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Stability ladder of various HC_2N conformers and their excitation energies

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The molecular structure of various stationary points of HC_2N has been studied using the quadratic configuration interaction including single and double substitutions with triples contributions (QCISD(T)). A Huzinaga–Dunning double-zeta plus polarization (D95**) basis set was used. A stability ladder of these species is calculated using the configuration interaction including single and double substitutions (SDCI) with the Davidson correction (SDCI+Q). The general contraction scheme of the $[5s3p2d1f(C$ and $N)/3s2p1d(H)]$ atomic natural orbital basis set was chosen. The natural orbitals obtained in the preceding complete active space self-consistent field (CASSCF) calculations were applied to the open-shell SDCI. The triplet cyanomethylene is bent, and the barrier to linearity is 1.4 kcal/mol at the single-reference SDCI+Q level of theory in accord with the Schaefer and Roos' values (0.8–1.0 kcal/mol). The nine-reference SDCI+Q calculation increases the energy separation by 0.7 kcal/mol. The thermal energy change between the two (1 and 2) including the calculated zero-point vibrational energies is 1.4 kcal/mol. The enthalpy barrier ($\Delta H^{\neq}$) to linearize 1 to transition state 2 in a (hypothetical) reaction is predicted to be 0.0 kcal/mol using the single-reference SDCI+Q bent-linear energy separation. As a result, experiments might find no barrier to inversion of bent triplet 1. The most stable singlet species 6 (ring form of HC_2N) lies 7.7 kcal/mol above the triplet bent cyanomethylene. Vertical excitation energies from the ground-state ($^3A''$) of triplet bent cyanomethylene to $^1A'$ and $^1A''$ are studied using the CASSCF and SDCI methods; the SDCI+Q energies are 0.93 and 1.11 eV, respectively. These excitation energies are compared with those in the methylene and oxygen molecules having a qualitatively similar electronic structure to the present HCCN species, where two electrons occupy near-degenerate π-like (or degenerate π) highest occupied molecular orbitals (HOMO) forming a triplet ground-state. The excitation energies of 0.93 and 1.11 eV are close to the relative energies of the 3, 8, and 9 to the most stable triplet bent cyanomethylene.

I. INTRODUCTION

The molecular structure of HC_2N has been a subject of contention between theory and experiment, since two primary candidates of the carbene (1) and allenelike diradical (2) are proposed for a most probable species.[1]

In 1964, an electron paramagnetic resonance (EPR) study revealed the presence of a linear form of triplet HC_2N molecule.[2] Another EPR experiment also showed that the HC_2N molecule is linear, but that the CH_2 molecule is really strongly bent.[3] Using a transient species microwave spectroscopy, Saito, Endo, and Hirota reported that HC_2N is linear.[4] These early experiments all indicate a triplet linear ground state for HCCN.

Early theoretical studies supported the above experimental conclusions.[5] The recent higher level of theoretical studies, however, predicted that the HC_2N is bent. Rice and Schaefer performed the multireference SDCI (MR-SDCI) studies on the triplet HC_2N, reporting that the bent-linear separation is 0.8 kcal/mol.[6] This value was recently ascertained by the same authors[7] using a more elaborate coupled-cluster single and double excitation (CCSD(T)) level of theory.[8] Malmqvist *et al.* also re-

ported that the triplet cyanomethylene is bent, and that the barrier to linearity is 1.0 ± 0.5 kcal/mol.[9]

A recent experiment by Brown, Saito, and Yamamoto slightly remedied their previous experimental conclusion, suggesting a quasilinear structure instead of a strict linear one.[10]

There still exists a discrepancy between theory and experiment on the molecular structure of the most stable species. Furthermore no theoretical and experimental studies on other conformers and the excited states have been performed.

