Photoelectron Spectroscopy of the NCN\(^{-}\) and HNCN\(^{-}\) Ions

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We have used negative ion photoelectron spectroscopy to measure the electron affinities of the cyanonitrene and the cyanoano radical: EA(X \( ^3\Sigma_g^- \)) = 2.484 \pm 0.006 eV, EA(X \( ^2\Lambda'\nu \)) = 2.622 \pm 0.005 eV, and EA(X \( ^2\Lambda''\nu \)) = 2.622 \pm 0.005 eV. Our experimental findings are accurately reproduced by complete basis set (CBS) \textit{ab initio} electronic structure calculations: EA(X \( ^3\Sigma_g^- \)) = 2.51 \pm 0.03 eV and EA(X \( ^2\Lambda''\nu \)) = 2.60 \pm 0.03 eV. Our qualitative picture of these species is N≡C=\( \hat{N}\) \( ^3\Sigma_g^- \), [N≡C=\( \hat{N}\)] \( ^2\Pi\nu \) HNC≡N \( ^2\Lambda'\nu \), and [HNC≡N] \( ^2\Delta'\nu \). We make use of the electron affinities of NCN and HNCN, together with the gas phase acidity of cyanamides, \( \Delta_{\text{acid}}H_{298}(\text{H}^–\text{HNCN}) = 350 \pm 3 \text{ kcal mol}^{-1} \), to find the bond enthalpies of H\( _2\)NCN. We find \( \Delta H_{298}(\text{H}^–\text{HNCN}) = 96.9 \pm 3.0 \text{ kcal mol}^{-1} \) and \( \Delta H_{298}(\text{H}^–\text{NCN}) = 77 \pm 4 \text{ kcal mol}^{-1} \), which closely agree with the calculated values: \( \Delta H_{298}(\text{H}^–\text{HNCN}) = 95.5 \pm 0.7 \text{ kcal mol}^{-1} \) and \( \Delta H_{298}(\text{H}^–\text{NCN}) = 76.7 \pm 0.7 \text{ kcal mol}^{-1} \). We therefore use the CBS \textit{ab initio} electronic structure calculations to estimate \( \Delta_{\text{acid}}H_{298}(\text{H}^–\text{HNCN}) \approx 339 \text{ kcal mol}^{-1} \). Use of the experimental electron affinity, EA(NCN), leads to the NH bond enthalpy of the cyanoamino radical, \( \Delta H_{298}(\text{H}^–\text{NCN}) = 83 \pm 2 \text{ kcal mol}^{-1} \) and \( \Delta H_{298}(\text{NCN}) = 108 \pm 4 \text{ kcal mol}^{-1} \).

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I. Introduction

The NCN and HNCN radicals are interesting derivatives of the amidogen (NH) and amino (NH\(_2\)) radicals because the cyano group is likely to stabilize the unpaired electrons. Both of these species are also possible reactive intermediates in the chemistry of "active nitrogen". Cyanonitrene, NCN, was first implicated as an important intermediate in combustion chemistry in 1960, when a complicated emission at 329 nm was observed from hydrocarbon flames.\(^{1}\)

An important experimental means to study the neutral radicals (M) is to photodetach mass-selected beams of the corresponding negative ions (M\(^{-}\)). We have used negative ion photoelectron spectroscopy to study both the NCN\(^{-}\) and HNCN\(^{-}\) ions.

\[
\text{NCN}^- + h\omega_{351\text{nm}} \rightarrow \text{NCN} + e^- \quad (1a)
\]

\[
\text{HNCN}^- + h\omega_{351\text{nm}} \rightarrow \text{HNCN} + e^- \quad (1b)
\]

Our photoelectron spectra provide the molecular electron affinities EA(NCN) and EA(HNCN). Use of the EAs along with the gas phase acidities of the corresponding cyanamides enables us to determine the thermochemistry of the NCN and HNCN radicals. Our findings are accurately predicted by \textit{ab initio} electronic structure calculations; our CBS (complete basis set) calculations\(^2\)–\(^4\) completely describe the geometries and energetics of the [NCN\(^{-}\), HNCN\(^{-}\)] ions and [NCN, HNCN] radicals.

