A' HCNC is predicted in this study to be $\sum D_0 = 363.6 \pm 0.9$ kcal/mol, leading to the heat of formation at 0 K of $\Delta H_f^\circ = 140.5 \pm 0.9$ kcal/mol. As in the case of HCCN, the predicted heat of formation for X^1A' HCNC is much larger than the recent experimental value of Nimlos et al.[2] (133 ± 5 kcal/mol), as well as the best theoretical values therein (130.6 kcal/mol (CBS-APNO) and 131.1 kcal/mol (CBS-QB3)). However, using the CBS-APNO method,[17] the total atomization energy for X^1A' HCNC is predicted here to be $\sum D_0 = 364.2$ kcal/mol, leading to a heat of formation at 0 K of $\Delta H_f^\circ = 139.9$ kcal/mol. The latter value is 9.3 kcal/mol larger than that calculated from the acidity/EA thermodynamic cycle.[2] For both X^3A'' HCCN and X^1A' HCNC, the CBS-APNO method[17] and the theoretical technique applied in this study thus yield similar estimates of the heats of formation within the atomization energy approach.

Although the recent experimental values of the heat of formation for HCCN[1,2] and HCNC[2] carry large error bars, the substantial differences between these values and the theoretical predictions of this study are quite surprising. For X^3A'' HCCN, the predicted heat of formation at 0 K, $\Delta H_f^\circ = 116.8 \pm 0.9$ kcal/mol, is located at the upper end of the experimental range of 112.6 ± 5 kcal/mol that was determined by Poutsama et al.[1] However, it is clearly above the upper limit of the experimental value of 110 ± 4 kcal/mol that was reported by Nimlos et al.[2] As just mentioned, this is also the case for X^1A' HCNC. For a molecule of this size, it is still difficult to estimate the correlation energy corrections that are not accounted for by the CCSD(T) approach applied in this study. The results of recent benchmark calculations for some diatomic molecules[56,60] indicate that the corrections to a dissociation energy are of the order of ±1 kcal/mol. Interestingly, among 11 molecules that were studied by Feller and Sordo,[60] the two most problematic cases were found to be C_2 and CN. The differences in a dissociation energy between the best FCI estimate and the CCSD(T) calculated value, both with the cc-pVTZ basis set, were determined to be 1.1 and 1.4 kcal/mol for the C_2 and CN molecules,[60] respectively. The coupled-cluster T_1 diagnostics[61] were determined to be 0.039 and 0.054 for the C_2 and CN molecules, respectively, thus indicating the strong nondynamical correlation effects for the CN radical. For the X^3A'' HCCN and X^1A' HCNC molecules, the T_1 diagnostics were calculated in this study to be 0.034 and 0.019, respectively. Therefore, the nondynamical correlation effects can be expected to be weaker than those for the C_2 molecule (see below). It is also reasonable to conclude that the cumulative effect of the higher excitations that are not accounted for by the CCSD(T) approach may introduce, in this case, a maximum error of approximately ±2 kcal/mol to the atomization energies (±1 kcal/mol each for the CC and CN bonds) and, hence, the calculated heats of formation. As shown by Peterson and Dunning,[41] the effect of the higher excitations is <0.2 kcal/mol for the CH bond dissociation energy. This suggests a quite conservative error estimate of ±2 kcal/mol for the heats of formation determined in this work. We thus believe that, for the X^3A'' HCCN and X^1A' HCNC molecules, the true values of the heats of formation must be located at the upper end of their experimental ranges.[1,2] It is worth noting that the relative energy of the zero-point energy levels of the ground electronic states for the HCCN and HCNC molecules is predicted in this study to be 23.7 kcal/mol, which is in good agreement with the experimental value of 23 kcal/mol.[2]

The CBS limit for the energy difference between the X^1A' and a^3A'' states of HCNC is estimated in this study to be ΔE_{ST} = 516 ± 17 cm^{-1}. The correction for the core−electron correlation effects was calculated to be −141 cm^{-1}, whereas that for the scalar relativistic effects was calculated to be +29 cm^{-1}. It is worth noting that these corrections are essentially identical (in absolute value) to those for HCCN: they just have opposite signs, because of reversed ordering of the singlet and triplet states. Thus, the best estimate of the vibrationless singlet−triplet splitting is $T_e = 404 \pm 20$ cm^{-1}. The harmonic zero-point vibrational energy for the excited $^3A''$ state was calculated at the RCCSD(T)/cc-pVTZ level of theory to be 3956 cm^{-1}, leading to a singlet−triplet splitting of the zero-point energy levels of $T_0 = 463 \pm 20$ cm^{-1} (1.3 ± 0.1 kcal/mol). The predicted T_0 splitting for HCNC agrees with the experimental value of 1.4 ± 0.6 kcal/mol,[2] to within the error bars. It is also consistent with the best theoretical values of Nimlos et al.[2] (1.8 kcal/mol (CBS-APNO) and 3.3 kcal/mol (CBS-QB3)).

