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A Gaussian-2 Study of Isomeric C_2H_2N and $C_2H_2N^+$

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The structures and energetics of the C_2H_2N and $C_2H_2N^+$ isomers have been investigated using a modified Gaussian-2 (G2) method, which takes into account the energy correction due to spin contamination. At the QCISD(Full)/6-31G(d) level, C_2H_2N may exist as 12 stable isomers. In the order of decreasing stabilities, they are CH_2CN (**1**), CH_2NC (**2**), CHCNH (**3**), c-CH_2CN (**4**), c-NCHCH (**5**), CHNCH (**6**), NH_2CC (**7**), NHCHC (**9**), c-NHCHC (**10**), *cis*-CHCHN (**12**), *cis*-CHNHC (**13**), and *trans*-CHNHC (**14**). On the other hand, there are seven $C_2H_2N^+$ isomers. In the order of decreasing stabilities, they are c-$NCHCH^+$ ($\mathbf{5}^+$), CH_2CN^+ ($\mathbf{1}^+$), CH_2NC^+ ($\mathbf{2}^+$), $CHCNH^+$ ($\mathbf{3}^+$), $CHNCH^+$ ($\mathbf{6}^+$), c-$NHCHC^+$ ($\mathbf{10}^+$), and NH_2CC^+ ($\mathbf{7}^+$). The G2 result for the ionization energy of **1** and the $\Delta H°_{f298}$ values of **1** and $\mathbf{1}^+$ are in good agreement with the available experimental data. However, the G2 results for radicals **2** and **5** as well as cations $\mathbf{2}^+$ and $\mathbf{5}^+$ do not agree with the experimental data in the literature. This calls for a reexamination of the experimental results. Furthermore, in a recent study of the reaction between nitrogen atom and vinyl radical, a C_2H_2N radical was formed with an ionization energy < 9.64 eV. On the basis of our calculations and known reactivity of the reactants, it is concluded that the unidentified isomer is likely to be **2**.

Introduction

Recently, Thorn and co-workers published a photoionization efficiency (PIE) spectroscopic study of cyanomethyl radical, CH_2CN, produced by the reaction $F + CH_3CN \rightarrow CH_2CN + HF$, using a discharge-flow-photoionization mass spectrometer coupled to a dispersed synchrotron radiation source.[1] They reported a values of 10.28 ± 0.01 eV for the adiabatic ionization energy (IE) of CH_2CN. In the same measurements, they also reported that there was an unidentified C_2H_2N radical isomer with IE < 9.64 eV, and that unidentified isomer was formed in the reaction between nitrogen atom and the vinyl radical:

$$N\,(^4S) + CH{=}CH_2 \rightarrow C_2H_2N + H \qquad (1)$$

However, the assignment of PIE spectrum for the unidentified isomer was made difficult by the possible existence of numerous C_2H_2N and $C_2H_2N^+$ isomers.

On the theoretical front, so far there has not been a systematic study of all the isomeric C_2H_2N radicals and $C_2H_2N^+$ cations. However, there are a few reports on a selected number of isomers. For instance, calculations were carried out at HF/4-31G[2] and MP4SDQ/6-311G(d,p)//HFDZ+P[3] levels of theory for $C_2H_2N^+$ isomers. Recently, Radom and co-workers[4] applied several G2- and CBS-based methods to cyanomethyl radical, isocyanomethyl radical, and 1*H*-azirinyl radical, as well as to their corresponding cations and anions. In other words, these studies reported the results of only a small number of C_2H_2N/$C_2H_2N^+$ isomers. In the present work, we have carried out G2 calculations[5] for a large number of C_2H_2N and $C_2H_2N^+$ isomers. In addition, we also report the G2 heat of formation at 0 K ($\Delta H°_{f0}$) and 298 K ($\Delta H°_{f298}$) for all the isomers. Where possible, we will compare these results with the available experimental data.

Theoretical Methods

All calculations were carried out on IBM RS6000/390 and SGI10000 workstations, and SGI Origin 2000 High Performance Server, using the Gaussian 94 package of the programs.[6] All structures were optimized at the second-order Mϕller−Plesset theory (MP2) using the 6-31G(d) basis set with all electrons included, i.e., at the MP2(Full)/6-31G(d) level. The G2 theoretical procedure[5] is an approximation to the ab initio level of QCISD(T)/6-311+G(3df,2p). It involves single-point energy calculations at the QCISD(T)/6-311G(d,p), MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-311G(2df,p), and MP2/6-311+G-(3df,2p) levels based on the optimized geometry at MP2(Full)/6-31G(d). A small empirical correction is added to include high-level correction effects in the calculation of the total electronic energies (E_e). The HF/6-31G(d) harmonic vibrational frequencies, scaled by 0.8929, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e +$ ZPVE).

