Thermochemistry of CH_3CN, CH_3NC, and Their Cyclic Isomers and Related Radicals, Cations, and Anions: Some Curious Discrepancies between Theory and Experiment

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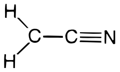
The heats of formation of four C_2H_3N molecules and the three most stable C_2H_2N cations, namely, cyanomethyl, isocyanomethyl, and azirinyl, together with their corresponding radicals and anions, have been calculated at the G2, G2(//QCI), CBS-Q, and CBS-RAD levels of theory. In addition, bond dissociation enthalpies and gas-phase acidities of the molecules and the electron affinities and ionization energies of the free radicals have been derived. Comparison of the theoretical results with available experimental values shows generally good agreement with directly measured experimental data but significant discrepancies in several instances for derived quantities.

1. Introduction

The determination of the thermochemical properties of small organic molecules remains a fundamental goal in chemistry. In particular, the bond strengths, proton affinities, and acidities of molecules are key values in understanding chemical behavior. The experimental determination of such properties is often difficult and fraught with large potential uncertainties, and so theory can make important contributions. In particular, ab initio calculations at the G2 level of theory[1] have contributed significantly to the thermochemical knowledge of small molecules, including heats of formation,[1,2c−e,g−j] proton affinities,[1,2b,h−j] gas-phase acidities,[2a,f,j] and bond dissociation enthalpies.[1,2e,g−i]

One of the most common solvents in chemistry is acetonitrile, CH_3CN. While the heats of formation of acetonitrile and its isomer, isocyanomethane, are known to reasonable precision,[3] the C−H bond dissociation enthalpies in these two molecules are less certain, owing primarily to the uncertainities in the experimentally determined heats of formation of the free radicals, $^{\bullet}CH_2CN$ and $^{\bullet}CH_2NC$.[3−5] There is very little known about the thermochemistry of the cyclic isomers of CH_3CN and CH_3NC such as 1*H*- or 2*H*-azirine.

A key to determining some of the thermochemical properties of these molecules is knowledge pertaining to the C_2H_2N family of radicals, cations, and anions (see also Figure 1):



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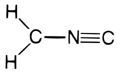

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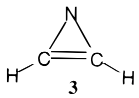

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The cyanomethyl radical (**1**) has been included in many theoretical[6] and experimental[5e,f,7] investigations of free radical stability. Similarly, the cyanomethyl cation ($\mathbf{1}^+$) has been the subject of investigations concerning the stability of substituted methyl cations.[5e,f] These species are also of significance to interstellar chemistry since $^{\bullet}CH_2CN$ is an interstellar species and the related HC_nN species have been detected in interstellar clouds.[8] The ionization energies of $^{\bullet}CH_2CN$ and $^{\bullet}CH_2NC$ have been determined through recent high-level ab initio calculations,[9] and there have been very recent experimental investigations[10] of the ionization energy of $^{\bullet}CH_2CN$. The 1*H*-azirin-1-yl cation ($\mathbf{3}^+$) is a prototype example of an aromatic species, while the anion $\mathbf{3}^-$ is an example of a potentially antiaromatic species.

We present here a high-level ab initio study of the thermochemistry of the C_2H_3N molecules acetonitrile (CH_3CN, **1H**), isocyanomethane (CH_3NC, **2H**), and two cyclic isomers, 2*H*-azirine ($\mathbf{3H_a}$) and 1*H*-azirine ($\mathbf{3H_b}$). The heats of formation of the C_2H_3N molecules and the cyano- and isocyano-substituted methyl radicals, cations, and anions, along with corresponding values for the 1*H*-azirin-1-yl isomer (referred to for simplicity in this paper simply as azirinyl), are calculated at several levels of theory. In addition, the C−H bond dissociation enthalpies and gas-phase acidities of the C_2H_3N molecules and the electron affinities and ionization energies of the free radicals are derived. The calculated values are compared with available experimental data.

2. Computational Methods

Standard ab initio molecular orbital calculations[11] were carried out using the GAUSSIAN 94[12] suite of programs. Geometry optimizations were performed at the HF. MP2(full), B3-LYP, and QCISD levels of theory with the 6-31G(d) basis set. The composite methods G2,[1] G2(//QCI),[13] CBS-Q,[14] and CBS-RAD[15] were employed to calculate the total energies of each species. Extensive testing has shown these methods to be generally reliable to within 10 kJ mol^{-1}. The lack of diffuse functions in the basis set for the optimization of the geometry of $\mathbf{1}^-$ has previously been found not to introduce significant errors[2j] and thus should not present a problem in the present work.

