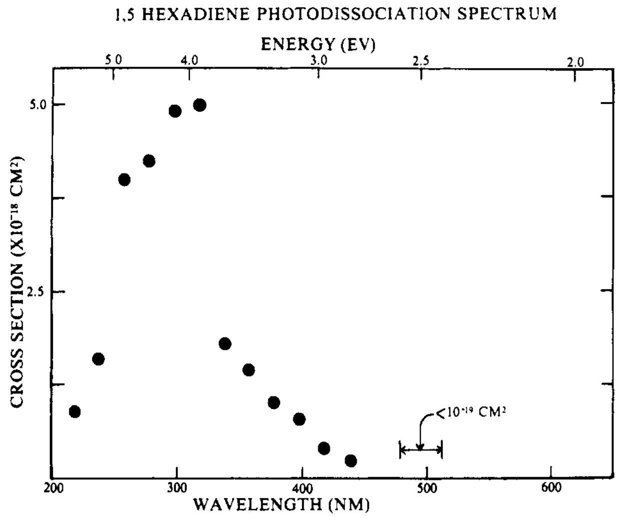

Figure 5. Monochromator spectrum at ~40-nm resolution for 1,5-hexadiene ion (**6**).

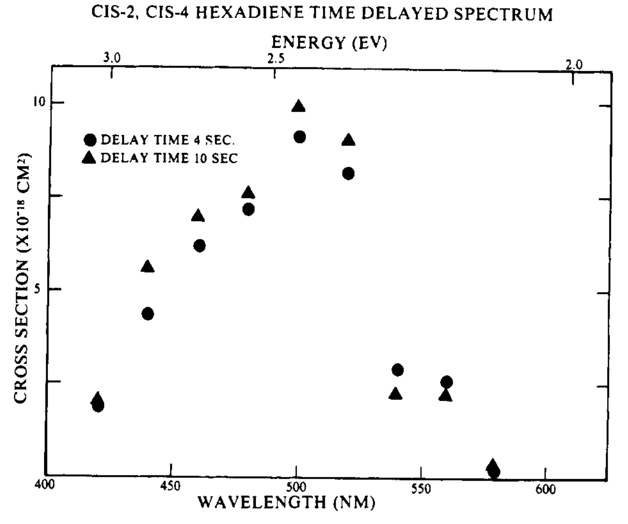

Figure 6. Interference-filter spectra of ion **1c**: (●) shows the spectrum at 4-s trapping time and 3×10^{-8} torr; (▲) shows the spectrum at 10-s trapping time and 10^{-7} torr.

the visible spectrum in Figure 3 suggests two separate peaks. The separation of about 0.04 eV (8 nm) between these maxima is in accord with the shifts found for the 2,4 isomers, and it seems reasonable to take this spectrum as showing the presence of both cis–trans isomers.

Table I. Orbital Spacing for 2,4-Hexadiene Isomers

	spectral peak position, eV	diff, eV	theor, eV
trans–trans	2.47	0.03	0.03
cis–trans	2.50	0.04	0.03
cis–cis	2.54		

Conclusions

The experimental results indicate that there is no rotation around the double bonds in the ionization of 2,4-hexadiene isomers. Each ion structure has a unique photodissociation spectrum, and spectral differences are in accord with the molecular orbital calculations. The spectral differences of the 2,4 isomers are greater in the visible region than those seen for the 1-chloropropene isomers,[10] and there are also differences, though smaller, in the UV region. It would be of interest to reexamine the two isomers of 2-butene[13] at a higher spectral resolution to see if the two spectra are really identical or if there is a shift too small to be seen at low resolution.

Where rearrangement occurred, in the case of 1,4-hexadiene, the 2,4-hexadiene structure was apparently formed. The double bond shift from 1,4 to 2,4 is similar to that seen in the rearrangement of allylbenzene to 1-phenylpropene[14] and most likely the mechanism of rearrangement involves a 1,3-hydrogen shift.[15]

There is no evidence of any conjugated ions formed from 1,5-hexadiene, which is consistent with results for the unconjugated phenylalkenes.[14] A double-bond shift of two positions has not been observed in any spectra except for 1,5-octadiene.[16] In that case, the amount of rearrangement has been estimated to be 30% and must occur as a result of the cyclic nature of the chain.