In this work, to make certain the existence of the C_2H_2N and $C_2H_2N^+$ isomers, we also performed structural optimization at the QCISD(Full)/6-31G(d) level for all isomers found at the

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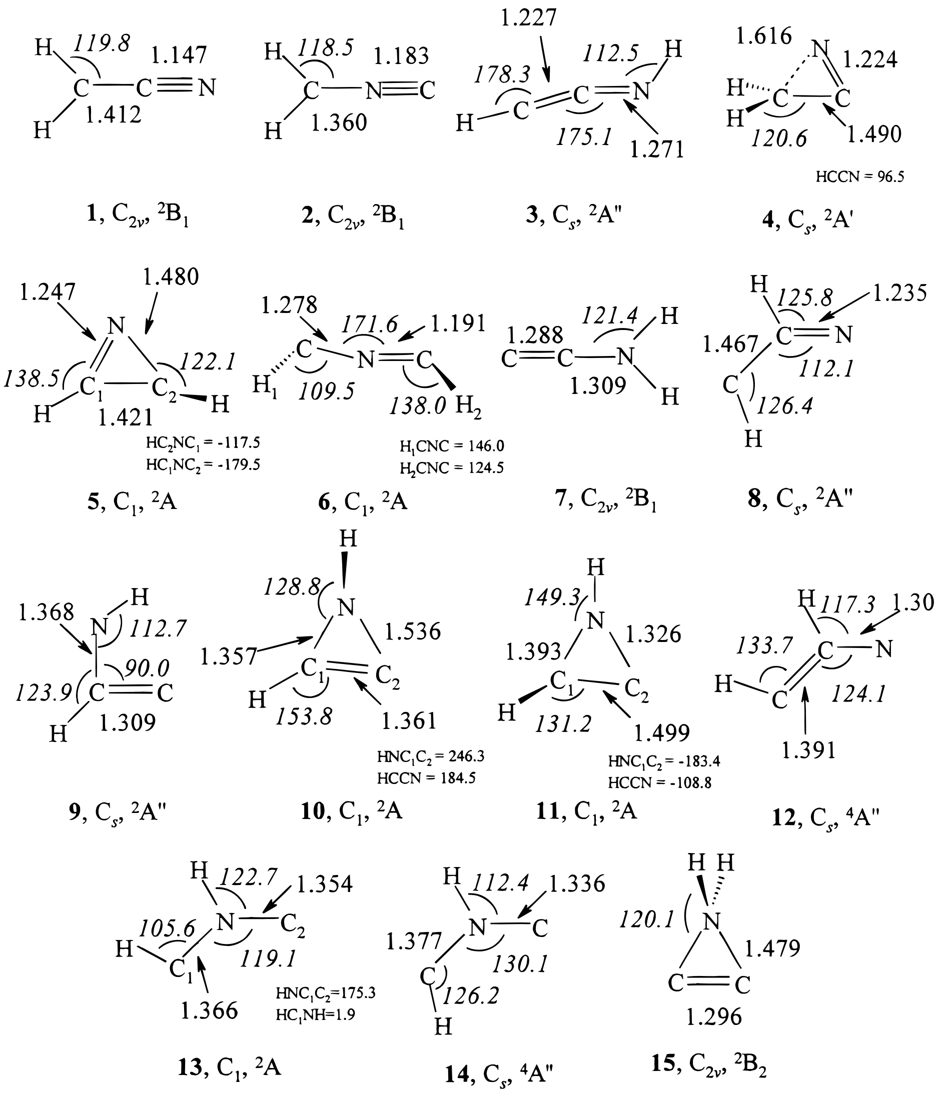


1, C_{2v}, $^2B_1$ **2**, C_{2v}, $^2B_1$ **3**, C_s, $^2A''$ **4**, C_s, $^2A'$

5, C_1, ^2A **6**, C_1, ^2A **7**, C_{2v}, $^2B_1$ **8**, C_s, $^2A''$

9, C_s, $^2A''$ **10**, C_1, ^2A **11**, C_1, ^2A **12**, C_s, $^4A''$

13, C_1, ^2A **14**, C_s, $^4A''$ **15**, C_{2v}, $^2B_2$

Figure 1. Selected structural parameters of C_2H_2N isomers optimized at the levels of MP2(Full)/6-31G(d) (**1**−**11**, **13**, and **15**) and QCISD(Full)/6-31G(d) (**12** and **14**). All bond lengths are in angstroms, and angles are in degrees. It is noted that **8**, **11**, and **15** do not exist at the QCISD(Full)/6-31G(d) level.

