International Journal of Mass Spectrometry 185/186/187 (1999) 179–187

Conjugate base of a cyclic hydrazine: formation and energetics of *N*-diaziridyl anion

Katherine M. Broadus, Steven R. Kass*

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

Received 25 May 1998; accepted 24 July 1998

Abstract

N-Diaziridyl anion (**1**), the conjugate base of a simple hydrazine, has been generated in a Fourier transform mass spectrometer (FTMS) by reduction of the nitrogen–nitrogen double bond in diazirine. The acidity of its conjugate acid (390 ± 3 kcal mol^{-1}) and the electron affinity of its corresponding radical (0.50 ± 0.10 eV) were measured. These data are combined in a thermodynamic cycle to afford the N–H bond strength in *trans*-diaziridine (**2**, 88 ± 4 kcal mol^{-1}). This value represents one of the few such bond energies reported for a hydrazine. High-level ab initio complete basis set-quadratic configuration interaction/atomic pair natural orbital (CBS-QCI/APNO) calculations on **1** and the parent hydrazyl anion (NH_2NH^-) are presented. These results provide strong confirming evidence for Berkowitz's recent determination of the N–H bond strength in hydrazine. (Int J Mass Spectrom 185/186/187 (1999) 179–187) © 1999 Elsevier Science B.V.

Keywords: Hydrazine; Diaziridine; Thermochemistry; Ion cyclotron resonance (ICR); CBS-QCI/APNO

1. Introduction

Hydrazines are an extensively used class of compounds whose applications range from agriculture and rocket fuel to polymers and medicine [1]. Despite their utility, the published thermochemistry of hydrazines appears limited mainly to heats of formation and ionization potentials. Very few N–H bond dissociation energies (BDEs) have been reported, and many of these results are unreliable. For example, published values for the N–H bond strength in hydrazine (H_2NNH_2) span a 41 kcal mol^{-1} range from 76–117 kcal mol^{-1} [2]. Part of the problem in measuring this quantity is that the $H_2N–NH_2$ bond (BDE = 65 kcal mol^{-1}) is weaker than the $H_2NNH–H$ bond [3,4]. It also has proven difficult to accurately determine the ionization potential of hydrazyl radical ($H_2NNH^{\cdot}$), although Ruscic and Berkowitz have reported a precise measurement of this quantity that when used in a thermodynamic cycle leads to BDE($H_2NNH–H$) = 80.8 ± 0.3 kcal mol^{-1} [2a]. This bond energy is in excellent accord with high-level ab initio calculations [5] and appears to be reliable, but has yet to replace the commonly listed value of 87.5 kcal mol^{-1} [6]. The situation for methylhydrazine and dimethylhydrazine is not as well resolved, and it is likely that most, if not all, of the literature values are incorrect; reported bond energies are as follows: BDE(MeNHNH–H) = 66 ± 5 [7a]

---

* Corresponding author.

Dedicated to Michael T. Bowers on the occasion of his 60th birthday and in honor of his seminal contributions to gas-phase ion chemistry.

1387-3806/99/$20.00 © 1999 Elsevier Science B.V. All rights reserved
PII S1387-3806(98)14164-7

and 112 [7b] kcal mol^{-1}, BDE(H_2NN(Me)–H) = 124 [7b] kcal mol^{-1}, and BDE(Me_2NNH–H) = 85 ± 5 [7a] and 113 [7b] kcal mol^{-1}).

Liquid-phase bond dissociation energies for some phenylhydrazine derivatives ($ArNHNH_2$) were reported recently [4]. These values were obtained by measuring the pK_{HA} of the hydrazine and the oxidation potential of its conjugate base, and combining this data as shown in Eq. (1):

$$\text{BDE(HA)} = 1.37\, pK_{HA} + 23.1\, E_{ox}(A^-) + 73.3 \tag{1}$$

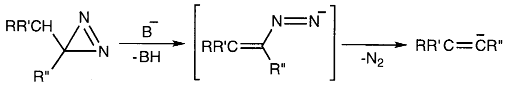
The N–H bonds for these compounds were found to be weaker than in the corresponding aniline derivatives ($ArNH_2$) by 18 kcal mol^{-1}, on average, as a result of the stabilizing two-center three-electron bonding in the hydrazyl radicals ($ArNNH_2^{\cdot}$). This methodology, however, is limited to acidic hydrazines (i.e. hydrazine and alkylhydrazines are not acidic enough to be studied) and solvation effects must be considered.