Acknowledgment. The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, of the National Science Foundation, and of the U.S. Air Force Geophysics Laboratory is gratefully acknowledged. R.C.D. was a John Simon Guggenheim Memorial Fellow, 1978–1979.

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Photodetachment of the Azide Anion in the Gas Phase. Electron Affinity of the Azide Radical

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Abstract: We report the formation of the azide anion, N_3^-, in the gas phase using azidotrimethylsilane as the source. The azide anion is formed as a product of a fast ion–molecule reaction between the trimethylsilylnitrene anion, $(CH_3)_3SiN^-$, and azidotrimethylsilane. A photodetachment threshold for N_3^- is obtained which can be equated with the adiabatic electron affinity of the azide radical, N_3, giving EA = 62.1 ± 2.8 kcal/mol.

Introduction

The azide anion, N_3^-, has been the subject of a number of chemical and theoretical studies. It is often employed in the synthesis of organic and inorganic azides, the importance of which is underscored by the volumes completely devoted to describing their chemistry.[1,2] The azide anion is a classical example of a strong nucleophile and is frequently used as a mechanistic probe in physical organic studies of nucleophilic displacement reactions.[3] In addition, N_3^- is small enough to be studied by sophisticated theoretical techniques.[4]

The electron affinity of the corresponding neutral azide radical, N_3, is still unknown, however. There have been various estimates over the years, but most of them come from thermochemical cycles based on data obtained in solution,[5] where it is generally not possible to remove accurately the contributions from solvent effects. Other estimates of the electron affinity are based on solid- or solution-phase spectroscopic data,[6] which again include unknown contributions from crystalline or solvent effects. An accurate gas-phase electron affinity would greatly aid in more fully characterizing N_3^-.

A good scheme for generating N_3^- in the gas phase has thus far not been reported. This ion has been observed upon electron impact on CH_3N_3[7] and HN_3[7,8] but its appearance potential is significantly higher than that of the nitrene anions,[7] CH_3N^- and HN^-, formed by loss of N_2. We have been able to form N_3^- efficiently in an ion cyclotron resonance (ICR) spectrometer by using azidotrimethylsilane, $(CH_3)_3SiN_3$, as a precursor. The azide anion is formed as the product of a fast ion–molecule rection between the initial electron impact product, $(CH_3)_3SiN^-$, and azidotrimethylsilane.

We report photodetachment experiments on N_3^- in this paper from which we assign an electron affinity for N_3. The electron affinity is lower than expected, based on some previous estimates and the "pseudohalide" behavior of N_3^- in solution.

Experimental Section

Materials. Azidotrimethylsilane was obtained from Aldrich and was used as received. It was transferred to an evacuated Pyrex bulb under an inert atmosphere to ensure the exclusion of moisture and oxygen. The bulb was degassed and stored at 0 °C when not in use. Nitrogen trifluoride was obtained from Ozark-Pennwalt; samples used in these experiments were prepared by transferring a small amount to an evacuated bulb on a glass vacuum line.

Instruments. The photodetachment cross section for N_3^- was measured with the use of a Varian V-5900 drift mode ICR spectrometer with a modified square analyzer cell. This apparatus and the method of data collection has been previously described.[9] Pressures of azidotrimethylsilane were $<10^{-7}$ torr, as measured by monitoring the current flow through the ion pump. Cell potentials were as follows: 2.8–3.0-V trapping, 0.0–0.50-V source, and 0.0–0.6-V analyzer. The electron beam current traversing the cell in the source region was kept under 0.1 μA, with an energy of 0.8–1.2 eV (electron energy minus trapping). Trapping-plate ejection of electrons was employed at 10 MHz with use of 0.5–1.5-V (root mean square).

Reaction pathways leading to the formation of N_3^- were established by standard double-resonance techniques.[10] Variable-frequency radio frequency voltages were applied to the source and analyzer plates with potentials of 0.2–0.5 V (peak-to-peak).

Photodetachment of N_3^- was examined qualitatively by use of a pulsed mode ICR spectrometer. This instrument has been previously described in detail.[11] Pressures of azidotrimethylsilane for these experiments were $\sim 2 \times 10^{-6}$ torr as measured with an ionization gauge. Conditions typical for negative ion formation in this apparatus were used. Irradiation of the ions was controlled with a shutter (response time ≤ 5 ms), opened and closed by TTL pulses. The opening pulse was set to coincide with the end of all reactions forming N_3^-, and the closing pulse was set just prior to the detect pulse.