HF/6-31G(d) and MP2(Full)/6-31G(d) levels. Indeed, with this additional structural optimization, several isomers were eliminated.

For the isomeric C_2H_2N radicals, unrestricted wave functions were used in all geometry optimizations and single-point energy calculations. For the $C_2H_2N^+$ isomers, a number of closed-shelled cationic structures (**1**$^+$, **3**$^+$, **6**$^+$, **7**$^+$, and **10**$^+$) were found to have unrestricted Hartree−Fock (UHF) energies lower than the corresponding restricted Hartree−Fock (RHF) energies, i.e., RHF instabilities occur. For these cations, except **7**$^+$ and **10**$^+$, the unrestricted wave functions were first constructed. Then these unrestricted wave functions were employed in the geometry optimizations at the UHF/6-31G(d) and UMP2(Full)/6-31G(d) levels. The eventual UMP2(Full)/6-31G(d) geometries were then used for single-point energy calculations. For **7**$^+$ and **10**$^+$, the unrestricted wave functions reverted to the restricted wave functions during UHF/6-31G(d) optimizations. Therefore, the original RHF wave functions were used for energy calculations. For the remaining cationic species (**2**$^+$ and **5**$^+$), their wave functions are RHF stable and hence the restricted wave functions were used in the subsequent G2 calculations.

In our calculations, spin contamination in the UHF wave functions is significant for some radicals, e.g. the $\langle S^2 \rangle$ values of UHF/6-31G(d) wave functions for **1** and **3** are 0.924 and 0.939, respectively. Hence, we employed the method proposed by Chiu and co-workers[7] to correct the spin contamination in UHF wave functions. Energy correction term, $\Delta E(\langle S^2 \rangle)$, for the spin contamination is approximated by:

$$\Delta E(\langle S^2 \rangle) = E[\text{PUMP4/6-311G(2df,p)}] - E[\text{UMP4/6-311G(2df,p)}] \quad (2)$$

The energy correction term for spin contamination is added to the G2 energy in order to yield the projected (corrected) G2 energy, PG2, according to the following expression:

$$\text{PG2} = \text{G2} + \Delta E(\langle S^2 \rangle) \quad (3)$$

This method has been applied to all radical and cationic isomers with RHF instabilities.

Additionally, it is noted that G2 heats of formations in this work were calculated in the following manner.[7] For molecule AB, its G2 heat of formation at T ($\Delta H^\circ_{f,T}$) is calculated from the G2 heat of reaction $\Delta H^\circ_{r,T}$ ($A + B \rightarrow AB$) and the respective experimental $\Delta H^\circ_{f,T}(A)$ and $\Delta H^\circ_{f,T}(B)$ for elements A and B.

Before proceeding to presenting and discussing the results, we note that the G2 predictions for ΔH°_f's and IE's are usually

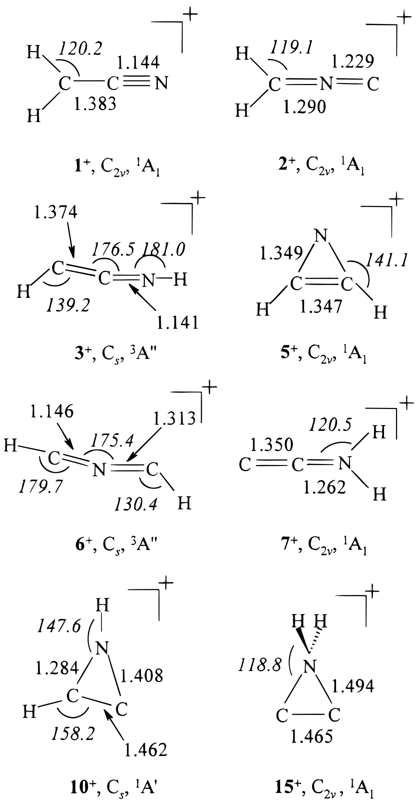


Figure 2. Selected structural parameters of $C_2H_2N^+$ isomers ($\mathbf{1^+}-\mathbf{3^+}$, $\mathbf{5^+}-\mathbf{7^+}$, $\mathbf{10^+}$, and $\mathbf{15^+}$) at the MP2(Full)/6-31G(d) level. All bond lengths are in angstroms, and angles are in degrees. It is found that $\mathbf{15^+}$ does not exist at the QCISD(Full)/6-31G(d) level.