An alternative approach is to obtain bond dissociation energies in the gas phase by relating ΔH°_{acid}(HX), IP($H^\cdot$), and EA($X^\cdot$) in a thermodynamic cycle [Eq. (2)]. To our knowledge, only one

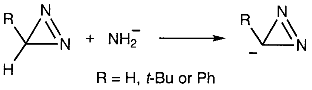
$$\text{BDE(HX)} = \Delta H^\circ_{acid}(\text{HX}) - \text{IP}(H^\cdot) + \text{EA}(X^\cdot) \tag{2}$$

conjugate base of a hydrazine, N,N'-diphenylhydrazyl anion ($PhNHN^-Ph$) has been reported [8]. This stabilized species was generated by Nibbering et al. via deprotonation of hydrazobenzene (PhNHNHPh). Thermodynamic measurements revealed a 15 kcal mol^{-1} weakening of the hydrazine N–H bond relative to aniline (i.e. the bond energies are 73 and 88 kcal mol^{-1}, respectively) that is similar to the stabilization observed in solution. Unfortunately, the same approach is not useful for preparation of the conjugate bases of hydrazine and 1,1-dimethylhydrazine, presumably because the resulting anions are thermodynamically unstable with respect to electron loss (i.e. they are unbound) [9]. A similar situation exists for a number of alkyl anions, but the electron affinities of the corresponding radicals can be increased by incorporating them into strained small-membered rings.

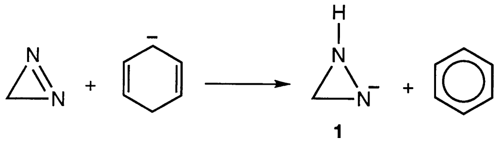
3*H*-Diazirines (or simply diazirines) are cyclic isomers of diazo compounds with a nitrogen–nitrogen double bond. Numerous derivatives are known [10], and we have previously exploited these compounds to prepare vinyl anions [$RR'C{=}CR''^-$, Eq. (3)] [11] and cyclic 4π electron systems in the gas phase (Eq. 4) [12]. [Deprotonation of phenyldiazirine also affords a small amount of a $C_7H_5^-$ ion (M–H–N_2).] Herein, we describe the reduction of diazirine (c-CH_2N_2) to afford *N*-diaziridyl anion (**1**), a simple alicyclic hydrazyl anion (Eq. 5). The reactivity and thermodynamic properties of **1** are reported, the N–H bond strength in *trans*-diaziridine (**2**) is presented, and the experimental results are compared to high-level ab initio molecular orbital calculations at the complete basis set-quadratic configuration interaction/atomic pair natural orbital (CBS-QCI/APNO) [13] level of theory.



(3)



(4)



(5)

2. Experimental

Caution: Diazirine is explosive, particularly upon freezing to liquid nitrogen temperatures.

Diazirine was prepared by oxidation of methylenediamine sulfate [14]. In one portion, 0.5 g of $3CH_2(NH_2)_2 \cdot 4H_2SO_4$ was added to a stirred solution of 150 ml of 0.7 N NaOCl and 5 ml of saturated NaOH at 0°C. (This amount of oxidant is sufficient for 8.0 g of sulfate salt.) The resulting gaseous product was carried in a stream of argon through a saturated sodium hydroxide solution and then collected in 20 ml of decalin at −78°C. Argon was allowed to flush through the apparatus for 15 min following dissolution of the salt, and then the system was opened to atmosphere and the decalin trap was closed. The product was kept cold (freezer temperatures or below) at all times. In this procedure, no ground glass joints were used; the reaction flask, sodium hydroxide bubbler, and decalin trap were connected with 1/4″ glass tubing and Cajon union fittings. [This safety precaution was taken despite no known reports of denotation of diazirine upon contact with glass joints or scratches (in comparison to diazomethane). We have safely prepared diazirine several times using a setup that contained ground glass joints.]

A dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3.0 T superconducting magnet was used to carry out the gas-phase experiments. In order to introduce diazirine into the instrument, a freeze–pump–thaw cycle of the decalin solution was required. *Extreme caution* was used because of the explosive nature of diazirine during the gaseous to solid state transition [15]. The problematic nature of this transition was verified in a few explosive incidents. To circumvent the problem, only about 80% of the decalin solution was frozen. The top portion was maintained as a liquid to serve as a buffer preventing gaseous diazirine from condensing onto solid decalin and forming high local concentrations. By taking this necessary precaution, we were able to safely degas diazirine solutions.

Hydroxide was generated by electron ionization of H_2O at 6 eV and was allowed to react with 1,4-cyclohexadiene in one cell of the FTMS to afford cyclohexadienide ($C_6H_7^-$). This ion was isolated using a stored waveform inverse Fourier transform (SWIFT) [16] and transferred to the second cell where it was allowed to react with a static pressure (1×10^{-7} Torr) of diazirine for 7 s. The reduced ion at m/z 43 corresponding to $CH_3N_2^-$ subsequently was isolated by ejecting the residual cyclohexadienide and any other ions in the cell (Fig. 1). A static pressure of argon, 1×10^{-7} Torr, was maintained in the cell to serve as a cooling gas while reactions were carried out by pulsing in probe reagents at pressures of 3×10^{-6} Torr. The resulting product ions were monitored as a function of time.