G2 theory[1] effectively corresponds to a QCISD(T)/6-311+G(3df,2p) energy calculation on a geometry optimized at the MP2(full)/6-31G(d) level of theory. A zero-point vibrational energy (ZPE) correction is made using the scaled (by 0.8929) harmonic vibrational frequencies calculated at the HF/6-31G(d) level. An

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empirical higher level correction (HLC) is also included to account for residual basis set deficiencies. The standard G2 approach has been found to generally predict molecular $\Delta_f H°$ values to within ±10 kJ mol^{-1} accuracy (and typically does better than this), but it performs less well for highly spin-contaminated situations.[15] The G2(//QCI)[13] variant of G2 theory incorporates a geometry optimized at the QCISD/6-31G(d) level. It has been found that improvement of the level of theory used to optimize the geometry for open-shell species showing significant spin contamination can lead to considerable improvement in the predicted thermochemistry.[15]

CBS-Q[14] is a method that attempts to approximate the energy of a species at the infinite basis set limit by performing an extrapolation of the energies of pair natural orbitals at the MP2 level. The effects of going from MP2 to QCISD(T) are accounted for with an additivity scheme. The geometry is obtained at the MP2/6-31G† level of theory, while the ZPE used is the scaled (by 0.9135) HF/6-31G† value. For open-shell systems, there is also a correction for spin contamination in the unrestricted Hartree–Fock wave function. The CBS-Q method has been shown generally to yield reliable $\Delta_f H°$ values for small molecules.[14]

The CBS-RAD procedure was formulated with a view to obtaining reliable free radical heats of formation for severely spin-contaminated species.[15] It differs from CBS-Q in that it employs an improved geometry and ZPE and replaces the QCISD(T)/6-31+G† single-point calculation with a CCSD(T) calculation with the same basis set. The spin-correction factor of CBS-Q is retained in CBS-RAD and is a key factor in the good performance of CBS-RAD for spin-contaminated radicals. The particular CBS-RAD variant used in the present study is CBS-RAD(QCISD,B3-LYP),[15] which employs a geometry optimized at QCISD/6-31G(d) and a ZPE calculated from scaled (by 0.9806)[16] B3-LYP/6-31G(d) harmonic vibrational frequencies. For simplicity, these calculations are referred to as CBS-RAD in the present paper, but it should be emphasized that the CBS-RAD(QClSD,B3-LYP) variant was used throughout.

Heats of formation at 0 K ($\Delta_f H°_0$) were derived from the G2, G2(//QCI), CBS-Q, and CBS-RAD total energies using the atomization method as outlined by Nicolaides et al.[17] We note that for charged species this entails balancing the ionization reaction with an electron, which of course has zero energy. G2 heats of formation at 298 K were obtained from the 0 K values using the calculated scaled (by 0.8929) HF/6-31G(d) vibrational frequencies of the species of interest together with the $H°_{298} - H°_0$ thermal corrections of the elements in their standard states.[18] CBS-Q values were corrected to 298 K employing scaled (by 0.9135) HF/6-31G† frequencies, while CBS-RAD values at 298 K were obtained with scaled (by 0.9989)[16] B3-LYP/6-31G(d) frequencies.

Theoretical bond dissociation enthalpies were obtained as the calculated ΔH values of reaction 1:

$$AH \rightarrow A^\bullet + H^\bullet \tag{1}$$

Gas-phase acidities at 298 K were obtained as the calculated ΔH values of reaction 2:

$$AH \rightarrow A^- + H^+ \tag{2}$$

Since the HLC in G2 theory is the same on both sides of reaction 2, all G2 calculations of acidities presented in this paper are purely ab initio. The same cannot be said of the two CBS methods, for which the corrections for the parent molecule and product anion are distinct. The electron affinities (EA) of the free radicals were obtained as the negative of the calculated enthalpy changes of reaction 3:

$$A^\bullet + e^- \rightarrow A^- \tag{3}$$

Their ionization energies (IE) were obtained as the calculated enthalpy changes of reaction 4:

$$A^\bullet \rightarrow A^+ + e^- \tag{4}$$

Unrestricted reference wave functions were used in all calculations on open-shell species. All calculations involving electron correlation employed a frozen core, except for the MP2/6-31G(d) geometry optimizations, which incorporated correlation of all electrons (MP2(full)). For simplicity, the term MP2 is used throughout the text instead of MP2(full).

Unless otherwise stated, all geometric parameters mentioned in the paper are QCISD/6-31G(d) values.

3. Results and Discussion

3.1. Structural Information. The optimized geometric parameters of the C_2H_3N molecules and C_2H_2N radicals, cations, and anions, as obtained at the QCISD, MP2, and B3-LYP levels of theory with the 6-31G(d) basis set, are shown in Figure 1.

a. The C_2H_3N Molecules. The parent molecules CH_3CN (**1H**) and CH_3NC (**2H**) both have C_{3v} symmetry, and each are similarly described at all three levels of theory (Figure 1).[19] Acetonitrile displays a QCISD/6-31G(d) C–C bond length of 1.470 Å and a C≡N bond length of 1.168 Å, which are in reasonable agreement with experimental values (from microwave spectroscopy) of 1.457 and 1.156 Å, respectively.[20a] Isocyanomethane has C–N and N≡C bond lengths of 1.430 and 1.183 Å, respectively, again in reasonable agreement with experimental values of 1.426 and 1.166 Å.[20b]