In this paper the molecular structure of ten stationary points was studied using the QCISD(T)[11] method with the Huzinaga–Dunning D95** basis set.[12] (Only the open-shell singlet linear structure 8 was studied using the SDCI+Q method.) To obtain a stability ladder of these species, we performed the subsequent single-point energy calculations using the SDCI method[13] with the Davidson correction[14] (SDCI+Q). The general contraction scheme (GCS) of the $[5s3p2d1f/3s2p1d]$ atomic natural orbital (ANO) basis set[15] was chosen. The triplet bent-linear energy separation was further studied using the MR-SDCI method. We calculated the harmonic frequencies of the two stationary points (1 and 2) using the QCISD(T)/ D95** method both to characterize them and obtain their

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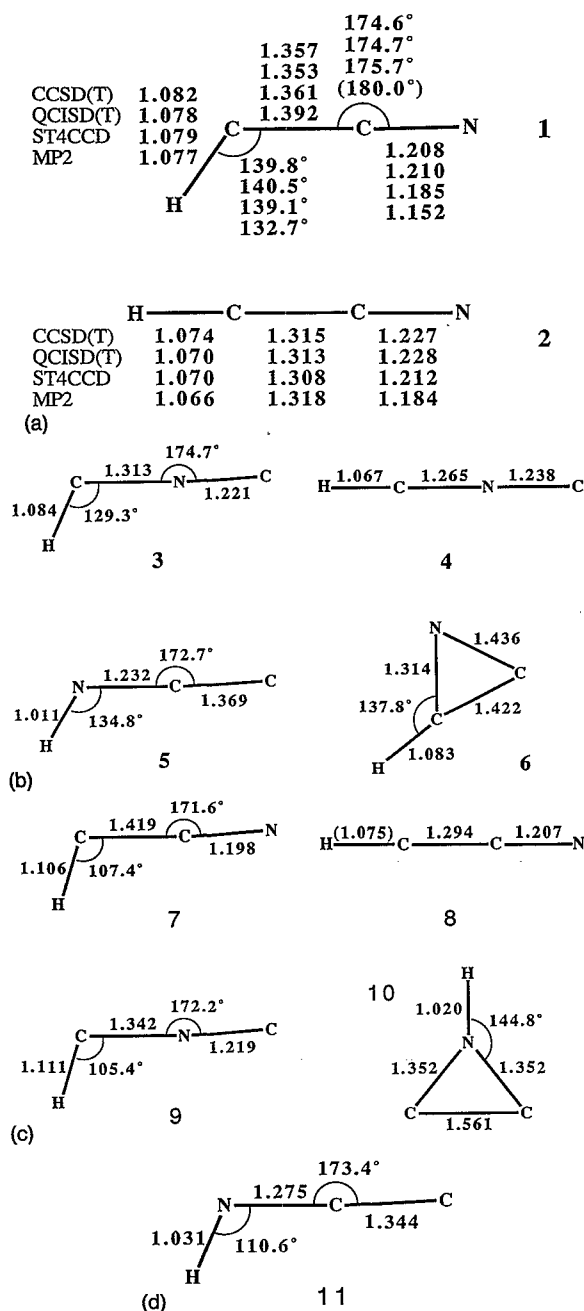[a)]To whom all correspondences should be addressed.

FIG. 1. Molecular structure of the 11 HC₂N stationary points optimized using the QCISD(T)/D95** method. For the 8 the SDCI+Q method with the GCS of ANO basis set was used. The values in parentheses (in 1 and 8) were fixed in the optimizations. The species from 1 through 5 are triplet, but those from 6 through 11 singlet.

TABLE I. Rotational constants (in GHz) and dipole moment (in a.u.) of the 11 HC₂N stationary points.[a]

	Rotational constants (GHz)			Dipole moment (in a.u.)[b]
1	10.603	10.687	1337.775	1.3037
2	10.615	10.615	0.0	1.4072
3	11.739	11.900	870.278	1.0486
4	11.789	11.789	0.0	1.5103
5	10.567	10.663	1177.547	1.5892
6	18.159	33.615	39.493	1.2849
7	10.505	10.725	510.262	0.9318
8	10.959	10.959	0.0	1.4202
9	11.758	12.044	495.333	0.7005
10	17.862	34.583	36.944	1.4166
11	10.292	10.317	4289.381	1.5229

[a]The QCISD(T)/D95** geometries were used in ten species except 8 (see the text).
[b]Dipole moments were calculated at the SDCI level of theory with the ANO basis set.

the triplet bent cyanomethylene and methylene molecules, two electrons are distributed in near-degenerate π-like orbitals forming $^3A'(^3B_1)$, $^1A'(^1A_1)$, and $^1A''(^1B_1)$, where the electronic states in the parentheses correspond to the methylene molecule. In the oxygen molecule, two electrons are distributed in degenerate π HOMO orbitals forming $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$.