Ab initio calculations were carried out using GAUSSIAN 94 [17] on UNIX-based workstations or Cray supercomputers. The CBS-QCI/APNO theoretical model was selected for our system because we found it successfully reproduces a number of ammonia's thermodynamic properties (vide infra), and it accurately describes several isomeric CH_2N_2, $^{\cdot}CHN_2$, and $^{-}CHN_2$ species [18]. In order to obtain accurate molecular energy calculations, convergence of the one electron and the many electron expansion is needed. Pople's quadratic configuration interaction (QCI) approach [19] adequately approximates the latter requirement while the CBS models were developed to address the former problem (i.e. to reduce errors arising from truncation of the basis set). Details of the CBS-QCI/APNO model (denoted as CBS/APNO from here on) are well documented [13], but it is worth noting that this additive approach makes use of a QCISD/6-311G(d,p) geometry and a HF/6-311G(d,p) zero-point energy correction using 0.9251 as the scale factor. Higher-order correlation is obtained by a single point energy determination at the QCISD(T)/6-311++G(2df,p) level of theory in most cases whereas estimates of the CBS limit are achieved

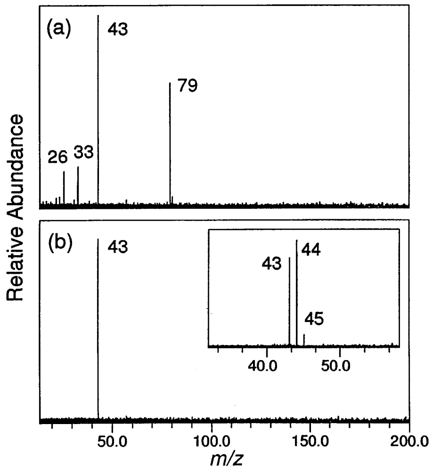
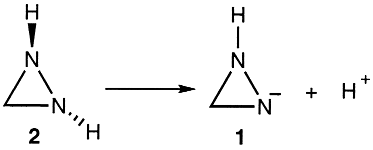


Fig. 1. (a) Reaction of cyclohexadienide (m/z 79) with diazirine; (b) isolation of N-diaziridyl anion (**1**, m/z 43). The inset shows the reaction of **1** with D_2O.

by extrapolating MP2 calculations to infinite order pair energies. The computational demands of this approach are reported to be somewhat greater than G2 theory, but so is the accuracy [i.e. the mean absolute deviations from experiment for the G2 test set are 1.2 kcal mol^{-1} (G2) and 0.5 kcal mol^{-1} (CBS/APNO)] [13a]. In this work, temperature corrections from 0–298 K were made by scaling the computed HF/6-311G(d,p) harmonic frequencies by an empirical factor of 0.8929 [20].

3. Results and discussion

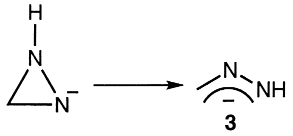
Some years ago we reacted diazirine with cyclohexadienide or HNO^- in a variable temperature flowing afterglow device at subambient temperatures, but these reactions were too slow and no more than a trace of an ion corresponding to the mass of a reduced product was detected [21]. By carrying out this transformation in the low pressure environment of a Fourier transform mass spectrometer, it was found that cyclohexadienide slowly reduces diazirine [Eq. (5)] and the resulting *N*-diaziridyl anion (**1**) can be readily isolated after a reaction period of 7 s (Fig. 1). This ion undergoes hydrogen–deuterium (H/D) exchange with D_2O ($\Delta H^\circ_{acid} = 392.9 \pm 0.1$ kcal mol^{-1}) [22] and incorporates up to two deuteriums, but no OD^- is observed. The first exchange takes place significantly faster than the second one indicating that there are two nonequivalent incorporation sites, which is consistent with the proposed structure for **1** [23]. Stronger acids such as fluorobenzene ($\Delta H^\circ_{acid} = 387.2 \pm 2.5$ kcal mol^{-1}) and MeOD ($\Delta H^\circ_{acid} = 383.5 \pm 0.7$ kcal mol^{-1}) [24] protonate (deuteronate) **1** that enables us to assign the acidity (ΔH°_{acid}) of the conjugate acid as 390 ± 3 kcal mol^{-1} (Eq. 6). (*trans*-Diaziridine is calculated to be 6.5 kcal mol^{-1} more stable than its *cis* isomer at the MP2/6-31+G(d)//HF/6-31+G(d) + ZPE level (see [25]) and, therefore, is the expected protonation product of **1**.) This result is in excellent agreement with the CBS/APNO value of 389.5 kcal mol^{-1}. The H/D exchange data are also in accord with the 16.5 kcal mol^{-1} calculated $\Delta\Delta H^\circ_{acid}$ difference between the nitrogen and carbon acidities in *trans*-diaziridine (**2**).