We can anticipate the structures and states of both species by use of the following diagrams.\(^5\) Cyanonitrene is a diradical and will have three low-lying states, \( \tilde{X} \tilde{\Sigma}_g^- \), \( \tilde{a} \tilde{\Delta}_g \), and \( \tilde{b} \tilde{\Sigma}^+ \), as well as a pair of \( \Pi \) states, \( \tilde{A} \tilde{\Pi}_u \) and \( \tilde{c} \tilde{\Pi}_g \). The triplet state is expected to be the ground state, \( \tilde{X} \tilde{\Sigma}_g^- \), and one can write this as a resonating formula:

\[
\begin{array}{c}
N=\tilde{C}=-\tilde{N} \\
\tilde{\Sigma}_g^- \\
\end{array}
\quad (3)
\]

The lowest singlet state will be \( \tilde{a} \tilde{\Delta}_g \); the \( \tilde{1} \Delta^+_g \) component might be represented as

\[
\begin{array}{c}
N=\tilde{C}=-\tilde{N} \\
\tilde{\Sigma}_g^- \\
\end{array}
\quad (3)
\]

The negative ion, NCN\(^{-}\), is isoelectronic with NCO and is anticipated to be a \( \tilde{2} \Pi_u \) state:

\[
\begin{array}{c}
N=\tilde{C}=-\tilde{N} \\
\tilde{\Pi}_u \\
\end{array}
\quad (4)
\]

Formulae 4 and 2 suggest that there will be little geometry change upon detachment of the NCN\(^{-}\) ion. The electron affinity of NH is very well known\(^6\)–\(^7\) from spectroscopic studies of the NH\(^{-}\) ion, \( \tilde{X} \tilde{\Pi} \), and it is found that EA(NH) is 0.370 \pm 0.004 eV. We expect the CN group to stabilize the anion by about 1 eV while resonance effects will stabilize the ion even further. Consequently we anticipate a nearly vertical photodetachment spectrum for NCN as in NH, with an EA(NCN) of roughly 2 eV.

The amino radical, NH\(_2\), has a \( \tilde{X} \tilde{2}B_1 \) ground state and a low-lying\(^8\) excited state, \( \tilde{A} \tilde{1}A_1 \); \( T_0(\tilde{A} \text{ NH}_2) = 1.271 \text{ eV} \). We
anticipate that the HNCN radical will have a \( \tilde{X}^2A'' \) ground state and an \( \tilde{A}^2A' \) excited state.

One would write the HNCN\(^-\) ion as a closed shell species, \( \tilde{X}^1A' \):

The photoelectron spectrum of the amide ion has been studied\(^9\) and it was found that \( E_A(NH_3) = 0.771 \pm 0.006 \text{ eV} \). Again we anticipate the cyano group to stabilize the negative ion and estimate \( E_A(NHCN) \approx 2 \text{ eV} \). A nearly vertical photodetachment spectrum is expected as well since detachment of the \( \tilde{X}^1A' \) HNCN\(^-\) ion in (6) involves ejection of a non-bonding electron.

The NCN and HNCN radicals have been studied previously. The gas phase optical spectrum of the NCN radical has been obtained following the photolysis of diazomethane.\(^{10}\) A rotational analysis of the bands indicated a triplet/triplet absorption at 30 383.74 \text{ cm}^{-1} which was assigned as NCN (\( \tilde{A}^3\Pi_u \rightarrow \tilde{X}^3\Sigma_g^+ \)). From the rotational constant, \( B_0'' = 0.3968 \text{ cm}^{-1} \), the C=N bond length was reported to be \( r_0(\tilde{X}^3\Sigma_g^+) \text{ NCN} = 1.232 \text{ \AA} \). Very recently\(^{11}\) laser-induced fluorescence (LIF) spectra have yielded a set of refined rotational constants and show the excited \( \Pi \) state to be inverted, \( \tilde{A}^3\Pi_u \). From the optical spectrum, the NCN bending frequency was estimated to be \( \nu_2' \approx 370 \pm 50 \text{ cm}^{-1} \). Subsequently NCN \( \tilde{X}^3\Sigma_g^+ \) was detected by EPR spectroscopy\(^{12}\) in a matrix at 4 K. Singlet states of NCN have been observed\(^{13,14}\) by flash photolysis as well; \( T_0(\tilde{1}\Pi_u \rightarrow \tilde{1}\Delta_g \text{ NCN}) = 30.046 \text{ cm}^{-1} \). Some hints of UV transitions originating from NCN \( \tilde{B}^3\Sigma_g^+ \) have also been reported.\(^{15}\) Dynamical studies of the quenching of NCN (\( \tilde{A}^3\Pi_u \rightarrow \tilde{X}^3\Sigma_g^+ \)) have been reported\(^{16}\) and the lifetime of NCN \( \tilde{A}^3\Pi_u \) was measured to be 183 \pm 6 ns. To the best of our knowledge, no singlet/triplet splittings have been measured.