The lowest energy cyclic neutral is 2*H*-azirine (**3H$_a$**), having C_s symmetry. It is characterized by a formal C═N double bond of 1.264 Å, a long C–N single bond of 1.551 Å, and a slightly shortened C–C single bond of 1.451 Å. A second cyclic isomer, 1*H*-azirine (**3H$_b$**), also has C_s symmetry.[21] It displays two formally single C–N bonds of 1.521 Å and a short C═C double bond of 1.284 Å. The N–H bond lies out of the CNC plane by 81.8°, while the two C–H bonds are slightly out of the plane by 7.8°. Optimization under a C_2 symmetry constraint leads to a C_{2v} structure with one imaginary frequency (corresponding primarily to out-of-plane motion of the N–H bond).

b. The C_2H_2N Free Radicals. The cyanomethyl radical (**1**) has C_{2v} symmetry and a $^2B_1$ ground state at the HF, MP2, RMP2, B3-LYP, QCISD, QCISD(T), and CCSD(T) levels of theory.[9,15,19a,22] The QCISD/6-31G(d) structure has a C≡N length of 1.182 Å, a C–C length of 1.399 Å and an ∠HCC angle of 120.0°, which may be compared with the results of a recent microwave study which yielded a C≡N length of 1.192 Å and a C–C length of 1.368 Å.[23] The elongated C≡N bond and shortened C–C bond in **1** compared with **1H** may be attributed to delocalization involving the unpaired electron and the π and π^* orbitals of the C≡N triple bond.

The isocyanomethyl radical (**2**) also has C_{2v} symmetry and a $^2B_1$ ground state at the HF, MP2, B3-LYP, and QCISD levels of theory.[9,22] The QCISD/6-31G(d) structure has an N≡C bond length of 1.196 Å, a C–N bond length of 1.353 Å, and an ∠HCN bond angle of 118.8°. The N≡C bond is only slightly longer than that in **2H**, but the shortened C–N bond (1.353 vs 1.430 Å) indicates significant delocalization of the unpaired electron.

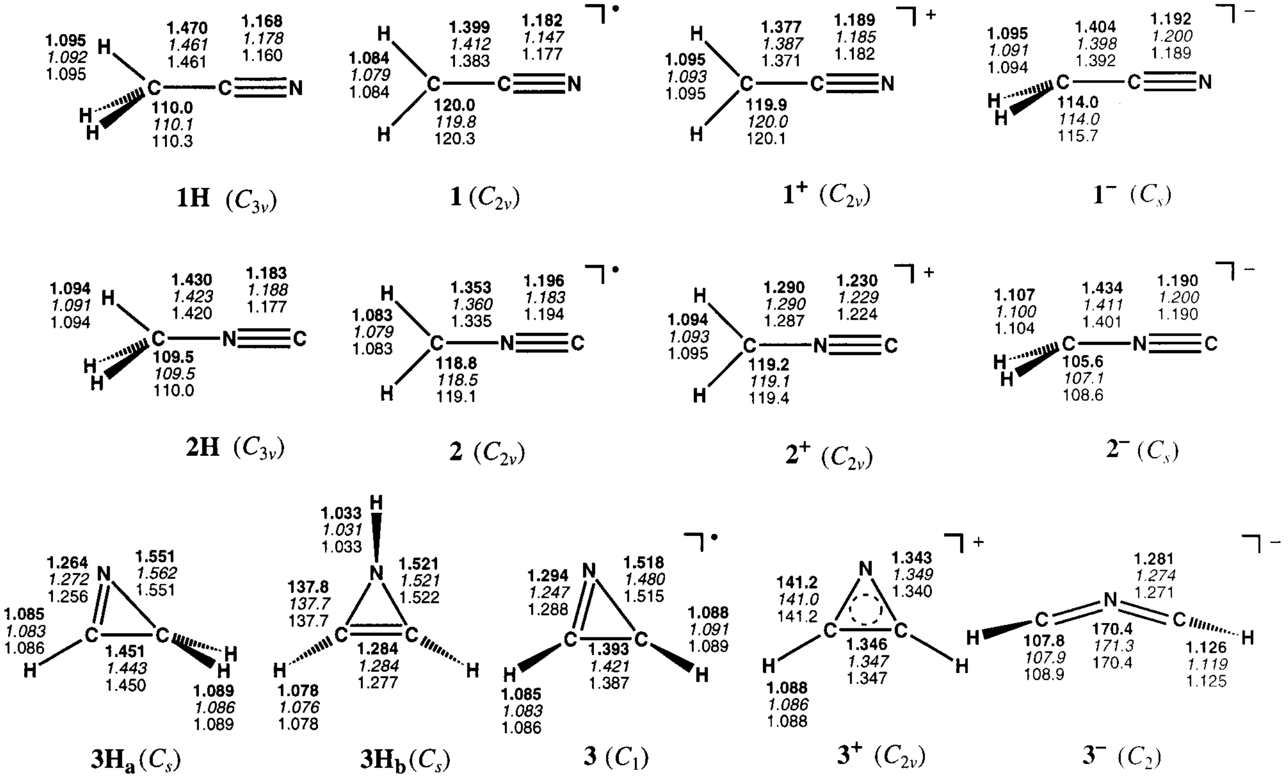

Figure 1. Selected optimized geometric parameters for the C_2H_3N molecules **(1H−3H)** and the C_2H_2N radicals (**1**−**3**), cations ($\mathbf{1}^+$−$\mathbf{3}^+$), and anions ($\mathbf{1}^-$−$\mathbf{3}^-$). QCISD/6-31G(d) values are shown in bold print, MP2(full)/6-31G(d) values in italics, and B3-LYP/6-31G(d) values in normal type.