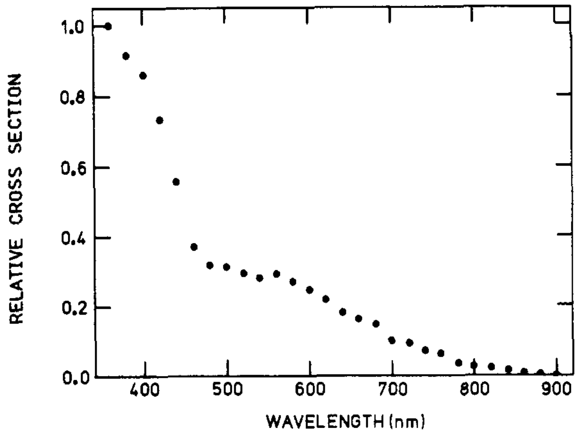

Figure 1. Apparent photodetachment cross section of N_3^-.

Pulsed ICR photodetachment data was obtained in essentially the same manner as that used in previously reported photodissociation experiments:[12] by monitoring the marginal oscillator response through a boxcar integrator in the presence and absence of irradiation. Substantial improvement in the signal to noise ratio was obtained, however, by collecting and averaging data with a Commodore PET computer and an A/D converter. Signal decreases due to photodetachment were measured by irradiating the ion population on alternate duty cycles, thereby storing the boxcar response to each duty cycle separately. The time constant of the boxcar was lowered to a value that ensured a complete response to signal changes from one duty cycle to the next, essentially reducing the function of the boxcar to integration, sample, and hold. The stored value corresponding to the boxcar output from the first duty cycle (light on) was divided by the value from the second duty cycle (light off), giving F_p: the fraction of the ions undergoing photodetachment. The logarithm of F_p was then found and could be directly translated into a relative photodetachment cross section by correcting for the photon flux.[12] This sequence is repeated many times, averaging the logarithms as the process continues. Repeating the sequence 200 times allowed signal decreases smaller than 0.5% to be reproducibly measured.

Light Source. All photodetachment experiments were performed with the use of a 1000-W Xe arc lamp as the light source. Wavelengths for the drift mode ICR photodetachment of N_3^- were selected by a $^1/_4$-m calibrated grating monochromator (resolution 58-nm fwhm). Long-pass filters were used to block diffraction higher than first order. Wavelengths for the drift mode ICR photodetachment of $(CH_3)_3SiN^-$ and the pulse mode ICR photodetachment of N_3^- were selected with sharp-cut long pass filters. Signal decreases were not large enough in the pulsed mode experiments to permit the use of the monochromator.

Results

Formation of N_3^-. Double resonance experiments in the source region of the drift mode ICR indicate that N_3^- is almost exclusively formed by reaction of azidotrimethylsilane with an ion of mass 87. This corresponds to the trimethylsilylnitrene anion, $(CH_3)_3SiN^-$, formed as a result of dissociative electron capture by azidotrimethylsilane. Reaction of this nitrene anion to form N_3^- is extremely efficient. At reasonably long trapping times (>1 s), the nitrene anion completely reacts before it can drift into the analyzer region, and it is thus not detected in the negative ion mass spectrum. The formation and subsequent decay of trimethylsilylnitrene can be observed by pulsed ICR but only at pressures of $\geq 1 \times 10^{-6}$ torr where the reaction to form N_3^- is complete within ~ 30 ms. This suggests that the reaction between the nitrene anion and azidotrimethylsilane is nearly unit efficient. The back-reaction forming trimethylsilylnitrene anion from N_3^- does not occur.

The azide anion can be produced by the reaction of azidotrimethylsilane and F^-, formed by electron impact on NF_3. Partial pressures of both NF_3 and azidotrimethylsilane as low as 2×10^{-8} torr were sufficient to form large amounts of N_3^- in the drift ICR spectrometer. Producing N_3^- from F^- does not eliminate the double-resonance signal from the trimethylsilylnitrene anion,

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however. Including large partial pressures of CCl_4 also fails to quench the nitrene anion double resonance, although the Cl^- produced does react to form N_3^-.

Photodetachment. The photodetachment cross section as a function of wavelength for N_3^- is shown in Figure 1. Each point was measured three times and averaging was employed, with use of a previously described technique to obtain the final spectrum.[13] The wavelength resolution is 58-nm fwhm. Maximum signal decreases in each run were ~5%.