The infrared absorption spectrum of NCN was measured\(^{17}\) in a N\(_2\) matrix at 14–20 K following irradiation of cyanogen azide. Analysis of the IR spectrum yielded values\(^{18}\) for the bending frequency, \( \nu_2 = 423 \pm 3 \text{ cm}^{-1} \), and the asymmetric stretch, \( \nu_3 = 1475 \pm 3 \text{ cm}^{-1} \); the IR inactive symmetric stretch was estimated to be \( \nu_1 \approx 808 \text{ cm}^{-1} \). These matrix studies suggest that irradiation of NCN at wavelengths below 2800 \( \AA \) leads to dissociation to produce molecular nitrogen: NCN (\( \tilde{X}^3\Sigma_g^+ \)) + \( h\nu \approx 4.4 \text{ eV} \) \( \rightarrow \) C (\( ^3\Pi \)) + N\(_2\) (\( ^3\Sigma_u^+ \)). In subsequent studies,\(^{19}\) matrix spectroscopy revealed a weak band at 2672 \text{ cm}^{-1} which was interpreted as a combination (\( \nu_1 + \nu_3 \)); this provided a refined value for \( \nu_1(\text{NCN}) = 1197 \text{ cm}^{-1} \). Very recent gas phase FTIR absorption studies in a White cell following pyrolysis of NCN\(_3\) with a CO\(_2\) laser have provided values\(^{20}\) for the two IR allowed bands for NCN \( \tilde{X}^3\Sigma_g^+ \): \( \nu_2 \approx 395 \text{ cm}^{-1} \) and \( \nu_3 = 1466.5 \text{ cm}^{-1} \). Besides these experimental studies, the NCN molecule has been studied by \textit{ab initio} electronic structure calculations.\(^{21,22}\) A quadratic CI calculation ([UHF-QCISD/6-31G*]) has yielded\(^{23}\) harmonic frequencies for NCN and HNCN. All of these results are summarized in Table 1.

II. Experimental Procedures

Our photoelectron spectra were taken on a spectrometer that has been described elsewhere.\(^{27,28}\) We have used oxide ion chemistry\(^{29}\) to generate the NCN\(^-\) from cyanamide; NH\(_2\)CN was acquired from Aldrich Chemical and used without further purification. The chemistry used to produce our target ions is

\[
\text{O}^- + \text{NH}_2\text{CN} \rightarrow \text{OH}_2 + \text{NCN}^- \quad (m/z \ 40) \tag{7a}
\]

\[
\text{OH}^- + \text{NH}_2\text{CN} \rightarrow \text{OH}_2 + \text{HNCN}^- \quad (m/z \ 41) \tag{7b}
\]
TABLE 2: Molecular Constants for HNCN

<table>
<thead>
<tr>
<th></th>
<th>Aν/GHz</th>
<th>Bν/GHz</th>
<th>Cν/GHz</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>634.900 ± 3.100</td>
<td>11.087 ± 8.4 ±</td>
<td>10.881 ± 73.5 ±</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>638.5 ± 0.7</td>
<td>11.1 ± 0.7</td>
<td>10.9 ± 0.7</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>636.2</td>
<td>11.1</td>
<td>10.9</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>r_CN = 2.470 ± 0.002 Å; r_NH = 1.034 ± 0.020 Å;</td>
<td>θ_CNH = 116.5° ± 2.7°</td>
<td></td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ν/N−C−N sym sta'' = 1140 cm⁻¹</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν/N−C−N out-of-plane bend'' = 440 cm⁻¹</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tilde{X}^{2}A''$</td>
<td></td>
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</tr>
</tbody>
</table>

Ab Initio Electronic Structure Calculations for $\tilde{X}^{2}A''$

| harmonic vibrational frequencies (unscaled) | | |
| MP2/6-311G(2d,2p)* | | |
| r_CN/A = 1.166 | $\omega$ν(N−H) | 3552 | 43 |
| r_CN/A = 1.291 | $\omega$ν(NC) | 1937 | 73 |
| r_CN/A = 1.017 | $\omega$ν(NC) | 1179 | 116 |
| $\theta$CN = 175.0° | $\omega$ν(NCN) | 981 | 12 |
| $\theta$CN = 110.8° | $\omega$ν(NCN) | 526 | 22 |
| $\omega$ν(NCN) | 535 | 13 |
| Aν/GHz = 628.0 | | | |
| $B_ν/\text{GHz} = 11.2$ | | | |
| Cν/GHz = 11.1 | | | |
| $\text{energy/eu} = -147.779$ | | | |

* MP2 calculations from ref 26.