The cyclic azirinyl radical (**3**) has C_1 symmetry and a geometry similar to that of $\mathbf{3H_a}$, with the removal of a hydrogen atom from the methylene group.[21] There is one formal C═N double bond (1.294 Å) and one formal C−N single bond (1.518 Å). The C−C bond has partial double-bond character (1.393 Å) due to delocalization of the unpaired electron. However, as in the isoelectronic cyclopropenyl radical, full cyclic delocalization does not take place.[24]

In a recent assessment of theoretical procedures for the study of free radicals, we found that in cases of high spin contamination, UMP2 geometries can differ significantly from the results of higher level treatments such as QCISD.[15] In that study, the $^\bullet CH_2CN$ radical (**1**, $\langle S^2\rangle = 0.978$) was explored in some detail, and differences between UMP2 and QCISD geometries were noted. We find here that this is also the case for radicals **2** ($\langle S^2\rangle = 0.835$) and **3** ($\langle S^2\rangle = 0.938$), though the differences are not as pronounced for **2**. We also find that B3-LYP reasonably approximates the QCISD results for these two radicals, in agreement with the conclusions reached in our earlier study.

c. The C_2H_2N Cations. In contrast to the above results for the free radicals, we find that the geometries of the three cations are not very sensitive to level of theory, there being only moderate geometric changes in going from MP2 and B3-LYP to QCISD.[9,19a,25] The cyanomethyl and isocyanomethyl cations ($\mathbf{1}^+$ and $\mathbf{2}^+$) have C_{2v} structures and show evidence of cumulenic contributions. Thus, the C−C bond in $\mathbf{1}^+$ has a length almost characteristic of a double bond (1.377 Å), while the C≡N bond is lengthened slightly to 1.189 Å. This reflects π-donation by the cyano group, as a result of which there is a significant contribution to the bonding in this cation from the cumulenic resonance contributor $CH_2{=}C{=}N^+$. The geometry of $\mathbf{2}^+$ suggests an even greater contribution from the cumulenic form, $CH_2{=}N{=}C^+$, as reflected in the very short C−N bond of 1.290 Å and elongated N≡C bond (1.230 Å).

The cyclic azirinyl cation ($\mathbf{3}^+$) also has C_{2v} symmetry, associated with the cyclic delocalization of the two π electrons in a formally aromatic species.[25] The structure is characterized by three similar bond lengths, two C−N bonds of 1.343 Å and one C−C bond of 1.346 Å. The MP2, B3-LYP, and QCISD geometries are in close agreement.

d. The C_2H_2N Anions. The anions $\mathbf{1}^-$ and $\mathbf{2}^-$ exhibit C_s symmetry due to the competing influences of interaction between the formal lone-pair orbital on C and the π* orbital on CN or NC, which would favor a planar C_{2v} structure, and four-electron repulsion between the carbanion lone pair and the π orbital on CN or NC, which would favor retention of pyramidalization at the carbanion carbon (Figure 1).[22] The short C−C and long C≡N lengths in $\mathbf{1}^-$ (1.404 and 1.192 Å, respectively) do nevertheless indicate significant delocalization of the lone pair to the CN group. It is clear from Figure 1 that $\mathbf{2}^-$ exhibits less delocalization than $\mathbf{1}^-$, since the C−N and N≡C bond lengths are very similar to those in the parent molecule **2H**, and the degree of pyramidalization at the carbanion carbon is greater in $\mathbf{2}^-$ than in $\mathbf{1}^-$. This is probably due to the partial negative charge already present on the terminal carbon in the isocyano species, making a further contribution of negative charge density unfavorable.

The addition of an electron to the azirinyl radical can lead to anion $\mathbf{3}^-$, which has a ring-opened structure. The ring-opened anion $\mathbf{3}^-$ has C_2 symmetry and is almost linear, having a ∠CNC angle of 170.4°. A second ring-opened isomer with an N−CH−CH skeleton (and C_1 symmetry) lies more than 70 kJ mol^{-1} higher in energy than $\mathbf{3}^-$ (at the G2 level of theory) and was not pursued further. We were unable to isolate a ring-closed anion at the levels of theory used in this study.