We also calculated the triplet-singlet energy gap $(^3B_1\rightarrow{}^1A_1)$ in methylene using the same level of theory to find out the accuracy of the present calculations.

II. METHOD

The molecular structure of ten stationary points (except 8) was studied using the QCISD(T) method[11] with the Huzinaga–Dunning D95** basis set.[12] Geometry optimization of the 1 and 2 was further performed, for comparison, by the second-order Møller–Plesset perturbation (MP2)[17] and the coupled cluster using double substitutions (CCD) and evaluation of the contribution of single and triple excitations through fourth-order using the CCD wave function (ST4CCD).[18]

A (open-shell) singlet linear structure 8 was studied using the SDCI+Q method; an A_2 irreducible representation of a C_{2v} point group was assumed.

To obtain the relative stability ladder, the subsequent single-point energy calculations were performed using the SDCI+Q method. The general contraction scheme (GCS) of the $[5s3p2d1f(\mathrm{C}$ and $\mathrm{N})/3s2p1d(\mathrm{H})]$ ANO basis sets, which are based on the primitive set of $(14s9p4d3f/8s4p3d)$ Gaussian functions, was chosen.

The natural orbitals obtained in the preceding CASSCF (six electrons in six orbitals) were applied to the open-shell SDCI calculations; for the closed-shell singlets, SCF MO's were used. We used the C_{2v} point group for the linear species and C_s for the bent and ring ones.

Three $1s$ and the corresponding virtual orbitals were deleted in the excitations; 101 orbitals were thus correlated. To clarify the most stable conformer, we also used the four- and nine-reference SDCI methods, where the numbers of the configurations (for the triplet bent 1) were

zero-point vibrational energies (E_{zp}). A thermal energy change between the two including their E_{zp} was computed.

The enthalpy $(\Delta H^{\neq})$ and free energy $(\Delta G^{\neq})$ barrier to linearize 1 to transition state 2 in a (hypothetical) reaction were predicted using the single, four-, and nine-reference SDCI+Q bent-linear energy separations.

We studied the lower exited states of the triplet-bent cyanomethylene (1) using the CASSCF[16] and SDCI methods. The calculated excitation energies were compared with those in the methylene and oxygen molecules. Both in

TABLE II. Total and relative energies in the 11 HC$_2$N stationary points.[a]

Conformer	CASSCF[b]		SDCI		SDCI+Q	
	Total energy	ΔE[c]	Total energy	ΔE[c]	Total energy	ΔE[c]
1	−130.787 933	0.00	−131.106 209	0.0	−131.167 375	0.00
2	−130.777 476	6.56	−131.100 266	3.73	−131.165 164	1.39
3	−130.742 133	28.7	−131.071 846	21.6	−131.127 515	25.0
4	−130.721 157	41.9	−131.056 140	31.4	−131.117 573	31.2
5	−130.710 842	48.4	−131.051 384	34.4	−131.110 375	35.8
6	⋯	⋯	−131.097 103	5.71	−131.155 032	7.74
7	−130.767 635	12.7	−131.083 517	14.2	−131.145 306	13.8
8	−130.742 474	28.5	−131.070 349	22.5	−131.131 184	22.7
9	−130.739 378	30.5	−131.068 878	23.4	−131.128 123	24.6
10	⋯	⋯	−131.047 254	37.0	−131.106 086	38.5
11	−130.674 732	71.0	−131.010 586	60.0	−131.075 797	57.5

[a]QCISD(T)/D95** geometries were used except 8. For open-shell systems (1–5 and 8) the (six electrons in six orbitals) CASSCF natural orbitals were applied to the SDCI calculations. Total energies in hartrees.
[b]The CASSCF calculations on the ring conformers (6 and 10) have not been performed, since the same CASSCF space as the linear and bent structures cannot be defined due to the ring formation. Two π_y-orbitals form a new σ-bond.
[c]Relative energies to the conformer 1 in kcal/mol.