The two ions at m/z 40 and 41 were separated by a Wien velocity filter and were photodetached by a CW Ar II ion laser that provides 50–100 W of 351.1 nm light in the circulating build-up cavity. The photodetached electrons are focused and pass through a hemispherical energy analyzer, with an instrumental resolution (FWHM) of 6–10 meV. In order to reduce rotational broadening in the photodetachment spectra, we bathe the part of the flow tube with liquid N₂. We estimate (vide infra) that the rotational temperature of our ions is roughly 200 K. The deuterated precursor, D₂NCN, was prepared by washing the H₂NCN with methanol-d₄ (CH₃OD) and evaporating the solvent; the extent of D₂NCN formation was verified by electron impact mass spectrometry.

Our electron spectra are calibrated with respect to O⁻ and transformed to the center of mass (CM) frame by a standard expression where E is the CM kinetic energy (eV) of an electron detached from an ion of mass M (amu) which is passed by the energy analyzer when the slit voltage is V. The beam energy is W, mₑ is the mass of an electron, and γ is the dimensionless scale compression factor (typically 1.000 ± 0.006):

$$E = E_{\text{cat}} + \gamma(V - V_{\text{cat}}) + m_{e} W \left( \frac{1}{M_{\text{cat}}} - \frac{1}{M} \right)$$

III. Results

Figure 1 presents the photoelectron spectrum of the HNCN⁻ ion on the top panel and the NCN⁻ ion on the bottom. Because of limited mass-resolution, each spectrum is slightly contaminated with the other ion. The HNCN⁻ ion (m/z 41) is prepared by reaction of cyanamide with hydroxide ion while the NCN⁻ species (m/z 40) results from the interaction of oxide anion with cyanamide. As expected from eqs 2 and 4 and 5 and 6, both photoelectron spectra are essentially vertical transitions. The intense feature in the HNCN⁻ spectrum is the (0,0) band for HNCN $\tilde{X}^{2}A''$ → HNCN⁻ $\tilde{X}^{2}A'$; and it occurs at center-of-mass kinetic energy = 0.908 ± 0.002 eV. This corresponds to a value for the uncorrected or "raw" EA(HNCN) = 2.623 ± 0.002 eV. The strong band in the NCN⁻ spectrum is the (0,0) transition for NCN $\tilde{X}^{2}Σ_{e}^+ →$ NCN⁻ $\tilde{X}^{2}Π$ occurring at center-of-mass kinetic energy = 1.052 ± 0.003 eV and corresponding to a "raw" EA(NCN) = 2.479 ± 0.003 eV.

The yields of photodetached electrons are angular dependent. The distribution of scattered photoelectrons, I(θ), is approximated by the following expression:

$$I(\theta) = \frac{\beta}{4\pi} \left( 1 + \beta(3\cos^2 \theta - 1) \right)$$

In this expression, θ is the angle between E_s and the electron collection direction, $\bar{\sigma}$ is the average photodetachment cross section, and β is the anisotropy factor. The anisotropy factor β can vary from −1 to 2 (−1 ≤ β ≤ 2). The photoelectron spectra shown in Figure 1 were collected under conditions where θ was set to the "magic angle" of 54.7° so that I(θ) = $\bar{\sigma}/4\pi$ and is independent of β. If spectra are collected at θ = 0° (E_s and collection direction ⊥) and θ = 90° (E_s and collection direction ⊥), one can extract a value for the anisotropy factor.

$$\beta \approx \frac{I(0°) - I(90°)}{\frac{1}{2} I(0°) + I(90°)}$$

The value of β provides an important clue as to the nature of the photodetached electron. In atoms, detachment of an
s-electron leads to an outgoing p-wave (l = 1) and β = 2, independent of electron kinetic energy. Detachment of a p-electron results in a mixture of interfering s- and d-waves and leads to an energy dependent value for β. At photodetachment threshold, s-wave (l = 0) detachment dominates, giving β = 0 and yielding an isotropic photoelectron angular distribution. At photoelectron kinetic energies roughly 1 eV above threshold, d-wave detachment becomes important and β → −1.