3.2. Heats of Formation. The heats of formation at 298 K of the C_2H_3N molecules and the C_2H_2N radicals, cations, and anions are listed in Table 1 together with experimental values

TABLE 1: Comparison of Calculated and Experimental $\Delta_f H^\circ_{298}$ Values[a]

	G2	G2(//QCI)	CBS-Q	CBS-RAD	experiment
1H	75.6	74.4	78.3	78.1	74 ± 1[b]
2H	174.6	174.2	177.5	178.6	173 ± 1[b]
3H$_a$	273.3	266.8	279.8	279.5	
3H$_b$	408.1	408.2	416.3	414.5	
1	267.2	263.1	261.8	262.6	245 ± 10,[b] 250 ± 8,[c] 243 ± 12,[d] 253 ± 9[e]
2	363.1	363.0	359.6	363.1	402 ± 12,[d] 310 ± 13,[f] 334 ± 8,[g] 336 ± 11[e]
3	497.0	490.3	498.8	491.1	≈339[d]
1$^+$	1249.0	1248.5	1255.9	1257.9	1218 ± 8,[d] 1246 ± 18,[h]
2$^+$	1265.0	1264.7	1268.8	1269.9	1203 ± 21[d]
3$^+$	1198.0	1198.4	1208.0	1207.0	≤1138[d]
1$^-$	114.1	113.3	117.5	118.1	105 ± 12,[b] 101 ± 8[c]
2$^-$	248.7	248.5	255.5	256.8	208 ± 13,[f] 232 ± 8[g]
3$^-$	357.0	357.8	364.1	368.3	

[a] In kJ mol^{-1}. [b] Lias et al.[3] [c] Moran et al.[5a] [d] Holmes and Mayer.[5f] [e] Calculated from data in Berkowitz et al.[4] See also Shea et al.[10a] [f] Moran et al.[5b] [g] Matimba et al.[5d] [h] Shea et al.[10a]

from the literature.[3,4,5a,b,d,f,10a] In the discussion that follows, the range of values predicted by our four high-level theoretical procedures is generally presented. For comparisons involving open-shell systems, we believe that the CBS-RAD values are the most reliable.[15]

a. The C_2H_3N Molecules. Both the G2-based and CBS-based values for the heats of formation of CH_3CN and CH_3NC agree well with experiment (Table 1). The 2*H*-azirine molecule **3H$_a$** is predicted to lie almost 100 kJ mol^{-1} higher in energy than CH_3NC, though the $\Delta_f H^\circ_{298}$ value depends moderately on level of theory, ranging from 266.8 kJ mol^{-1} at G2(//QCI) to 279.8 kJ mol^{-1} at CBS-Q. 1*H*-Azirine (**3H$_b$**) is significantly less stable than **3H$_a$**, with a predicted $\Delta_f H^\circ_{298}$ range of 408.1−416.3 kJ mol^{-1}. The high energy of **3H$_b$** may be associated with the fact that this species would be formally antiaromatic in a hypothetical planar structure.

b. The C_2H_2N Free Radicals. The $^\bullet CH_2CN$ radical (**1**) is the lowest energy isomer on the C_2H_2N surface, having a $\Delta_f H^\circ_{298}$ of 262.6 kJ mol^{-1} at the CBS-RAD level of theory (Table 1). This value is almost 20 kJ mol^{-1} higher than the value quoted in Lias et al.[3] (245 ± 10 kJ mol^{-1}), which was derived from gas-phase pyrolysis studies of cyanoethane and cyanopropane, and the value derived by Holmes et al.[5f] (243 ± 12 kJ mol^{-1}) from the monoenergetic electron impact appearance energy measurements for the formation of $HOCH_2^+$ from $HOCH_2CH_2CN$ and CH_3OCO^+ from $CH_3OC(=O)CH_2CN$. Somewhat closer is a value obtained by Moran et al.[5a] (250 ± 8 kJ mol^{-1}), derived by combining their experimentally measured electron affinity of $^\bullet CH_2CN$ (1.543 ± 0.014 eV) with the acidity of CH_3CN (1557 ± 8 kJ mol^{-1})[26] and $\Delta_f H^\circ_{298}$ of CH_3CN (74 kJ mol^{-1}).[3] Finally, Shea et al.[10a] derive a $\Delta_f H^\circ_{298}$ for $^\bullet CH_2CN$ of 253 ± 9 kJ mol^{-1} from the heat of formation of acetonitrile (74 kJ mol^{-1})[3] and its C−H bond dissociation enthalpy (397 kJ mol^{-1}).[4] This is within 10 kJ mol^{-1} of the CBS-RAD value of 262.6 kJ mol^{-1}. We note that in a recent evaluation of theoretical procedures for obtaining free radical thermochemistry[15] we found that further increasing the level of theory does not change the calculated $\Delta_f H^\circ_{298}$ of **1** to any significant extent.

The $^\bullet CH_2NC$ radical (**2**) has a calculated $\Delta_f H^\circ_{298}$ of 363.1 kJ mol^{-1} at the CBS-RAD level (Table 1). This differs substantially from an experimental determination by Holmes and Mayer[5f] of 402 ± 12 kJ mol^{-1} (derived from the monoenergetic electron impact appearance energy of CH_3OCO^+ from $CH_3OC(=O)CH_2NC$) and also differs significantly from the values determined by Matimba et al.[5d] of 334 ± 8 kJ mol^{-1} (derived using their experimentally measured gas-phase acidity of CH_3NC, 1589 ± 8 kJ mol^{-1}) and Moran et al.[5b] of 310 ± 13 kJ mol^{-1} (derived using their experimentally measured electron affinity of $^\bullet CH_2NC$, 1.059 ± 0.024 eV) and the value of 336 ± 11 kJ mol^{-1} derived from the bond dissociation enthalpy reported by Berkowitz et al.[4] It is intriguing that the calculated value of 363.1 kJ mol^{-1} lies in the middle of the range spanned by the four experimental values.