well within ±0.15 eV (or about ±15 kJ mol^{-1}) of the experimental data.[5] So far we have applied the G2 method to determine the $\Delta H°_f$'s of C_2H_5S[7,8] and $C_2H_5S^+$ [9] isomers, $CH_3S_2^+$, CH_3S_2, and $CH_3S_2^-$ isomers,[10,11] CH_3O^+, CH_3O, and CH_3O^- isomers,[12−14] SF_n^+, SF_n, and SF_n^-, $n = 1-6$,[15,16] CH_3SF and CH_3SSCH_2,[17] and Cl_2O_2 and $Cl_2O_2^+$ isomers as well as their fragments.[18] In addition, we have applied the same method to determine the energies of the dissociation reaction involving CH_3S, CH_2SH, and their cations and anions,[19] $HSCH_2CH_2SH$,[20] C_2H_3Cl, and $C_2H_3Cl^+$,[21] as well as Cl_2O_2 and $Cl_2O_2^+$ isomers.[18] In all instances, the calculated results are in good to excellent agreement with the experimental data. Indeed, there are also cases we use the G2 results to suggest preferred values where the experimental data are either not very accurate or in conflict with each other.[16] There are also examples where the G2 results are used to revise experimental data.[22]

Results and Discussion

In our notation, numerals **1**, **2**, etc., refer to C_2H_2N radicals, while their corresponding cations are denoted as $\mathbf{1^+}$, $\mathbf{2^+}$, etc. At the MP2(Full)/6-31G(d) level, there are 15 C_2H_2N isomers (**1**−**15**, in order of decreasing stability) and eight $C_2H_2N^+$ isomers ($\mathbf{1^+}-\mathbf{3^+}$, $\mathbf{5^+}-\mathbf{7^+}$, $\mathbf{10^+}$, and $\mathbf{15^+}$) found on their respective potential energy surfaces. The geometries of the radicals and cations, optimized at the MP2(Full)/6-31G(d) level, are displayed in Figures 1 and 2, respectively. However, it should be noted that, at the QCISD(Full)/6-31G(d) level, radicals **8**, **11**, and **15** no longer exist. In trying to locate these species at the higher level, we found **5**, **10**, and **7**, respectively. Also, at the higher level, cation $\mathbf{15^+}$ does not exist. In its optimization, we found $\mathbf{7^+}$ instead.

The G2 energies at 0 K (E_0), enthalpies at 298 K (H_{298}), heat of formation at 0 and 298 K ($\Delta H°_{f0}$ and $\Delta H°_{f298}$) for the C_2H_2N and $C_2H_2N^+$ isomers are summarized in Tables 1 and 2, respectively. Where available, experimental values are included for ready comparison. Also included in Table 1 are the G2 IE's of the radicals, and the energy corrections due to spin contamination [$\Delta E(\langle S^2\rangle)$].

To gain further validity for the modified G2 method employed in this work, especially regarding the energy correction due to spin contamination, we also carried out analogous calculations for two C_3H_3 isomers and their corresponding cations, for which thermodynamics data are available in the literature. The C_3H_3 isomers are CH_2CCH and c-C_3H_3, which are isoelectronic to **1** and **5**, respectively. In other words, cations CH_2CCH^+ and c-$C_3H_3^+$ are isoelectronic to $\mathbf{1^+}$ and $\mathbf{5^+}$, respectively. Results for these four species are summarizied in Table 3.

The C_2H_2N and $C_2H_2N^+$ Isomers. The most stable C_2H_2N isomer is the cyanomethyl radical, CH_2CN (**1**), with C_{2v} symmetry. Among the remaining isomers, **2** and **7** also have C_{2v} symmetry. But they have different skeletons in that **2** has the CNC linkage and that of **7** is CCN. Isomer **3** (C_s) and **6** (C_1) have terminal hydrogens at both ends. Isomer **4** has a partially closed ring in which the nitrogen atom is weakly bonded to the methylenic carbon. Isomer **5** is the most stable species among the five cyclic isomers. Radicals **8** and **12** form a pair of cis and trans geometrical isomers. However, at the QCISD(Full)/6-31G(d) level, for **8**, ring closure takes place to form **5**. Radicals **10** and **11** are two cyclic isomers in which the nitrogen atom in **10** is sp^3-hybridized, while in **11** it is the carbon atom that is sp^3-hybridized instead. At the aforementioned higher level, **11** reverts to **10**. Isomer **9** has a planar structure with the two hydrogens in trans arrangement. [We could not locate the *cis*-isomer]. Also, **13** and **14** are another pair of cis−trans isomers. The cyclic radical **15** is the least stable C_2H_2N isomer and it becomes **7** at the QCISD(Full)/6-31G(d) level. Finally, it is noted that, at the HF/6-31G(d) and MP2(Full)/6-31G(d) levels, all C_2H_2N isomers, except **12**, have a doublet ground state. For **12**, the ground state is a spin quartet. On the other hand, at the QCISD(Full)/6-31G(d) level, both **12** and **14** have a quartet ground state, while those for all other isomers are doublets.