Electron detachment from molecular ions is more complicated than the atomic case, but β is generally found to be positive for detachment from σ (s-like) electrons and negative for detachment from π (p-like) orbitals. Use of (9) leads to the following values: β(σ-HNCN) = 0.59 ± 0.15 and β(π-HNCN) = −0.53 ± 0.15. Both β values are suggestive of ejection of a π-like electron from both the NCN− and HNCN− anions and are in qualitative agreement with our pictures of these negative ions in eqs 4 and 6.

There are two small features in the HNCN− spectrum and we ascribe them to vibrational excitation in the HNCN radical. To identify these modes, we need to compare the spectrum of the d0 and d1 ions. Figure 2 is an overlay of the photoelectron spectra of HNCN− and DNCN−. The two small features at a and b correspond to vibrational excitations in the cyanoamino radical. Since these two spectra are identical, the HNCN/DNCN vibrations a and b do not involve motion of either the H or D atoms. The splitting of a from the (0,0) band is 1049 ± 177 cm−1 while that of b is 1813 ± 128 cm−1 and is assigned as 2u1.

Electron detachment from molecular ions is more complicated than the atomic case, but β is generally found to be positive for detachment from σ (s-like) electrons and negative for detachment from π (p-like) orbitals. Use of (9) leads to the following values: β(σ-HNCN) = 0.59 ± 0.15 and β(π-HNCN) = −0.53 ± 0.15. Both β values are suggestive of ejection of a π-like electron from both the NCN− and HNCN− anions and are in qualitative agreement with our pictures of these negative ions in eqs 4 and 6.

In order to interpret our photoelectron spectra, we need a consistent set of molecular geometries and vibrational frequencies of the NCN and HNCN radicals as well as for the NCN− and HNCN− ions. In addition to the earlier ab initio electronic structure calculations, we report the results of our own density functional calculations. These 3BLYP calculations in a 6-311++G(2df,p) basis. The 3BLYP/6-311++G(2df,p) calculations give us a balanced set of results with which to compare the negative ion and the neutral, and these findings are collected in Table 4.

Table 3: Photoelectron Bands

<table>
<thead>
<tr>
<th>feature</th>
<th>com kinetic energy/eV</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.908 ± 0.002</td>
<td>EA(X 2A′′ HNCN)</td>
</tr>
<tr>
<td>b</td>
<td>0.778 ± 0.020</td>
<td>ν3(X 2A′′ HNCN) = 1049 ± 162 cm−1</td>
</tr>
<tr>
<td></td>
<td>0.675 ± 0.013</td>
<td>ν2(X 2A′′ HNCN) = 1879 ± 106 cm−1</td>
</tr>
<tr>
<td>a</td>
<td>0.908 ± 0.002</td>
<td>EA(X 2A′′ DNCN)</td>
</tr>
<tr>
<td>b</td>
<td>0.779 ± 0.020</td>
<td>ν3(X 2A′′ DNCN) = 1049 ± 162 cm−1</td>
</tr>
<tr>
<td></td>
<td>0.684 ± 0.013</td>
<td>ν2(X 2A′′ DNCN) = 1879 ± 106 cm−1</td>
</tr>
</tbody>
</table>

The features for NCN are reproducible within ±0.003 eV and this molecule requires a rotational correction (∆rot = 0.0004 eV), a spin-orbit correction (0.005 eV), and accommodation for the uncertainty in the energy linearizer of the analyzer (0.005 eV). Consequently we apply the correction: raw EA(NCN) = EA(NCN) − (E f + Δspin-orbit) + Δrot. Applying these corrections, we find EA(X 2A′′ NCN) = 2.484 ± 0.006 eV or 57.3 ± 0.1 kcal mol−1. The transitions of HNCN are reproducible within ±0.002 eV and this molecule requires a rotational correction (∆rot = 0.001 eV) and no spin-orbit correction. Consequently we apply the correction: EA(HNCN) = raw EA(HNCN) − Δrot. Applying these corrections, we find EA(X 2A′′ HNCN) = 2.622 ± 0.005 eV (60.5 ± 0.1 kcal mol−1) and EA(X 2A′′ DNCN) = 2.622 ± 0.005 eV (60.5 ± 0.1 kcal mol−1).