The azirinyl radical (**3**) is calculated with CBS-RAD to have a $\Delta_f H^\circ_{298}$ of 491 kJ mol^{-1}. This is much higher than the only previous estimate of 339 kJ mol^{-1} by Holmes and Mayer.[5f] The latter was based on their measured heat of formation of $^\bullet CH_2CN$ (243 ± 12 kJ mol^{-1}) and the known difference in $\Delta_f H^\circ_{298}$ (96 kJ mol^{-1}) between the propargyl radical, $^\bullet CH_2C{\equiv}CH$ ($\Delta_f H^\circ_{298} = 343$ kJ mol^{-1}),[3] and the cyclopropenyl radical, c-$C_3H_3^\bullet$ ($\Delta_f H^\circ_{298} = 439$ kJ mol^{-1}).[3,27] The present results indicate that the azirinyl radical is considerably less stable relative to the acyclic isomer than is the cyclopropenyl radical.

c. The C_2H_2N Cations. The theoretical values in Table 1 for $\Delta_f H^\circ_{298}$ of **1**$^+$ range from 1249 to 1258 kJ mol^{-1}. These are significantly higher than the experimental value of 1218 ± 8 kJ mol^{-1} reported by Holmes and Mayer.[5f] Their experimental value is based on the appearance energy of CH_2CN^+ from ICH_2CN. Mass spectrometry experiments[5f] showed that this process probably occurs at threshold with little or no reverse energy barrier, and there was no reported evidence of a kinetic or competitive shift (though these effects in any case would make the experimental value too high rather than too low). One potential problem may be the heat of formation of ICH_2CN (151 kJ mol^{-1}), which was estimated from group additivity.[5f] However, we have calculated the $\Delta_f H^\circ_{298}$ of ICH_2CN at the G2 level of theory from the isodesmic reaction with CH_4 and found a similar value, 153 kJ mol^{-1}. There is much closer agreement between the theoretical $\Delta_f H^\circ_{298}$ for **1**$^+$ and the very recent experimental value of 1246 ± 18 kJ mol^{-1} derived by Shea et al.[10a] Their result was obtained from their $\Delta_f H^\circ_{298}$ for $^\bullet CH_2CN$ and their measured ionization energy for $^\bullet CH_2CN$ of 10.30 ± 0.04 eV.

The $\Delta_f H^\circ_{298}$ of **2**$^+$ reported by Holmes and Mayer[5f] (1203 ± 23 kJ mol^{-1}) is based on their experimentally determined $\Delta_f H^\circ_{298}$ for **1**$^+$ coupled with earlier theoretical evaluations of the relative energies of **1**$^+$ and **2**$^+$.[25] It is considerably lower than the present calculated range of 1265−1270 kJ mol^{-1}.

The azirinyl cation (**3**$^+$) is predicted by theory to be the lowest energy $C_2H_2N^+$ isomer with a $\Delta_f H^\circ_{298}$ of 1198−1208 kJ mol^{-1}. This is significantly higher than the experimentally estimated upper limit of 1138 kJ mol^{-1} reported by Holmes and Mayer,[5f] obtained from the measured appearance energy of the cation from l*H*-1,2,3-triazole. The experimental value is reported as an upper limit to the true value due to the competition from a lower energy dissociation. It is difficult to understand the discrepancy between the experimental and theoretical values, especially since the experimental value is the lower of the two. Quite apart from the lower energy dissociation complication, factors such as the presence of a kinetic shift or a reverse energy barrier would also make the experimental value too high rather than too low. One possibility is that there is another, lower energy C_2H_2N cation that is being formed in the dissociative ionization of l*H*-1,2,3-triazole. However, previous studies of the cation surface give no indication of an isomer with energy lower than that of **3**$^+$.[25] Another potential source of uncertainty is the $\Delta_f H^\circ_{298}$ of l*H*-1,2,3-triazole used in the experimental study. The value listed by Lias et al.[3] (247 kJ mol^{-1}) was derived by

TABLE 2: Comparison of Calculated and Experimental C−H and N−H BDE$_{298}$ Values[a]

	G2	G2(//QCI)	CBS-Q	CBS-RAD	experiment
1H	409.6	406.7	401.5	402.5	389 ± 10,[b] 394 ± 8,[c] 389 ± 12,[d] 397 ± 9[e]
2H	406.5	406.8	400.1	402.5	447 ± 12,[d] 355 ± 13,[f] 379 ± 8[g] 381 ± 9[e]
3H$_a$[h]	441.7	441.5	437.0	429.6	
3H$_b$	306.9	300.1	300.5	294.6	

[a] In kJ mol^{-1}. [b] Using the radical $\Delta_f H^\circ_{298}$ value from Lias et al.[3] [c] Moran et al.[5a] [d] Using the radical $\Delta_f H^\circ_{298}$ value of Holmes and Mayer.[5f] [e] Berkowitz et al.[4] [f] Moran et al.[5b] [g] Matimba et al.[5d] [h] Methylene C−H BDE forming **3**.