1 925 005 and 1 870 054, respectively. In the four-reference SDCI calculation, the natural orbitals (NO's) with the populations less than 0.5×10^{-4} in the preceding single-reference SDCI calculations were deleted. In the nine-reference SDCI calculation, NO's with populations less than 1.5×10^{-4} were deleted. Thus 81 and 69 orbitals were correlated in the four- and nine-reference SDCI, respectively. These MR-SDCI using the natural orbitals obtained in the preceding SDCI is very useful, since the energy loss due to these virtual orbital deletions is almost quantitatively recovered by the successive SDCI method.[19]

The harmonic frequency only for the 1 and 2 stationary points was calculated using the QCISD(T) method with the D95** basis set to characterize them and obtain their zero-point vibrational energies. The vibrational analysis for other stationary points has not been performed, since it will take very large CPU times. Thus some of the stationary points, obtained in the present study, might be transition state. The thermal energy change (including the zero-point vibrational energies) was obtained. The enthalpy ($\Delta H^{\neq}$) and free energy ($\Delta G^{\neq}$) changes in the $1 \rightarrow 2$ (hypothetical) reaction were predicted, to find the barrier to linearization of triplet 1.

The vertical excitation energies from the ground-state ($^3A''$) of triplet bent cyanomethylene to $^1A'$ and $^1A''$ were calculated at the SDCI+Q level of theory using the (six electrons in six π-like orbitals) CASSCF natural orbitals. The CASSCF excitation energies (six electrons in seven orbitals, i.e., one σ and six π-like MO's) were also calculated using the preceding ground-state SDCI natural orbitals. The vertical excitation energies in the methylene and oxygen molecules were also studied, for comparison, using the same levels of theory.

All the calculations were performed with the MOLCAS2[20] and GAUSSIAN92[21] program systems at the Computer Center of Tokyo Metropolitan University. IBM3090/300J, IBM RS6000, and VAX9210 VP computers were used.

III. RESULTS AND DISCUSSION

A. Relative stability ladder

The molecular structure of 11 stationary points in the HC$_2$N molecule is shown in Fig. 1. Ten structures (1–11 except 8) were optimized using the QCISD(T) method with the D95** basis set, but that of the 8 using the SDCI+Q method with the GCS of the ANO basis set. The CCSD(T) parameters recently obtained by Schaefer (for 1 and 2) are included for comparison; the MP2 and ST4CCD parameters obtained in the present study are also illustrated. The calculated rotational constants and dipole moments are summarized in Table I. The structures obtained with the QCISD(T) method are in good agreement with Schaefer's CCSD(T) ones. One can see that the slightly different parameters are obtained in the MP2 optimizations. The total energies of these 11 stationary points, subsequently calculated at the CASSCF, SDCI, and SDCI+Q levels of theory with the GCS of the ANO basis set, are listed in Table II. The natural orbitals obtained in the preceding CASSCF were applied to the open-shell SDCI calculations.

To clarify the triplet bent-linear energy separation, we also performed the four- and nine-reference SDCI calculations. The CASSCF (six electrons in six orbitals), SDCI, and SDCI+Q energy differences are summarized in Table III. The energy separations, obtained with the segmented contraction scheme (SCS) of the $[7s4p2d1f(C \& N)/5s2p1d(H)]$ basis set,[22] are also included for comparison. The SCS energies do not show any difference from the GCS values.

The single-reference SDCI+Q energy differences (1.2–1.4 kcal/mol) are close to Schaefer's estimate of 0.8 kcal/mol. The four- and nine-reference SDCI+Q calculations only in the π-orbital reference space increase the energy difference by only 0.2–0.7 kcal/mol. Although we could not succeed in the MR-SDCI including σ orbitals as a reference space, these results may indicate that the bent-

TABLE III. The triplet bent (1)-linear (2) energy separations in kcal/mol.[a]

(i) Single-reference			
Basis set...Method	CASSCF	SDCI	SDCI+Q
$[7s4p2d1f/5s2p1d]$	5.1	3.6	1.2
$[5s3p2d1f/3s2p1d]$	5.1	3.7	1.4
(ii) Four reference			
Basis set...Method		SDCI	SDCI+Q
$[5s3p2d1f/3s2p1d]$		1.6	1.6
(iii) Nine reference			
Basis set...Method		SDCI	SDCI+Q
$[5s3p2d1f/3s2p1d]$		1.7	2.1