A similar experiment was attempted under conditions where F^- was used to form N_3^- and double-resonance ejection of trimethylsilylnitrene anion was performed in the source region. The radio frequency potentials necessary for complete ejection, however, reduced the signal to noise ratio to a level unacceptable for measuring small photodecreases.

Photodetachment of trimethylsilylnitrene anion could be observed by employing experimental conditions which reduced the ion trapping times to ~0.1 s. Long-pass filters were used to select the wavelength since we were only interested in a rough determination of the photodetachment onset of this ion. Sizable signal decreases were observed with long-pass filters out to 850 nm. The 950-nm long-pass filter produced no detectable photodecrease in the trimethylsilylnitrene anion signal.

We also used long-pass filters to observe photodetachment of N_3^- in the pulsed ICR spectrometer. This does not allow a spectrum such as the one shown in Figure 1 to be obtained, but it does allow a rough determination of the threshold for N_3^- photodetachment in the absence of interfering photodetachment of precursors. A sizable decrease in the N_3^- signal was observed when a 440-nm long-pass filter was used when we waited until all the trimethylsilylnitrene anion had reacted before opening the shutter and irradiating the contents of the cell. In contrast, no decrease was observed under the same conditions when a 500-nm long-pass filter was used.

Discussion

Two thresholds are observed in the photodetachment spectrum measured for N_3^-, shown in Figure 1. A threshold is observed at ~460 nm with a very large increase in the cross section toward shorter wavelengths. A tail extends to longer wavelengths and terminates in a threshold of ~900 nm. It is doubtful that this long-wavelength threshold can be attributed to the onset of N_3^- photodetachment since this would require a much smaller value for the electron affinity of N_3 than can reasonably be expected.

Indeed, we have found that the longer wavelength tail does not represent photodetachment of N_3^- but rather corresponds to photodetachment of the trimethylsilylnitrene anion, $(CH_3)_3SiN^-$, which serves as the precursor to N_3^- in our experiments. A threshold for the nitrene anion has been established by following its photodetachment qualitatively with use of long-pass filters to select wavelengths. We find a threshold for this anion between 850 and 950 nm, in agreement with the long-wavelength threshold of the tail in Figure 1.

There is the possibility that the shorter wavelength threshold in Figure 1 actually corresponds to photodetachment of trimethylsilylnitrene anion as well and represents the threshold for producing trimethylsilylnitrene in an excited electronic state. By analogy with methyl nitrene,[14] which presumably has the same symmetry (C_{3v}), trimethylsilylnitrene is expected to be a ground-state triplet ($^3A_2$) and to have an excited singlet state (^1E) about 1 to 2 eV higher in energy. The energy difference between the thresholds in Figure 1 is ~1.3 eV, which is in the proper energy range. In addition, while the triplet to singlet transition is forbidden, transitions to both the singlet and the triplet are allowed from the ^2E anion.

Our pulsed mode ICR photodetachment results show, however, that the second threshold actually represents the onset for N_3^-. Photodetachment in the pulsed ICR spectrometer permits a delay time between the grid pulse forming the ions and the trigger pulse initiating irradiation of the ions and thus allows complete reaction of all precursors prior to irradiation. Photodetachment of N_3^- at wavelengths selected by long-pass filters, under conditions where all the trimethylsilylnitrene anion has reacted prior to irradiation, indicates that a threshold exists between 440 and 500 nm but that no longer wavelength tail is present. Thus, we confirm our earlier result that the long-wavelength tail arises from photodetachment of a precursor to N_3^-, and we find that the shorter wavelength threshold in Figure 1 corresponds to the onset of N_3^- photodetachment.

Table I. Equilibrium Geometry and Vibrational Frequencies for N_3^- and N_3[a]

	N_3^-	N_3
r_{N-N}, Å	1.187[b]	1.1815[c]
∠NNN, deg	180	180
ν_{sym}, cm^{-1}	1350	
ν_{bend}, cm^{-1}	640[d]	~500[b]
ν_{asym}, cm^{-1}	2020	

[a] Based in part on solid-phase data for N_3^-. [b] Pringle, G. E.; Noakes, D. E. *Acta Crystallogr., Sect. B* 1968, *B24*, 262. [c] Douglas, A. E.; Jones, W. J. *Can. J. Phys.* 1965, *43*, 2216. [d] Lamoreaux, R. T.; Dows, D. A. *Spectrochem. Acta, Part A* 1975, *31A*, 1945.