Although 15 C_2H_2N radical isomers were found, we only located eight cationic equilibrium structures for $C_2H_2N^+$ at the MP2(Full)/6-31G(d) level. Furthermore, at the QCISD(Full)/6-31G(d) level, $\mathbf{15^+}$ no longer exists. Radical isomers outnumber cationic isomers because some of the radical isomers ionize to the same cation. Rather surprisingly, the cyclic cation $\mathbf{5^+}$ is most stable among the $C_2H_2N^+$ isomers. Compared with $\mathbf{1^+}$, $\mathbf{5^+}$ is more stable by 30 kJ mol^{-1}. However, when their radical counterparts are compared, **1** is more stable than **5** by 240 kJ mol^{-1}. Thus, the presence or absence of one electron changes the relative stabilities of these isomers by about 270 kJ mol^{-1}. The extra stability of $\mathbf{5^+}$ may be due to its considerable aromatic stabilization, as two π-electrons are delocalized into the vacant p orbital of nitrogen. Cation $\mathbf{5^+}$ is the ionized product for both radicals **5** and **12**. Isomers $\mathbf{2^+}$, $\mathbf{3^+}$, $\mathbf{6^+}$, $\mathbf{7^+}$, and $\mathbf{10^+}$ are the cations of their corresponding radicals. They have structures similar to their radicals. It is worth noting that, in **3**, the nitrogen atom is sp^2-hybridized and the terminal carbon is sp-hybridized. On the other hand, for $\mathbf{3^+}$, just the opposite is true: the terminal carbon is sp^2-hybridizied while the nitrogen atom is sp-hybridized. Cation $\mathbf{1^+}$ is the ionized product of both **1** and **4**. Additionally, the cyclic cation $\mathbf{10^+}$ is the common ionized product of radicals **9**, **10**, **13**, and **14**. Regarding the spin state of the cations, at all

TABLE 1: G2 Total Energies (E_0), Enthalpies (H_{298}), Standard Heats of Formation at 0 K (ΔH°_{f0}) and 298 K (ΔH°_{f298}), Energy Corrections for Spin Contamination [ΔE ($\langle S^2 \rangle$)], Expectation Values of S^2 ($\langle S^2 \rangle$), and Ionization Energies (IE) of C_2H_2N Isomers

species	E_0 (G2)[a] (hartree)	ΔH°_{f0}(G2)[a] (kJ mol^{-1})	H_{298} (G2)[a] (hartree)	ΔH°_{f298} (G2)[a,b] (kJ mol^{-1})	ΔE ($\langle S^2 \rangle$) (kJ mol^{-1})	$\langle S^2 \rangle$ (au)	IE[b] (eV)	ionization process
1, C_{2v}, $^2B_1$	−131.87769	248.3	−131.87298	246.5 (243 ± 13)[c] (245 ± 10)[d] (250 ± 8)[e] (253 ± 9)[f]	−21.4	0.924	10.18 (10.28 ± 0.01)[g] (10.30 ± 0.04)[h]	**1** → **1**$^+$
2, C_{2v}, $^2B_1$	−131.83820	351.9	−131.83317	351.1 (310 ± 13)[i] (334 ± 8)[j] (336 ± 11)[f] (402 ± 13)[c]	−12.7	0.861	9.48 (8.40)[k] (8.30−9.26)[l]	**2** → **2**$^+$
3, C_s, $^2A''$	−131.82797	378.8	−131.82298	377.8	−25.7	0.939	9.92	**3** → **3**$^+$
4, C_s, $^2A'$	−131.79022	477.9	−131.78598	475.0	−10.3	0.875	7.80	**4** → **1**$^+$
5, C_1, ^2A	−131.78644	487.8	−131.78229	484.6 (≈339)[c]	−12.9	0.919	7.41 (≤8.30)[c]	**5** → **5**$^+$
6, C_1, 2A	−131.77888	507.7	−131.77395	506.5	−28.6	1.140	8.75	**6** → **6**$^+$
7, C_{2v}, $^2B_1$	−131.77006	530.8	−131.76518	529.5	−4.0	0.767	9.46	**7** → **7**$^+$
9, C_s, $^2A''$	−131.74868	587.0	−131.74415	584.8	−19.8	0.985	7.87	**9** → **10**$^+$
10, C_1, 2A	−131.74611	593.7	−131.74148	591.8	−4.8	0.800	7.80	**10** → **10**$^+$
12[m], C_s, $^4A''$	−131.74471	597.4	−131.74028	594.9	−26.5	4.048	6.28	**12** → **5**$^+$
13, C_1,^2A	−131.68587	751.9	−131.68141	749.5	−19.1	1.202	6.16	**13** → **10**$^+$
14[m], C_s, $^4A''$	−131.66346	810.7	−131.65881	808.8	−9.3	3.808	5.55	**14** → **10**$^+$

[a] These results have been corrected for spin contamination (see text). [b] Experimental data, where available, are given in brackets beneath the G2 value. [c] Reference 23. [d] Reference 24. [e] Reference 25. [f] Calculated from ref 26. [g] Reference 1. [h] Reference 27. [i] Reference 28. [j] Reference 29. [k] Reference 30. [l] Using ΔH°_{f298} values for radical and cation in Tables 1 and 2, respectively. [m] Calculated at the G2//QCI level.