Considering the large differences between the theoretical and experimental values of the heats of formation for HCCN and HCNC, it was also interesting to calculate the EAs of both species. This was a key experimental quantity used by Nimlos et al.[2] to derive the heat of formation for the HCCN and HCNC molecules by the acidity/EA thermodynamic cycle. The equilibrium molecular parameters for the ground electronic state (X^2A'') of the $HCCN^-$ and $HCNC^-$ anions are given in Table 3. For both species, the energy difference between the equilibrium configurations of the anion and corresponding neutral molecule was found to be quite sensitive to the size of the one-particle basis set. The relatively slow convergence of the energy differences is likely due to the lack of diffuse functions in the one-particle basis sets for the anions. The CBS limit values for the energy differences were estimated to be 48.5 ± 0.8 and

TABLE 3: Equilibrium Molecular Parameters of the X^2A'' $HCCN^-$ and $HCNC^-$ Anions, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets[a]

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
		$HCCN^-$		
r(HC) (Å)	1.1284	1.1056	1.1028	1.1014
r(CC) (Å)	1.4179	1.3944	1.3895	1.3883
r(CN) (Å)	1.2072	1.1944	1.1915	1.1913
∠(HCC) (deg)	106.25	108.03	108.70	109.07
∠(CCN) (deg)	172.87	173.24	173.44	173.48
energy + 131 (hartree)	−0.116650	−0.250127	−0.292269	−0.306280
ΔE^b (kcal/mol)	27.40	39.44	44.15	46.32
		$HCNC^-$		
r(HC) (Å)	1.1395	1.1156	1.1125	1.1104
r(CN) (Å)	1.3994	1.3795	1.3724	1.3698
r(NC) (Å)	1.2130	1.1976	1.1942	1.1936
∠(HCN) (deg)	102.65	103.91	104.47	104.85
∠(CNC) (deg)	172.53	173.01	173.07	173.10
energy + 131 (hartree)	−0.074128	−0.205804	−0.247330	−0.261612
ΔE^b (kcal/mol)	25.00	35.20	39.12	41.34

[a] Both equilibrium structures are planar, with the trans conformations. [b] ΔE is the energy difference between the equilibrium configurations of the anion and neutral parent species (X^3A'' HCCN or X^1A' HCNC).

43.5 ± 0.7 kcal/mol for HCCN and HCNC, respectively. The harmonic zero-point vibrational energies were calculated at the RCCSD(T)/cc-pVTZ level of theory to be 3929 and 3815 cm^{-1} for the $HCCN^-$ and $HCNC^-$ anions, respectively. Using the zero-point vibrational energies of the neutral parent species, the valence-only adiabatic EAs for HCCN and HCNC were derived to be 48.3 and 43.7 kcal/mol, respectively. The corresponding total corrections for the core−electron correlation and scalar relativistic effects were calculated to be −0.2 and +0.2 kcal/mol, respectively. Thus, the best estimates for the adiabatic EA at 0 K for HCCN and HCNC are 48.1 ± 0.8 and 43.9 ± 0.7 kcal/mol, respectively. The corresponding experimental values were determined by Nimlos et al.[2] to be 46.2 ± 0.3 and 43.4 ± 0.3 kcal/mol, respectively. The EA value predicted for HCNC is almost within the error limits of the experimental value, whereas that for HCCN is overestimated by 1.9 kcal/mol. Note, however, that experimental identification of the origins of the photoelectron spectra of the $HCCN^-$ and $DCCN^-$ anions[2] is challenging, because of the large vibrational anharmonicity of X^3A'' HCCN and large differences in the equilibrium structures of X^3A'' HCCN and X^2A'' $HCCN^-$.