This threshold for N_3^- can be equated with the electron affinity of N_3, provided the Franck–Condon factors connecting N_3^- and N_3 are not significantly off-diagonal and provided N_3^- is not formed appreciably hot under our experimental conditions.[15] We cannot directly observe off-diagonal transitions and hot bands because our resolution is not sufficient to observe vibrational structure.

The Franck–Condon overlap between N_3^- and N_3 should be quite good, however. The photodetachment transition involves removing a nonbonding electron from N_3^-, which is not likely to have a significant effect on the vibrational force constants. These force constants are not known for N_3, but the similar equilibrium geometries of N_3^- and N_3 predict a minimal change induced by photodetachment (see Table I). Additional support for this argument comes from photoionization of the isoelectronic neutral CO_2. It is found that photoionization produces >90% of the CO_2^+ in the ground vibrational state[16] and that only the symmetric stretch is slightly off-diagonal.

It cannot be established that N_3^- is not formed hot under our experimental conditions since nothing is known about the thermodynamics of the reaction between trimethylsilylnitrene anion and azidotrimethylsilane. Trapping times are long enough to guarantee a large number of collisions of N_3^- with azidotrimethylsilane, but recent experiments indicate that collisional cooling of ions is rather inefficient in some cases.[17]

Even if some ions are vibrationally excited, they should not greatly offset the vertical threshold from the adiabatic electron affinity, however. By analogy with the photoionization in isoelectronic CO_2, the Franck–Condon factor involving the lowest frequency (bending) mode is essentially diagonal. Thus, only sequence bands (1–1, 2–2, etc.) will arise from photodetachment of ions with excess energy in the bending mode, and these will not be significantly shifted from the 0–0 band. While the Franck–Condon factor for the symmetric stretching mode may be somewhat off-diagonal, an unreasonably high vibrational temperature is required before a significant fraction of the N_3^- will exist in even $\nu = 1$ of this or the higher frequency asymmetric stretching mode. We therefore expect no problem from either hot bands or poor Franck–Condon overlap in equating our ob-

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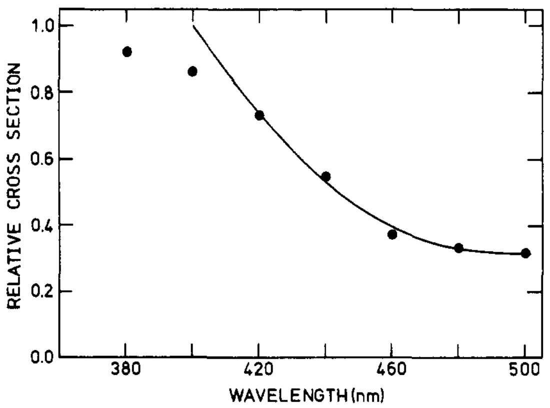


Figure 2. Theoretical fit to the photodetachment cross section for N_3^- near threshold.

served threshold with the adiabatic electron affinity of N_3.

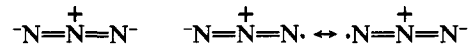
Assignment of the N_3^- threshold wavelength can be accomplished by using a technique we have previously described for locating photodetachment thresholds from low-resolution data.[18] This method involves fitting the experimental data to a theoretical cross section, calculated by the method of Reed,[19] which has been convoluted with the monochromator slit function. This technique gives the best fit for a threshold of 460 nm as shown in Figure 2, although adequate fits are obtained by using values as much as 20 nm to either side. We thus assign a threshold of 460 ± 20 nm,[20] corresponding to an electron affinity for N_3 of 2.70 ± 0.12 eV (62.1 ± 2.8 kcal/mol).

The calculations as well as the predictions of group theory indicate that the N_3^- cross section exhibits a p wave threshold dependence, rising as $E^{l+1/2}$ where $l = 1$, as observed. The threshold behavior can be understood in a simple way by examining the HOMO of N_3^- and assigning the lowest l value allowed for this orbital within the constraint of $D_{\infty h}$ symmetry. The HOMO of N_3^- is π_g, which can be assigned[21] $l = 2$ and can be considered to correspond to an atomic d orbital. Using the dipole selection rule $\Delta l = \pm 1$ to find l for the final states gives $l = 1$ or 3. Since the cross section rises much faster with $l = 1$ than with $l = 3$, we predict a p-wave dependence at threshold, as observed.