[a]Included molecular orbitals in the single-, four-, and nine-reference SDCI calculations are 101, 81, and 69, respectively. In the four- and nine-reference SDCI, natural orbitals obtained in the single-reference SDCI were used. The QCISD(T)/D95** geometries were used. Structure 2 is a transition state (Table IV).
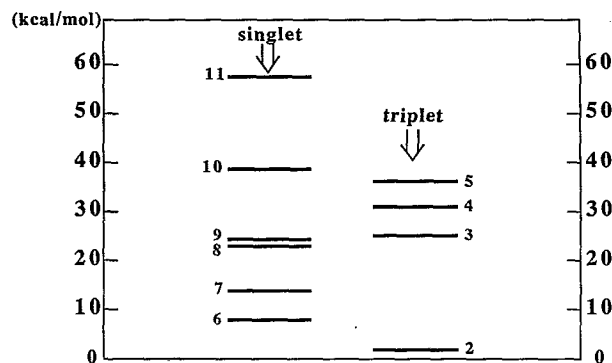

FIG. 2. Stability ladder of the 11 HC_2N stationary points relative to the most stable triplet bent cyanomethylene, calculated at the SDCI+Q level of theory with the GCS of the ANO basis set. (The structure for 2 is a transition state.)

linear energy difference without thermal energy corrections may be larger than Schaefer's estimate (0.8 kcal/mol) at more elaborate levels of theory.

The QCISD(T)/D95** harmonic frequencies are listed in Table IV. No correction factors are multiplied in the frequencies. The triplet linear 2 has one-degenerate π imaginary frequency (481 i) being a transition state, but the triplet bent conformer 1 has all the real frequencies. The thermal energy change between the two including the zero-point vibrational energies is 1.4 kcal/mol. To predict an enthalpy barrier ($\Delta H^{\neq}$) to linearize 1 to transition state 2 in the (hypothetical) reaction, this energy was subtracted from the triplet bent-linear energy differences. The predicted $\Delta H^{\neq}$ values are thus 0.0 (single-reference SDCI+Q), 0.2 (four-reference SDCI+Q), and 0.7 (nine-reference SDCI+Q) kcal/mol. The calculated entropy change resulting mainly from the rotational entropy is −4.1 cal/(mol K). We finally obtained the free energy barrier ($\Delta G^{\neq}$) in the 1→2 (hypothetical) linearization re-

action path to be 1.2–1.9 kcal/mol. These very small calculated $\Delta H^{\neq}$ and $\Delta G^{\neq}$ suggest that no experimental technique, now available, could detect whether 1 is actually bent, since the barrier to linearization via transition structure 2 is so small.

In Fig. 2 we give the SDCI+Q energies of 11 stationary points relative to that of the triplet bent cyanomethylene. (Other probable points having less stability will be reported in future.) The third triplet species 3 (bent HCNC) is 25.0 kcal/mol higher in energy than the 1. The most stable singlet structure is a ring 6, which is 7.7 kcal/mol higher in energy than the 1. The next stable singlet structure 7 is a bent HCCN, being 13.8 kcal/mol less stable than the 1.

The (open-shell) singlet linear structure 8, optimized using the SDCI+Q method, is 21.3 kcal/mol higher in energy than the triplet linear 2, or 22.7 kcal/mol less stable than the triplet bent cyanomethylene. Both the optimized

TABLE IV. Calculated harmonic frequencies and enthalpy ($\Delta H^{\neq}$) and free energy ($\Delta G^{\neq}$) barriers to linearize 1 to transition state 2 in the (hypothetical) reaction.

(i) Frequencies, zero-point vibrational energies, thermal energy, and entropy
   (a) Bent 1
      Frequencies (in cm^{-1})

a'	a''	a'	a'	a'	a'
376	408	689	1123	1818	3362

      Zero-point energy   11.12 kcal/mol
      Sum of thermal energy   13.38 kcal/mol
      Entropy   59.77 cal/(mol K)
   (b) Linear 2
      Frequencies (in cm^{-1})

π	π	σ	σ	σ
481i	408	1211	1635	3440

      Zero-point energy   10.15 kcal/mol
      Sum of thermal energy   12.03 kcal/mol
      Entropy   55.66 cal/(mol K)