For the sake of completeness, it is interesting to consider another isomer of cyanocarbene, namely, azacyclopropenylidene (HC(C)N). The ground electronic state of this planar cyclic isomer has been predicted to be the singlet A' state, lying ~8 kcal/mol[9] or 16 kcal/mol[11] higher in energy than X^3A'' HCCN. The HC(C)N molecule was proven to exist in solid argon and nitrogen.[58] The equilibrium molecular parameters calculated for X^1A' HC(C)N are given in Table 4. Using the CCSD(T)/cc-pV*n*Z results given in Table 1, the total energy for the X^1A' state of HC(C)N, relative to that for the X^3A'' state of HCCN, was determined to be 7.25, 6.23, and 5.72 kcal/mol for n = T, Q, and 5, respectively. The CBS limit for the relative total energy was then estimated to be 5.1 ± 0.3 kcal/mol. The correction for the core−electron correlation effects was calculated to be +0.51 kcal/mol, whereas that for the scalar relativistic effects was determined to be −0.04 kcal/mol. The harmonic zero-point vibrational energy was calculated at the CCSD(T)/cc-pVTZ level of theory to be 4471 cm^{-1}. Therefore, the best estimate of the relative total energy for X^1A' HC(C)N is predicted in this study to be 7.3 ± 0.3 kcal/mol, yielding a heat of formation at 0 K of 124.1 kcal/mol.

TABLE 4: Equilibrium Molecular Parameters of X^1A' HC(C)N, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets[a]

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
r(HC_a) (Å)	1.0936	1.0785	1.0779	1.0777
r(C_aN) (Å)	1.3135	1.3014	1.2973	1.2966
r(C_aC) (Å)	1.4259	1.4068	1.4022	1.4012
∠(HC_aN) (deg)	137.54	137.68	137.75	137.78
∠(HC_aC) (deg)	159.25	159.17	159.21	159.21
energy + 131 (hartree)	−0.057812	−0.175731	−0.211988	−0.223346

[a] C_a is the apex C atom of the CCN ring; the quoted valence angles are external to the ring.

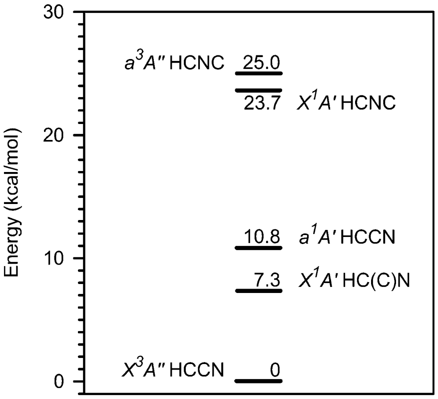

Figure 1. Relative energies of the zero-point energy levels of the ground electronic states for various cyanocarbene isomers.

Figure 1 summarizes the predicted relative energies of the zero-point energy levels of the ground electronic states for all the cyanocarbene isomers studied in this work. The calculated pattern is consistent with that determined by Aoki et al.[9] at the CISD+Q/ANO(spdf) level of theory.

Finally, it is interesting to address the question of the character of the electronic wave functions for HCCN and HCNC, especially in the context of the biradical nature[62] of both molecules. The wave functions and energetics of the $^1A'$ and $^3A''$ states were investigated using various multireference approaches, namely, the complete-active-space self-consistent field (CASSCF),[63] complete-active-space second-order perturbation (CASPT2),[64,65] and internally contracted multireference configuration interaction (icMRCI)[51,52] methods. For the icMRCI method, the multireference Davidson correction[66] to the calculated energy (icMRCI+Q) was employed to account approximately for the effects of higher excitations. The calculations were performed using the cc-pVQZ basis set and the equilibrium structural parameters determined at the RCCSD(T)/cc-pVQZ level. In the CASSCF and CASPT2 calculations, the reference wave function consisted of a full-valence complete active space. Thus, the wave function included all excitations of 14 valence electrons in 13 molecular orbitals, corresponding to the valence atomic *sp* orbitals of the C and N atoms and the 1*s* orbital of the H atom. Unfortunately, even the internally contracted MRCI calculations with such a large active space did not appear to be practically feasible. For the $^3A''$ and $^1A'$ states, the reference wave functions for the active space previously specified consist of 97 720 and 103 923 configurations, respectively. This observation leads to ~32 × 10^9 and 16 × 10^9 singly and doubly excited configurations for the corresponding multireference wave functions. Instead, a series of the icMRCI calculations was performed in which the reference space increased gradually