The longer wavelength threshold in Figure 1 gives an estimate of the electron affinity of the trimethylsilylnitrene anion, $(CH_3)_3SiN^-$. There is no reliable way to assess the effects of Franck–Condon factors or hot bands on the photodetachment threshold for this species, so the vertical threshold value may not correspond to the adiabatic electron affinity of trimethylsilylnitrene. We assign this vertical threshold as 1.43 ± 0.10 eV (32.8 ± 2.3 kcal/mol); the error limits are based on the experimental error rather than the difference between our threshold and the adiabatic electron affinity.

It is interesting to note that the electron detachment threshold for N_3^- is much lower than that for the isoelectronic "pseudohalide" NCO^-. We find that NCO^- has a threshold[22] greater than that of F^- (3.54 eV),[23] indicating that NCO^- is at least 0.78 eV more stable than N_3^- relative to their corresponding neutral radicals. This contrasts with their behavior in aqueous solution, where the oxidation potential of N_3^- is roughly equal to that of NCO^-.[6b]

A reasonable starting point in understanding the difference between these two isoelectronic species is provided by simple resonance theory. Reasonable canonical structures for N_3^- and N_3 are



$$^{-}N{=}\overset{+}{N}{=}N^{-} \qquad ^{-}N{=}\overset{+}{N}{=}N\cdot \leftrightarrow \cdot N{=}\overset{+}{N}{=}N^{-}$$

The canonical structure shown for N_3^- is a fairly accurate representation, as ab initio calculations indicate a large degree of charge alternation between the nitrogen atoms.[24] This is clearly energetically unfavorable. In contrast, canonical structures for NCO^- and NCO are

$$^{-}N{=}C{=}O \leftrightarrow N{\equiv}C{-}O^{-} \qquad \cdot N{=}C{=}O \leftrightarrow N{\equiv}C{-}O\cdot$$

Charge alternation does not occur in NCO^-; additional stabilization is provided by locating much of the negative charge on the more electronegative oxygen atom. One thus expects from this picture that NCO^- might be more stable than N_3^- relative to their corresponding neutral radicals, NCO and N_3.

The electron affinity found for N_3 is at the lower end of the scale set by the previous estimates based on thermochemical cycles[5] and spectroscopic data.[6] It does, however, agree with independent determinations of the heats of formation of N_3^- and N_3. Jenkins and Pratt find a value of $\Delta H_f^0(N_3^-) = 34.4 \pm 2$ kcal/mol based on thermochemical cycles.[25] A value of $\Delta H_f^0(N_3) = 99.7 \pm 5$ kcal/mol has been derived on the basis of the threshold for photodissociation of N_3CN to N_3 and CN radicals.[26,27] The difference between these numbers equals the electron affinity of N_3 minus a small correction,[28] giving 65.3 ± 7 kcal/mol. This agrees well with our electron affinity of 62.1 ± 2.8 kcal/mol.

Conclusion

We have reported the formation of N_3^- in the gas phase with use of azidotrimethylsilane as the source. The azide anion is formed via reaction of the initial electron impact product trimethylsilylnitrene anion, $(CH_3)_3SiN^-$, with azidotrimethylsilane. Photodetachment experiments have led to an electron affinity of neutral N_3 of 2.70 ± 0.12 eV (62.1 ± 2.8 kcal/mol).

Acknowledgment. We thank the National Science Foundation for support of this work and for fellowship support to M.J.P.

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(28) The electron affinity equals the difference between the enthalpies of the anion and the neutral plus a free electron at 0 K rather than at 298 K. The deviation will be small for N_3.

(29) Since this work was completed, we have obtained gas-phase acidity data (M. J. Pellerite, R. L. Jackson, and J. I. Brauman, manuscript in preparation) which allow determination of $\Delta H_f^0(N_3^-(g))$. Our value for this quantity differs substantially from the indirectly determined value mentioned above; thus, the agreement between our EA(N_3) and current literature values for $\Delta H_f^0(N_3^-(g))$ and $\Delta H_f^0(N_3(g))$ appears to be fortuitous.