TABLE 2: G2 Total Energies (E_0), Enthalpies (H_{298}), Standard Heats of Formation at 0 K (ΔH°_{f0}) and 298 K (ΔH°_{f298}), Energy Corrections for Spin Contamination [ΔE ($\langle S^2 \rangle$)], and Expectation Values of S^2 ($\langle S^2 \rangle$) of $C_2H_2N^+$ Isomers

species	E_0 (G2) (hartree)	ΔH°_{f0}(G2)[a] (kJ mol^{-1})	H_{298} (G2)[a] (hartree)	ΔH°_{f298} (G2)[a,b] (kJ mol^{-1})	ΔE ($\langle S^2 \rangle$) (kJ mol^{-1})	$\langle S^2 \rangle$ (au)
1$^+$, C_{2v}, $^1A_1$	−131.50344	1230.8	−131.49874	1229.1 (1218 ± 8)[c] (1246 ± 18)[d]	−33.7	0.352
2$^+$, C_{2v}, $^1A_1$	−131.48978	1266.7	−131.48493	1265.4 (1180−1226)[c]		
3$^+$, C_s, $^3A''$	−131.48741	1272.9	−131.48223	1272.4	−20.4	2.199
5$^+$, C_{2v}, $^1A_1$	−131.51410	1202.8	−131.51010	1199.3 (≤1138)[c]		
6$^+$, C_s, $^3A''$	−131.47494	1305.7	−131.46973	1305.3	−28.8	2.045
7$^+$, C_{2v}, $^1A_1$	−131.42253	1443.3	−131.41779	1441.6		
10$^+$, C_s, $^1A'$	−131.45942	1346.4	−131.45536	1343.0		

[a] Where applicable, the energies have been corrected for spin contamination (see text). [b] Experimental data, where available, are given in brackets beneath the G2 value. [c] Reference 23. [d] Reference 27.

TABLE 3: G2 Total Energies (E_0), Enthalpies (H_{298}), Standard Heats of Formation at 0 K (ΔH°_{f0}) and 298 K (ΔH°_{f298}), Energy Corrections for Spin Contamination [ΔE ($\langle S^2 \rangle$)], Expectation Values of S^2 ($\langle S^2 \rangle$), and Ionization Energies (IE) of Two C_3H_3 Isomers and Their Cations

species	E_0 (G2)[a] (hartree)	ΔH°_{f0}(G2)[a] (kJ mol^{-1})	H_{298} (G2)[a] (hartree)	ΔH°_{f298} (G2)[a,b] (kJ mol^{-1})	ΔE ($\langle S^2 \rangle$) (kJ mol^{-1})	$\langle S^2 \rangle$ (au)	IE[b] (eV)
CH_2CCH, C_{2v}, $^2B_1$	−115.78226	341.7	−115.77702	340.8 (343)[c]	−23.6	0.974	8.70 (8.68)[c]
CH_2CCH^+,[d] C_{2v}, $^1A_1$	−115.46238	1181.6	−115.45748	1179.7 (1179)[c]	−22.5	0.224	
c-C_3H_3, C_s, $^2A'$	−115.72303	497.2	−115.71862	494.1 (440 ± 17)[c]	−2.4	0.759	6.09 (6.6)[c]
c-$C_3H_3^+$, D_{3h}, $^1A_1'$	−115.49928	1084.7	−115.49517	1080.8 (1075)[c]			

[a] Where applicable, the energies have been corrected for spin contamination (see text). [b] Experimental data, where available, are given in brackets beneath the G2 value. [c] Reference 24. [d] Wave functions for this species are found to be RHF unstable.

three levels of theories employed in this work, **3**$^+$ and **6**$^+$ have triplet ground states, while those of the remaining cations are singlets.

In summary, at the QCISD(Full)/6-31G(d) level, we have located 12 C_2H_2N isomers and seven $C_2H_2N^+$ isomers.