(ii) Enthalpy barriers ($\Delta H^{\neq}$) in the 1→2 reaction in kcal/mol

Single-reference SDCI+Q	Four-reference SDCI+Q	Nine-reference SDCI+Q
0.0	0.2	0.7

(iii) Free energy barriers ($\Delta G^{\neq}$) in the 1→2 reaction in kcal/mol

Single-reference SDCI+Q	Four-reference SDCI+Q	Nine-reference SDCI+Q
1.2	1.4	1.9

TABLE V. Vertical excitation energies in the triplet bent cyanomethyl-ene, methylene, and oxygen (in eV).[a]

	CASSCF	SDCI	SDCI+Q	ACPF
$HC_2N(1)$				
$^1A''$	1.33	1.12	1.11	1.11
$^1A'$	0.95	0.95	0.93	0.94
$^3A''$	0.00	0.00	0.00	0.00
CH_2				
$^1B_1$	1.70	1.50	1.48	1.49
$^1A_1$	0.91	1.04	0.92	0.95
$^3B_1$	0.00	0.00	0.00	0.00
O_2				
$^1\Pi_g$	9.31	8.89	8.91	8.91
$^3\Pi_g$	7.63	7.40	7.52	7.50
$^1\Sigma_g^+$	1.72			
$^1\Delta_g$	0.99	1.07	0.98	0.99
$^3\Sigma_g^-$	0.00	0.00	0.00	0.00

[a]The CASSCF energy of $^1\Sigma^+$, $^1(\pi_x^2 + \pi_y^2)$, in O_2 was calculated as a second root of an A_1 irreducible representation in a C_{2v} point group.
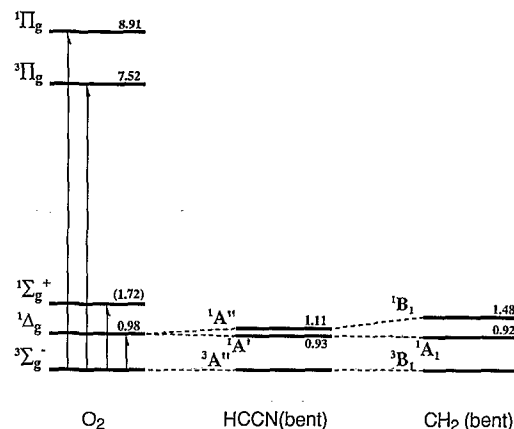

FIG. 3. Vertical excitation energies to the lower excited states in the triplet bent cyanomethylene are compared with those in oxygen and methylene. The energies were computed using the SDCI+Q method. The values in parentheses were calculated at the CASSCF level.

C–C and C–N bond lengths in the open-shell *singlet* 8 are about 0.02 Å shorter than those in the open-shell *triplet* 2. The shorter N–H bond lengths were obtained in the 5, 10, and 11, indicating the presence of ionic-bond characters.

B. Excitation energy

In Table V we give the calculated (vertical) excitation energies from the ground-state ($^3A''$) of triplet bent cy-anomethylene to the $^1A'$ and $^1A''$ excited states. The energies in CH_2 and O_2 are also included for comparison. The lower excited states are formed by the two electron distribution in near degenerate π-like (or degenerate π) HOMO orbitals. Although some of the CASSCF energies are slightly higher than the others [SDCI, SDCI+Q, and average coupled pair functional (ACPF)[23] values], the SDCI+Q excitation energies to $^1A'$ and $^1A''$ are 0.93 and 1.11 eV, respectively.

The $^1A'$ and $^1A''$ states correlate to the $^1\Delta$ states, $^1(\pi_x^2 - \pi_y^2)$, and $^1(\pi_x, \pi_y)$ having the same energies, at the linear structure of HCCN ($\theta(HCC) = \pi$). The open-shell singlet linear 8 ($^1(\pi_x, \pi_y)$) is 0.98 eV (22.7 kcal/mol) higher in energy than the triplet bent cyanomethylene. (The $^1\Delta$ states at the geometry of the 2 are 0.96 eV higher in energy than that of the 2 itself.) These energies are close to the excitation energies to $^1A'$ and $^1A''$, indicating that the potential energy curves in the excited states ($^1A'$ and $^1A''$) may be flat around their potential minima.