TABLE 3: Comparison of Calculated and Experimental $\Delta_{acid}H^\circ_{298}$ values[a]

	G2	G2(//QCI)	CBS-Q	CBS-RAD	experiment
1H	1569.2	1568.2	1568.0	1568.8	1560 ± 11,[b] 1557 ± 8[c]
2H	1604.8	1603.6	1606.8	1607.0	1565 ± 12,[d] 1589 ± 8[e]
3H$_a$[f]	1613.0	1620.3	1613.1	1617.7	
3H$_b$	1478.2	1478.9	1476.6	1482.7	

[a] In kJ mol^{-1}. [b] Lias et al.[3] [c] Bartmess et al.[26] [d] Filley et al.[5c] [e] Matimba et al.[5d] [f] Acidity of methylene hydrogens.

TABLE 4: Comparison of Calculated and Experimental EA Values[a]

	G2	G2(//QCI)	CBS-Q	CBS-RAD	experiment
1	1.58	1.54	1.49	1.49	1.543 ± 0.014[b]
2	1.17	1.17	1.06	1.08	1.059 ± 0.024[c]
3	1.45	1.37	1.40	1.27	

[a] In eV. [b] Moran et al.[5a] [c] Moran et al.[5b]

TABLE 5: Comparison of Calculated and Experimental IE Values[a]

	G2	G2(//QCI)	CBS-Q	CBS-RAD	experiment
1	10.18	10.21	10.30	10.32	10.03−10.11,[b] 10.30 ± 0.04,[c] 10.28 ± 0.01[d]
2	9.35	9.35	9.42	9.40	8.30−9.26[b]
3	7.27	7.34	7.35	7.42	>8.28[b]

[a] In eV. [b] Using $\Delta_f H^\circ$ values for the cation and radical in Table 1. [c] Shea et al.[10a] [d] Thorn et al.[10b]

Joshi from a bond energy additivity scheme.[28] We calculate the G2 $\Delta_f H^\circ_{298}$ to be 278 kJ mol^{-1}, accounting for 31 of the approximately 60 kJ mol^{-1} discrepancy between the theoretical and experimental values for the $\Delta_f H^\circ_{298}$ of **3**$^+$.[29]

d. The C_2H_2N Anions. The discrepancies between the present theoretical $\Delta_f H^\circ_{298}$ values for the anions **1**$^-$ − **3**$^-$ and experimental values reported by Moran et al.[5a,b] and Matimba et al.[5d] are less than those discussed above for the radicals and cations. The present results of 113.3−118.1 kJ mol^{-1} for $\Delta_f H^\circ_{298}$ (**1**$^-$) lie only about 10−15 kJ mol^{-1} higher than those reported in Lias et al.[3] and by Moran et al.[5a] and agree with the former experimental value within the quoted precision. The $\Delta_f H^\circ_{298}$ values for **2**$^-$ obtained in the present study (248.5−256.8 kJ mol^{-1}) are roughly 20 kJ mol^{-1} higher than the experimental value of 232 ± 8 kJ mol^{-1} reported by Matimba et al.[5d] and more than 40 kJ mol^{-1} higher than that of Moran et al.[5b] (208 ± 13 kJ mol^{-1}). The ring-opened anion **3**$^-$ is calculated to have a $\Delta_f H^\circ_{298}$ of between 357 and 368 kJ mol^{-1}.

3.3. Bond Dissociation Enthalpies. The 298 K C−H bond dissociation enthalpies (BDE$_{298}$) of **1H**, **2H**, and **3H$_a$** and the N−H BDE$_{298}$ of **3H$_b$** are shown in Table 2 along with available experimental values.[3,4,5a,b,d,f] The theoretical BDE values for CH_3CN and CH_3NC are very similar, ranging from 400 to 410 kJ mol^{-1}, depending on the level of theory. This indicates that the stabilizations of the two radicals **1** and **2** relative to **1H** and **2H** are similar (and would result in similar radical stabilization energy values). The results for the C−H BDE$_{298}$ in **1H** and **2H** are in closest agreement with the values of Berkowitz et al.[4] of 397 ± 9 and 381 ± 9 kJ mol^{-1}, respectively. The methylene C−H bond strength in 2*H*-azirine (**3H$_a$**) is larger than that for acetonitrile and isocyanomethane by roughly 30 kJ mol^{-1}. The BDE value ranges from 429.6 kJ mol^{-1} (CBS-RAD) to 441.7 kJ mol^{-1} (G2). Donation from a pseudo-π orbital on the methyl group to the π* orbital of the triple bond weakens the C−H bonds in **1H** and **2H**. The corresponding interaction with the π* orbital of the C═N bond in the cyclic isomer **3H$_a$** is much weaker on symmetry grounds. In addition, the greater s character in the C−H bonds of the strained three-membered ring would contribute to a greater bond strength. The N−H bond strength in **3H$_b$** is predicted to be 294.6−306.9 kJ mol^{-1}.