TABLE 5: Total Energies for HCCN and HCNC Determined at Various Levels of Theory[a]

	HCCN		HCNC	
level of theory	$^3A''$ energy (hartree)	ΔE_{ST}[b] (cm^{-1})	$^1A'$ energy (hartree)	ΔE_{ST}[b] (cm^{-1})
RHF	−130.695117	5556	−130.658668	−3014
CASSCF	−130.890178	4510	−130.849321	−516
CASPT2	−131.204394	5619	−131.156705	−1436
icMRCI (A)[c]	−131.192753	4119	−131.152418	−51
icMRCI (B)[c]	−131.197330	4090	−131.157333	127
icMRCI (C)[c]	−131.197563	4075	−131.157700	135
icMRCI+Q (A)[c]	−131.222483	3993	−131.183382	140
icMRCI+Q (B)[c]	−131.222562	3904	−131.183923	302
icMRCI+Q (C)[c]	−131.222548	3904	−131.183952	309

[a] Calculated with the cc-pVQZ basis set for the CCSD(T)/cc-pVQZ equilibrium structural parameters. [b] The singlet−triplet energy difference, calculated with reference to $^3A''$ HCCN or $^1A'$ HCNC. [c] The reference selection threshold of (A) 0.01, (B) 0.001, and (C) 0.0005.

TABLE 6: Leading Configurations of the CASSCF Wave Functions for HCCN and HCNC[a]

$^3A''$ configuration	weight	$^1A'$ configuration	weight
HCCN			
HF	0.8673	HF	0.8558
$(8a')(9a') \rightarrow (9a')(10a')$	0.0119	$(9a')^2 \rightarrow (2a'')^2$	0.0217
$(8a')^2 \rightarrow (10a')^2$	0.0090	$(9a')(1a'') \rightarrow (10a')(2a'')$	0.0112
$(1a'')(2a'') \rightarrow (2a'')(3a'')$	0.0089	$(1a'')^2 \rightarrow (2a'')^2$	0.0094
$(1a'')^2 \rightarrow (3a'')^2$	0.0077	$(9a')^2 \rightarrow (2a'')(3a'')$	0.0075
$(1a'') \rightarrow (3a'')$	0.0052	$(8a')^2 \rightarrow (10a')^2$	0.0070
		$(8a')(1a'') \rightarrow (10a')(3a'')$	0.0064
		$(1a'')^2 \rightarrow (2a'')(3a'')$	0.0051
HCNC			
HF	0.8899	HF	0.8749
$(8a')^2 \rightarrow (10a')^2$	0.0078	$(9a')^2 \rightarrow (2a'')^2$	0.0206
$(1a'')^2 \rightarrow (3a'')^2$	0.0074	$(9a')(1a'') \rightarrow (10a')(2a'')$	0.0075
$(1a'')(2a'') \rightarrow (2a'')(3a'')$	0.0070	$(8a')(1a'') \rightarrow (10a')(3a'')$	0.0074
$(8a')(9a') \rightarrow (9a')(10a')$	0.0055	$(8a')(9a') \rightarrow (2a'')^2$	0.0061
		$(8a')^2 \rightarrow (10a')^2$	0.0056
		$(1a'')^2 \rightarrow (3a'')^2$	0.0053

[a] In the natural orbital representation, weights greater than 0.005, calculated with the cc-pVQZ basis set for the CCSD(T)/cc-pVQZ equilibrium structural parameters.

toward the full-valence complete active space. The reference configurations were selected from the CASSCF wave function, according to several thresholds to their norms, namely (A) 0.01, (B) 0.001, and (C) 0.0005. The squared norms of the selected configurations were ∼0.987, 0.9988, and 0.99952 for thresholds A, B, and C, respectively, with a value of 1 being the limit for the CASSCF wave function.