These B3LYP/6-311++G(2df,p) calculations largely reproduce the experimental findings in Table 1. The ground state NCN X 3Σg+ is calculated to be very nearly a triplet with (S0) = 2.052 instead of the required value of 2 and the CN distance is found to be slightly smaller (1.224 Å) than the experimental value of 1.232 Å. The B3LYP harmonic frequencies for NCN X 3Σg+ are also qualitatively correct. We find unscaled frequencies of ω1 = 1274 cm−1, ω2 = 453 cm−1, and ω3 = 1557 cm−1, which can be compared with the experimental values in Table 1 of ω1 = 1197 cm−1, ω2 = 395 cm−1, and ω3 = 1466.5 cm−1 (notice that the value for ω1 is measured in a matrix). As predicted by eq 4, the properties of the NCN− X 2Πu ion are computed in Table 4 to be very close to those of the NCN X 3Σg− neutral species.

Likewise the properties of the HNCN X 2A′′ radical are found to be qualitatively correct. In Table 2 the UV spectroscopists report a larger CNH angle of θ = 116.5° ± 2.7° than we compute (113.6°) while the sum of the heavy atom distances is found to be 2.470 ± 0.002 Å, which is to be compared to the value found by the B3LYP calculation of 2.458 Å (1.188 Å + 1.270 Å). The GVB picture of HNCN X 2A′′ in (5) is essentially HNC≡N with a short HNC≡N bond and a longer HN−CN length. Our DFT ab initio calculation leads to an N−H bond length of 1.022 Å, which is to be compared with the experimental finding of 1.034 ± 0.020 Å. The only vibrational frequencies found for HNCN X 2A′′ are ν1 ≈ 1140 cm−1 and ν6 ≈ 440 cm−1; these values are plausibly close to the B3LYP harmonic frequencies of ω3 = 1202 cm−1 and ω6 = 474 cm−1. Our qualitative description for the HNCN− ion in (6) is compatible with the ab initio results in Table 4.

We can model the rotational contours of our photoelectron spectra for both NCN− and HNCN−. The peak shapes that we observe in Figure 1 are due to a convolution of the rotational envelope with our instrumental resolution. Since the center of the peak does not correspond with the (0,0) rotational transition, we estimate the true (0,0) transition from a simulation of the rotational contour which requires a rotational temperature and

Figure 2. An overlay of the negative ion photoelectron spectra of HNCN− (●) and DNCN− (s). Feature a is split from the origin by 1049 ± 177 cm−1 and is assigned 3u1 while peak b is split from the (0,0) band by 1813 ± 128 cm−1 and is assigned as 2u1.
rotational constants of the anion and the neutral species.\(^9\) We adopt (a) the known rotational constants for HNCN \(X^2\Sigma^+\) in Table 2 \(A_0' = 21.2 \pm 0.1\) \(\text{cm}^{-1}\), \(B_0' = 0.369 849 6 \pm 0.000 000 3\) \(\text{cm}^{-1}\), \(C_0' = 0.362 974 8 \pm 0.000 000 3\) \(\text{cm}^{-1}\), (b) \(T_{\text{rot}} = 200\) \(\text{K}\), and (c) an instrumental linewidth (FWHM) of 10 meV. We can account for the linewidth of the HNCN\(^-\) spectrum if we adopt the B3LYP rotational constants for the ion (see Table 4): \(A_0'' = 20.95\) \(\text{cm}^{-1}\), \(B_0'' = 0.37\) \(\text{cm}^{-1}\), \(C_0'' = 0.36\) \(\text{cm}^{-1}\). Figure 3a shows the fit of our simulation (--) and contrasts it with our observed data (- - -). The NCN\(^-\) spectrum is not as simple as that of HNCN\(^-\); Figure 3b clearly shows that the (0,0) peak is not a simple feature but is a composite (at least) of two bands. The NCN peak width is not consistent with a single rotational contour with \(T_{\text{rot}} = 200\) \(\text{K}\), and it does not change upon cooling, as one might expect for a rotational envelope. We are able to model the shape as being due to two transitions from the two spin-orbit states of NCN\(^-\) \(X^2\Sigma^+\) \(1/2 \pm 3/2\) state (see Figure 3b). The spin orbit splitting in the excited \(A^3\Pi_u\) state of NCN has been\(^11\) worked out \(A_0 = -37.566 64 \pm 0.000 60\) \(\text{cm}^{-1}\) and the \(\Pi\) state has been shown\(^10\) to be inverted, \(\Delta \text{NCN}^+ \Delta \Pi_u 3/2\). The neutral that is isoelectronic with the NCN\(^-\) ion is NCO and it is established\(^16\) that \(A = -96.7 \pm 1.5\) \(\text{cm}^{-1}\). We estimate that the spin orbit splitting in the NCN\(^-\) ion is \(|A| = 77 \pm 33\) cm\(^{-1}\). Adopting (a) the known rotational constant for NCN \(X^2\Sigma^+\) in Table 1 \(B_0' = 0.397 252 2 \text{ cm}^{-1}\), (b) \(T_{\text{rot}} = 200\) \(\text{K}\), and (c) an instrumental linewidth (FWHM) of 10 meV, we can reproduce the 16 meV FWHM band for NCN\(^-\) in Figure 3a if we adopt the B3LYP rotational constant for the ion (see Table 4): \(B_0'' = 0.40\) \(\text{cm}^{-1}\) and \(|A| = 77 \pm 33\) cm\(^{-1}\).