The Cyanomethyl Radical (1) and Cation (1$^+$). Examining Table 1, it is seen that the G2 IE (10.18 eV) of the cyanomethyl radical (**1**) is in good agreement with the latest experimental results of 10.28 ± 0.01 eV by Thorn and co-workers.[1] In addition, our G2 ΔH°_{f298} value of 246.5 kJ mol^{-1} is in good to excellent agreement with the various data found in the literature.[23–26] It is noted that the very good agreement between our result and the experimental data is achieved through the energy correction due to spin contamination as expressed in eqs 2 and 3. Without such a correction, the G2 ΔH°_{f298} value is 267.2 kJ mol^{-1}. Indeed, as pointed out by Radom et al.,[4] several G2- and CBS-based methods lead to essentially the same ΔH°_{f298} value for **1**, about 20 kJ mol^{-1} higher than the experimental result. As for the cyanomethyl cation (**1**$^+$), from Table 2, the G2 ΔH°_{f298} value of 1229.1 kJ mol^{-1} is about the average of the listed experimental data (1218 ± 8 kJ mol^{-1} by Holmes and Mayer[23] and 1246 ± 18 kJ mol^{-1} by Shea et al.[27]).

In short, by considering the correction due to spin contamination, our G2 method yields good to very good results for the thermodynamic data of the cyanomethyl cation and radical. It is further pointed out that the experimental results for these two species come from several independent investigations.[1,23−26]

Examining Table 3, it is seen that once again the spin contamination correction leads to very good results for CH_2CCH and CH_2CCH^+, species isoelectronic to **1** and **1**$^+$, respectively. Specifically, our G2 $\Delta H°_{f298}$ for CH_2CCH (340.8 kJ mol^{-1}) and CH_2CCH^+ (1179.7 kJ mol^{-1}) are in excellent agreement with the experimental data (343 and 1179 kJ mol^{-1}, respectively) listed in Lias's compendium.[24] As a result, our G2 IE for CH_2CCH (8.70 eV) is also in very good accord with the experimental results (8.68 eV[24]). The results obtained with our G2 model for **1** and **1**$^+$ as well as for their isoelectronic species lend confidence to the results for other C_2H_2N and $C_2H_2N^+$ isomers obtained with the same method.

The Isocyanomethyl Radical (2) and Cation (2$^+$). From Table 1, it is seen that there are four rather disparate experimental results in the literature for the $\Delta H°_{f298}$ of the CH_2NC radical (**2**), ranging from 310 ± 13 to 402 ± 13 kJ mol^{-1}.[23,26,28,29] Additionally, it is noted[4] that G2- and CBS-based methods yield essentially the same $\Delta H°_{f298}$ for **2**, about 360 kJ mol^{-1}. Our G2 value, 351.1 kJ mol^{-1}, is within the error range of the experimental data reported by Matimba et al.[29] (334 ± 8 kJ mol^{-1}) and by Berkowitz et al.[26] (336 ± 11 kJ mol^{-1}). As for the $\Delta H°_{f298}$ for the CH_2NC^+ cation (**2**$^+$), Holmes and Mayer[23] reported a value range of 1180−1226 kJ mol^{-1} for this quantity. Our G2 result for $\Delta H°_{f298}$ of **2**$^+$ is 1265.4 kJ mol^{-1}, while other G2- and CBS-based method lead to values between 1265 and 1270 kJ mol^{-1}. In view of the rather large disagreement between the calculated and experimental results, as well as the difference between the experimental data in the literature, the $\Delta H°_{f298}$ values for the isocyanomethyl radical and cation clearly deserve a reexamination.

In passing, it is mentioned that there also appears to be some confusion regarding the IE of **2**. In their experimental study for the IE of **1**, Thorn and co-workers[1] noted that the IE of **2** is 9.4 eV, quoting the work of Holmes and Mayer.[23] This value is in excellent agreement with our G2 result, 9.48 eV (Table 1). However, upon private communication, we have learned that the value of 9.4 eV is actually a misprint for 8.4 eV.[30] In other words, the G2 result is more than 1 eV off the experimental value in the literature. As discussed in the previous section, the error range for G2 result is usually well within ±0.15 eV. Hence our G2 result for the IE of **2** has cast some doubt on the accuracy of the experimental work.[23] Meanwhile, the G2- and CBS-based methods of Radom et al.[4] yield IE values between 9.35 and 9.42 eV.