The calculated total energies and singlet−triplet energy differences for HCCN and HCNC are given in Table 5. For the HCCN molecule, the singlet−triplet energy difference already is predicted quite reasonably at the RHF level of theory. Inclusion of the nondynamical correlation effects through the CASSCF framework decreases the ΔE_{ST} value by ∼1000 cm^{-1}. Surprisingly, by accounting for the dynamical correlation effects within the second-order perturbational procedure (CASPT2), the singlet−triplet energy difference is predicted to be larger by almost the same amount, thus becoming even larger than that determined at the RHF level. On the other hand, using the multireference configuration interaction approach, the ΔE_{ST} value is predicted to decrease further by ∼400 and ∼600 cm^{-1} for the icMRCI and icMRCI+Q methods, respectively. The calculated ΔE_{ST} values decrease monotonically with enlargement of the reference space. Even for the modest reference space (case A), the singlet−triplet energy difference is predicted by the icMRCI+Q method to be fairly close to that of 3699 cm^{-1} calculated at the RCCSD(T)/cc-pVQZ level. For the HCNC molecule, the situation is more complex. At the RHF level of theory, the $^3A''$ state of HCNC is predicted to be the ground electronic state, in contrast to the experimental[2] and theoretical (see Table 2) findings. Moreover, the singlet−triplet energy difference is calculated to be of the same order of magnitude as that for HCCN. Similarly, inclusion of the nondynamical correlation effects through the CASSCF approach decreases the ΔE_{ST} value by ∼2500 cm^{-1}, whereas inclusion of the dynamical correlation through the CASPT2 approach increases the ΔE_{ST} value (relative to the CASSCF approach) by ∼900 cm^{-1}. In regard to the RHF approximation, the $^3A''$ state is predicted by both CASSCF and CASPT2 methods to be the ground electronic state of HCNC. Thus, the low-order multireference perturbational approach does not provide an accurate (balanced) description of electron correlation in the $^3A''$ and $^1A'$ states of the HCCN and HCNC molecules. Although the CASSCF and CASPT2 results are reasonable for HCCN, this is clearly not the case for HCNC. A very high level of correlation treatment is required to reproduce the observed[2] ordering and splitting of the $^1A'$ and $^3A''$ states of the HCNC molecule. As shown in Table 5, using the icMRCI method with the modest reference space of 113/119 singlet/triplet configurations (case A), both states were found to be almost isoenergetic. However, the $^3A''$ state is still predicted to be somewhat more stable than the $^1A'$ state. Enlarging the reference space favors the $^1A'$ state over the $^3A''$ state, leading to the correct ordering and splitting of both states. This effect is more pronouced for the icMRCI+Q treatment, and the convergence of the calculated singlet−triplet energy differences is quite fast. For the largest reference space employed in this study, including 2933/2619 singlet/triplet configurations (case C), the singlet−triplet energy difference is predicted to be 309 cm^{-1}, compared to that of 417 cm^{-1} calculated at the RCCSD(T)/cc-pVQZ level of theory. It is worth noting that more than one-half of the ΔE_{ST} value predicted by the icMRCI+Q method is due to higher-than-double excitations that are accounted for by the multireference Davidson correction.[66]

Table 6 lists leading configurations of the CASSCF wave functions for the $^3A''$ and $^1A'$ states of HCCN and HCNC. The Hartree-Fock (HF) electronic configuration of the lowest $^3A''$ states of both molecules can be described as

$$[\text{core}](4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')(1a'')^2(2a'') \quad (1)$$

where [core] represents $(1a')^2(2a')^2(3a')^2$ and describes the 1s-like core orbitals of the C and N atoms. The HF electronic configuration of the lowest $^1A'$ states of both molecules can be described as

$$[\text{core}](4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(1a'')^2 \quad (2)$$

As shown in Table 6, the HF configurations account for ∼87% of the multiconfiguration wave functions for all the states under consideration. None of the excited-state configurations appeared to be particularly important. Similarly, in regard to the a^1A_1 state of CH$_2$,[42] the configuration $(9a')^2 \rightarrow (2a'')^2$ becomes as equally important as the HF configuration for linear conformations of a^1A' HCCN and X^1A' HCNC. However, both molecules are predicted to be bent definitively at equilibrium, and this excited-state configuration accounts for only ∼2% of the multiconfiguration wave function. For the lowest $^3A''$ and $^1A'$ states of HCCN and HCNC, the electronic wave functions thus are dominated by a single HF electronic configuration. Inspection of the CASSCF molecular orbitals and their occupation numbers indicates that the electron distribution in all these states resembles that characteristic of the bent carbenic form $H-\ddot{C}-C\equiv N$, rather than that of the linear allenic form $H-\dot{C}=C=\dot{N}$. Considering the close agreement between the RCCSD(T) and icMRCI results, it is reasonable to conclude that the single-reference coupled-cluster approach, including connected single through triple excitations, is shown to describe the electronic structure of the lowest $^3A''$ and $^1A'$ states of HCCN and HCNC accurately.

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