At the bottom of Table 3, we list the final corrected electron affinities for both ions: \(\text{EA}(X^2\Sigma^+ \text{NCN}) = 2.484 \pm 0.006\) eV, \(\text{EA}(X^2\Lambda'' \text{HNCN}) = 2.622 \pm 0.005\) eV, and \(\text{EA}(X^2\Lambda'' \text{DNCN}) = 2.622 \pm 0.005\) eV.
TABLE 5: Complete Basis Set Calculated *Ab Initio* Electronic Energies

<table>
<thead>
<tr>
<th>molecule</th>
<th>state</th>
<th>method</th>
<th>energy/hartree</th>
<th>$\Sigma D_d$/kcal mol$^{-1}$</th>
<th>$\Delta H_298$/kcal mol$^{-1}$</th>
<th>$\Delta H_{298}$/kcal mol$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>NCN</td>
<td>$^1\Delta_g$</td>
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<td>142.3 ± 2.5</td>
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<td>136.9 ± 0.7</td>
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<td>HNCN</td>
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TABLE 6

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<th>CBS <em>ab initio</em> calculated property/kcal mol$^{-1}$</th>
<th>experimental/kcal mol$^{-1}$</th>
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<td>$D_d$(H$^-$-HNCN)</td>
<td>93.1 ± 2.5</td>
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<td>$\Delta_{acdid}H_{298}$(H$^-$-HNCN)</td>
<td>348.4 ± 2.5</td>
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<td>$EA$(HNCN)</td>
<td>59.8 ± 2.5</td>
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<tr>
<td>$D_d$(HNCN)</td>
<td>82.2 ± 2.5</td>
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<td>$\Delta_{acdid}H_{298}$(HNCN)</td>
<td>339.8 ± 2.5</td>
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<td>$EA$(NCN)</td>
<td>59.6 ± 2.5</td>
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</table>

Figure 4. Calculated CBS-QCI/APNO *ab initio* thermochemical cycle for H$_2$NCN.

(NCN) of 2.484 eV suggests that the $^1\Delta_g$ state of NCN is at least 0.85 eV higher than $^2\Delta_g$ state. Likewise we estimate that the $^2\Delta_g$ (HNCN) is at least 0.70 eV above the HNCN $^1\Delta_g$ state. This is consistent with the LIF findings (in Table 2) that report $T_d(\tilde{A} \rightarrow \tilde{A}'$ HNCN) = 3.594 770 ± 0.000 002 eV.

IV. Thermochernometry

The chemistry and spectroscopy of negative ions provides a useful avenue to extract a number of thermochernometric parameters. If one can measure the enthalpy of deprotonation for a species RH [$\Delta_{acdid}H_{298}$(RH)] and separately find the electron affinity of the corresponding radical [EA(R)], then a simple cycle that uses the ionization potential of H atom can provide a value for the bond enthalpy [DH$_{298}$(RH)].

$$\Delta_{acdid}H_{298}$(RH) = DH$_{298}$(RH) + IP(H) − EA(R) − $\int_0^{298} d\tau[C_p(H) − C_p(R)] = C_p(H) − C_p(R)$