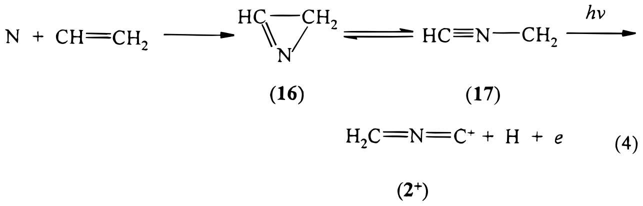
The 1*H*-Azirinyl Radical (5) and Cation (5$^+$). There are experimental *estimates*[23] for the $\Delta H°_{f298}$ values of **5** and **5**$^+$. They are ≈339 and ≤1138 kJ mol^{-1}, respectively, giving rise to an approximated IE of ≤8.30 eV for **5**. Since the results were obtained by various approximation and estimation,[23] we feel that our G2 results, 484.6 and 1199.3 kJ mol^{-1} for the $\Delta H°_{f298}$ values for **5** and **5**$^+$, respectively, and 7.41 eV for the IE of **5**, are very likely to be the more accurate estimates. Furthermore, it is pointed out that the computational results by Radom et al. are in better agreement with our results than with experimental estimates. They have also suggested possible sources for the experimental uncertainties.

In Table 3, we have listed the G2 results for c-C_3H_3 and c-$C_3H_3^+$, which are isoelectronic to **5** and **5**$^+$, respectively. It is seen that our G2 $\Delta H°_{f298}$ for c-$C_3H_3^+$ (1080.8 kJ mol^{-1}) agrees very well with the experimental result (1075 kJ mol^{-1}).[24] On the other hand, both our G2 $\Delta H°_{f298}$ (494.1 kJ mol^{-1}) and IE (6.09 eV) of c-C_3H_3 are not in agreement with the available experimental data, 440 ± 17 kJ mol^{-1} and 6.6 eV, respectively. Indeed, the disagreements are so large that they raise doubts on the accuracy of the experimental results. Actually, such discrepancies have already been reported by Glukhovtsev and co-workers.[31] In their work, the G2 $\Delta H°_{f298}$ of c-C_3H_3 was calculated using various atomization and isodesmic schemes; the results range from 479.2 to 495.5 kJ mol^{-1}, in good agreement with our G2 value. Also, their G2 IE for c-C_3H_3 was calculated to be 6.06 eV, very close to our result.

In summary, our modified G2 method, which takes into consideration energy correction due to spin contamination, gives results for the $\Delta H°_{f298}$ values of **1**, **1**$^+$, CH_2CCH, CH_2CCH^+, and c-$C_3H_3^+$, and IE values of **1** and CH_2CCH, which are in excellent agreement with the available experimental data. These agreements suggest that our G2 method should yield reliable results for the remaining C_2H_2N and $C_2H_2N^+$ isomers.

Other Isomers. There are nine other C_2H_2N isomers and four other $C_2H_2N^+$ isomers for which no experimental data are available. It is hoped that the results reported in Tables 1 and 2 will provide incentives for experimentalists to study these hitherto unknown species. Among the unknown C_2H_2N species, radicals **3** and **4**, which are more stable than **5** thermodynamically, appear to be prime candidates for experimental detection and other studies.

The Unidentified C_2H_2N Isomer Formed in N + CH=CH$_2$. In the reaction between nitrogen atom and vinyl radical (reaction 1),[1] Thorn and co-workers reported the possible formation of a C_2H_2N radical with an IE upper bound of 9.64 eV. Among the 12 C_2H_2N isomers studied in this work, there are two candidates that satisfy this IE requirement. They are **2** (isocyanomethyl radical, CH_2NC) and **7** (ethen-2-yl-1-iminium radical, NH_2CC) with IE's of 9.48 and 9.46 eV, respectively. Chemically, it is not clear to us how **7** or **7**$^+$ is formed in the aforementioned reaction. On the other hand, the following appears to be a plausible pathway for the formation of **2**$^+$ (reaction 4).



In reaction 4, the nitrogen atom inserts into the double bond of the vinyl radical to form azirine (**16**), which ring-opens to produce nitrile ylide (**17**). Ylide **17** then undergoes dissociative photoionization to produce **2**$^+$. Hence, it seems that **2** is likely to be the unidentified C_2H_2N isomer.

Conclusions

From the above discussion, the following conclusions may be drawn:

(1) The G2 method including energy correction due to spin contamination yields $\Delta H°_{f298}$ values for the cyanomethyl radical **1** and cation **1**$^+$ and IE results for **1** that are in very good agreement with the available data in the literature.

(2) However, the G2 results for the isocyanomethyl radical **2** and cation **2**$^+$ as well as for radical **5** and cation **5**$^+$ do not agree with the available experimental data. In addition, the various experimental data are not in good accord. This calls for a reexamination of the experimental results.

(3) On the basis of the G2 IE's of the C_2H_2N isomers listed in Table 1, it is suggested that the unidentified C_2H_2N isomer formed in the reaction between nitrogen atom and vinyl radical may be CH_2NC (**2**).

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