The excitation energies from $^3A''$ to $^1A'$ and $^1A''$ are also close to the relative energies of the 3, 8, and 9 to the triplet bent cyanomethylene (1).

In the methylene molecule, the calculated (vertical) $^1A_1$ state is 0.91 (CASSCF) and 0.92 (SDCI+Q) eV higher in energy than that of the ground state $^3B_1$. The $^1B_1$ state is 1.70 (CASSCF) and 1.48 (SDCI+Q) eV less stable than the $^3B_1$. We can compare the SDCI+Q energies [0.92 ($^1A_1$) and 1.48 ($^1B_1$) eV] in CH_2 with the corresponding values [0.93 ($^1A'$) and 1.11 ($^1A''$) eV] in triplet bent cyanomethylene. The similar energies in these

bent systems may result from the fact that near degenerate (two) π-like HOMO orbitals have similar chemical bonding characteristics, since the two bond angles [$\theta(HCH)$ in CH_2 and $\theta(HCC)$ in HC_2N] do not differ by much.[25]

It may be worth noting that the vertical *lowest* excitation energies from the ground states to the $^1A'$ in the triplet bent cyanomethylene and to the $^1A_1$ in CH_2 are in good agreement with the energy (0.98 eV) to the $^1\Delta_g$ ($^1(\pi_x^2 - \pi_y^2)$) in O_2 (Ref. 26) as shown in Fig. 3, indicating that the π character holds good even in the σ orbitals of these carbenes (correlate to the π-orbitals at the linear structure).

The triplet-singlet energy gap ($^3B_1 \rightarrow {}^1A_1$) in CH_2 was studied using the SDCI+Q and CASSCF (six electrons in four orbitals) methods with the same ANO basis set to find out the accuracy of the present calculations. The natural orbitals obtained in the preceding SDCI calculations were applied in the CASSCF. The calculated gap between the lowest two state is 10.0 (SDCI+Q) and 9.9 (CASSCF) kcal/mol; these values are in good agreement with the best current experimental estimate of 9.05 kcal/mol.[27]

The (vertical) electron affinity and ionization potential of the triplet bent cyanomethylene were calculated to be 1.50 and 10.7 eV, respectively, at the SDCI+Q level of theory.

IV. CONCLUSIONS

(i) The most stable conformer of HC_2N is triplet bent cyanomethylene (1), and the bent-linear energy separation is 1.5 ± 0.5 kcal/mol *without the thermal energy corrections*. This conclusion supports the previous results obtained by Schaefer[7] and Roos.[9]

(ii) Thermal energy change between the 1 and 2 (including the zero-point energies) is 1.4 kcal/mol. The entropy change resulting mainly from the rotational entropy is −4.1 cal/mol K.

(iii) The enthalpy and free energy changes in the 1→2 (hypothetical) linearization reaction path are, therefore, 0.0 and 1.2 kcal/mol, respectively, if one can apply the

single-reference SDCI+Q (bent-linear) energy difference. These energies change to 0.7 and 1.4 kcal/mol at the nine-reference SDCI+Q. No experimental techniques, available now, could prove HC$_2$N to have a bent ground state, since the enthalpy and free energy barriers to linearization are so small.

(iv) The vertical SDCI+Q excitation energy from $^3A''$ to the lowest excited state $^1A'$ (in the triplet bent cyanomethylene) is 0.93 eV. This excitation energy is very close to those in the CH$_2$ and O$_2$ molecules having a qualitatively similar electronic structure to the present HC$_2$N; in all of these systems two electrons occupy the near degenerate π-like (or degenerate π) HOMO orbitals forming the triplet ground states.

The excitation energy is also close to the relative energies of the 3, 8, and 9 to the triplet bent cyanomethylene.

ACKNOWLEDGMENTS

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[25] Both geometries ($^3B_1$ and $^1A_1$) were studied using the QCISD(T) method with the D95** basis set. The bond length of 1.0838 Å and the bond angle of 132.44 deg were obtained in $^3B_1$, and 1.1159 Å, and 101.89 deg in $^1A_1$.

[26] The SDCI+Q (vertical) excitation energies to $^1\Delta_g$ was calculated to be 0.98 eV at the same level of theory. (See Table V.)

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