Since the sum of the integrated heat capacities is always small (≤0.3 kcal mol$^{-1}$), the term in brackets will be ignored and we will use a more common expression, $\Delta_{acdid}H_{298}$(RH) = DH$_{298}$(RH) + IP(H) − EA(R). The gas phase acidity for cyanamide has been measured in a flowing afterglow device, and the enthalpy of deprotonation was reported to be $\Delta_{acdid}H_{298}$(H$^-$-HNCN) = 350 ± 2 kcal mol$^{-1}$. A separate set of ion experiments were interpreted to yield $\Delta_{acdid}H_{298}$(H$^-$-HNCN) = 349.8 ± 4 kcal mol$^{-1}$. Use of our electron affinity, EA(HNCN) = 60.5 ± 0.1 kcal mol$^{-1}$, leads to a value for the bond enthalpy of cyanamide, DH$_{298}$(H$^-$-HNCN) = 96.7 ± 2.3 kcal mol$^{-1}$. The bond enthalpy at 298 K and the bond energy at 0 K are related by the heat capacities.

$$DH_{298}$(RH) = $D_d$(RH) + $\int_0^{298} d\tau[C_p(H) − C_p(R)] = C_p(H) − C_p(R)$

Since the integrated heat capacity for H atom is just $\frac{1}{2}RT$, we find $DH_{298}$(H$^-$-HNCN) = 95.2 ± 2.3 kcal mol$^{-1}$. The most reliable heat of formation for cyanamide that we have found is $\Delta_H{298}$(NH$_2$CN) = 32 ± 2 kcal mol$^{-1}$. Consequently our value for DH$_{298}$(H$^-$-HNCN) leads to $\Delta_H{298}$(HNCN) = 77 ± 3 kcal mol$^{-1}$. If we can estimate the acidity of the HNCN radical, we could extract the second NH bond enthalpy of cyanamide, DH$_{298}$(H$^-$-NCN).

$$\Delta_{acdid}H_{298}$(H$^-$-NCN) = DH$_{298}$(H$^-$-NCN) + IP(H) − EA(NCN)
The acidity of the cyanoamino radical is not yet experimentally available, so we adopt a computational estimate extracted from our CBS ab initio electronic structure calculations (vide infra). Since the thermochemistry of many small radicals (N, C, NH, NH2, CN) is known, 42,37 one can assemble an entire family of bond enthalpies, DH298(RH)/kcal mol−1. Use of our experimental electron affinity, EA(NCN) = 57.3 ± 0.1 kcal mol−1, leads to the NH bond enthalpy of the cyanoamino radical, DH298(H−NCN) = 83.2 ± 1.0 kcal mol−1 and ΔHf298(HNCN) = 81.7 ± 1.0 kcal mol−1. From our value for ΔHf298(HNCN), we can use DH298(H−NCN) to extract ΔHf298(NCN) = 107.7 ± 3.2 kcal mol−1. JANAF tabulates43 a value of ΔH298(NCN) = 112.8 ± 5.0 kcal mol−1. The CBS calculations give ΔH298−(NCN) = 108.2 ± 0.7 kcal mol−1.

Since the thermochemistry of many small radicals (N, C, NH, NH2, CN) is known,42,37 one can assemble an entire family of bond enthalpies, DH298(RH)/kcal mol−1.

The collaboration between G.B.E. and G.A.P. is supported by a grant from Gaussian, Inc. To carry out the Gaussian 94 ab initio electronic structure calculations, we have used a cluster of RSC-6000 digital computers supported by NSF CHE-9412767. Throughout this work, we have benefited greatly from the insight of Prof. Steven Kass. We would particularly like to thank Prof. Geoffrey Duxbury for many fruitful discussions about the spin-orbit and Renner–Teller effects.

References and Notes

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(35) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. J. Phys. Chem. Ref. Data 1979, 8, 619. It is helpful to know the experimental bond lengths for some carbon/nitrogen bonds: \( r_e(N-N) = 1.098 \text{ Å}, r_e(C==N) = 1.172 \text{ Å}, r_e(HC==N) = 1.153 \text{ Å}, r_e(HN==C) = 1.172 \text{ Å}, r_e(H_2CN==N) = 1.140 \text{ Å}, r_e(\text{trans-HN==NH}) = 1.252 \text{ Å}, r_e(\text{H}_2\text{C==NH}) = 1.300 \text{ Å}, r_e(\text{H}_2\text{C==NH}) = 1.273 \text{ Å}, r_e(\text{H}(\text{C}==\text{N})) = 1.471 \text{ Å}.