3.4. Gas-Phase Acidities. The calculated 298 K gas-phase acidities are compared with available experimental values[3,5c,d,26] in Table 3. The acidities calculated for CH_3CN (1568−1569 kJ mol^{-1}) agree fairly well with the experimental value quoted by Lias et al.[3] (1560 ± 11 kJ mol^{-1}), being within the quoted uncertainty limits. The calculated $\Delta_{acid}H^\circ_{298}$ values of CH_3NC (1603.6−1607.0 kJ mol^{-1}) are somewhat higher than the experimental value of 1589 ± 8 kJ mol^{-1} reported by Matimba et al.[5d] and much higher than that reported by Filley et al.[5c] (1565 ± 12 kJ mol^{-1}). The agreement between theory and experiment for the acidities of **1H** and **2H** is nevertheless better than that observed tor the BDE values. It should be noted that the experimental $\Delta_{acid}H^\circ_{298}$ values are directly measured quantities and do not rely on ancillary thermochemistry, in contrast to the BDE values which are often indirectly obtained. The smaller $\Delta_{acid}H^\circ_{298}$ values for CH_3CN compared with CH_3NC are consistent with a greater stabilizing interaction with the carbanion center by CN compared with NC.

The $\Delta_{acid}H^\circ_{298}$ of the methylene hydrogens in 2*H*-azirine (**3H$_a$**) is predicted to be larger than the $\Delta_{acid}H^\circ_{298}$ values for **1H** and **2H**, the calculated values falling between 1613.0 and 1620.3 kJ mol^{-1}, while the N-centered acidity of 1*H*-azirine (**3H$_b$**) is predicted to lie in the range 1476.6−1482.7 kJ mol^{-1}.

3.5. Free Radical Electron Affinities. The electron affinities of **1**, **2**, and **3** are compared with experimental values in Table 4. The G2-based electron affinities of **1** (1.58 and 1.54 eV) are in close agreement with experimental values derived by Moran et al. (1.543 ± 0.014 eV) from photodetachment spectroscopy of the anion **1**$^-$.[5a] The CBS-based results (1.49 eV) are slightly lower. In the case of **2**, it is the CBS-based results that are in good agreement with experiment, 1.06−1.08 eV as compared with 1.059 ± 0.024 eV measured by Moran et al.[5b] The EA of the azirinyl radical (**3**) is calculated to lie between 1.27 and 1.45 eV. This spread in values is attributable to the range of values obtained for the $\Delta_f H^\circ_{298}$ of **3** and **3**$^-$. As with the acidities, we note good agreement between theory and experiment for the directly measured experimental EA values.

3.6. Free Radical Ionization Energies. The ionization energies of the free radicals **1**, **2**, and **3** are listed in Table 5. The CBS-based results are consistently slightly higher than the G2-based values. The cyanomethyl radical is predicted to have the highest IE of the three (10.18−10.32 eV), while that of the isocyanomethyl radical is almost 1 eV lower (9.35−9.42 eV), and the IE of **3** almost 3 eV lower (7.27−7.42 eV). These very different values reflect the change in relative stabilities of the radicals and cations. The cyanomethyl radical is the most stable radical, while the cyclic cation $\mathbf{3}^+$ is the most stable cation. Our calculated IEs for **1** and **2** are close to recent high-level ab initio predictions of Botschwina and co-workers[9] of 10.20 ± 0.03 and 9.36 ± 0.03 eV, respectively. Agreement between theory and experiment is quite poor in the cases where the experimental values are derived from the differences in the heats of formation of the neutral and cation.[5f] Agreement is greatly improved for $^\bullet CH_2CN$ when the theoretical value is compared with two very recent direct experimental measurements of the ionization energy.[10]

4. Concluding Remarks

The heats of formation of four C_2H_3N molecules and three C_2H_2N radicals, cations, and anions have been calculated at four levels of theory, G2, G2(//QCI), CBS-Q, and CBS-RAD-(QCISD,B3LYP). Extensive testing has shown these levels of theory to generally produce thermochemical data with an accuracy of within 10 kJ mol^{-1}. Bond dissociation enthalpies and gas-phase acidities of the C_2H_3N molecules and electron affinities and ionization energies of the free radicals were derived.

The theoretical acidities, electron affinities, and ionization energies were found generally to be in fair agreement with directly measured experimental values. However, the results for the heats of formation of the radicals and cations (and consequently molecular bond dissociation enthalpies and derived radical ionization energies) showed discrepancies between theory and experiment much greater than the expected 10 kJ mol^{-1} accuracy of the theoretical predictions. A pertinent observation is that, in contrast to the directly measured acidities, electron affinities, and ionization energies, the properties showing significant differences between theory and experiment are not directly measured by experiment, but rather have been derived indirectly from experimentally measured quantities such as dissociative ionization appearance energies or reaction rate constants.

Our results are in close agreement with very recent measurements of the ionization energy of the $^\bullet CH_2CN$ radical, and we believe that it would also be worthwhile to experimentally revisit the thermochemistry of the other C_2H_2N radicals and cations. It would seem unlikely, on the basis of the established performance of the theoretical methods used in the present study, that more elaborate theoretical treatments will alter the present results to any great extent. The eventual agreement between theory and experiment for these simple species derived from acetonitrile and its isomers is a highly desirable goal.

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