(6)

ΔH°_{acid} = 390 ± 3 kcal/mol (expt)
= 389.5 kcal/mol (CBS/APNO)

Ring-opening of *N*-diaziridyl anion to 1,2-diazallyl anion (**3**) needs to be considered as the rearrangement is calculated to be exothermic at the CBS/APNO level by 30.5 kcal mol^{-1} [Eq. (7)]. The observed ion, however, is too basic to be a 1,2-diazallyl anion and its reactivity (vide infra) is inconsistent with the known chemistry of 3-methyl-1-azallyl ion ($CH_3CH{=}CH{-}NH^-$, **4**) [26]; **4** is a reasonable model for **3** since a nitrogen at the central position in an allylic anion only has a small effect on the system and it is stabilizing [27]. In comparing their behavior, **1** reacts completely with MeOD to give MeO^- whereas **4** undergoes two H/D exchanges and does not afford any methoxide. CBS/APNO calculations also indicate that 1,2-diazallyl anion is not basic enough to deprotonate methanol (i.e. the predicted proton affinity is 375.2 kcal mol^{-1} at nitrogen and 369.5 kcal mol^{-1} at carbon) and its electron binding energy is too large (vide infra). Significant barriers for isomerizations of this type have been reported as well [28].

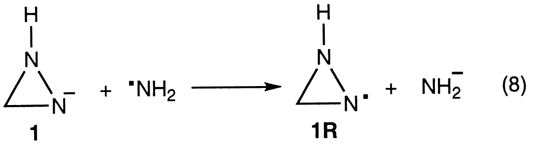


(7)

ΔH°_{rxn} = -30.5 kcal/mol (CBS/APNO)

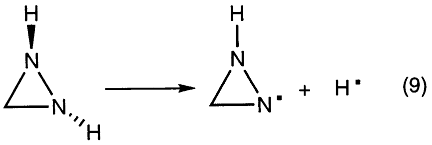
The electron affinity of *N*-diaziridyl radical (**1R**) was bracketed by monitoring the occurrence or nonoccurrence of electron transfer with standard references. A value of 0.50 ± 0.10 eV was determined based upon the following data: electron transfer is observed upon reaction of **1** with *m*-$CF_3C_6H_4CN$ (EA = 0.67 ± 0.10 eV) and CS_2 (EA = 0.51 ± 0.10 eV), but not observed with *p*-FC_6H_4CHO (EA =

0.486 ± 0.017 eV), CH_3NO_2 (EA = 0.48 ± 0.10 eV) or COS (EA = 0.46 ± 0.20 eV). These results and our assignment are in good accord with the calculated CBS/APNO values obtained by comparing the direct energy difference between **1** and **1R** (0.45 eV) and using the isogyric approach shown in Eq. (8) (0.46 eV).



$$EA(1R) = \Delta H^{\circ}_{rxn}(CBS/APNO) + EA_{expt}(^{\cdot}NH_2)$$

Given our experimental data for the proton and electron affinities of **1** and **1R**, the N–H bond dissociation energy in *trans*-diaziridine is found to be 88.0 ± 4 kcal mol^{-1} [Eq. (9)] by the application of the thermodynamic cycle shown in Eq. (2). This result is in good accord with the predicted CBS/APNO bond energy of 86.1 kcal mol^{-1}.

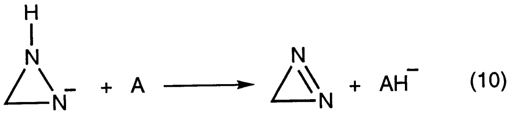


BDE = 88.0 ± 4 kcal/mol (expt)
= 86.1 kcal/mol (CBS/APNO)

N-Diaziridyl anion reacts with CS_2, COS, and N_2O predominantly via hydride transfer to afford HCS_2^-, $HCOS^-$, and HN_2O^- [Eq. (10)]. These reagents have hydride affinities (HA) of 67.3, 67.3, and ≥37.3 kcal mol^{-1} [29], respectively, which covers too broad a range to make any reasonable assignment of diazirine's hydride affinity. Therefore, **1** was reacted with benzaldehyde (HA = 45.9 kcal mol^{-1}) and nitric oxide (HA = 40.2 kcal mol^{-1}) in order to bracket the hydride affinity more accurately. In both instances there is a significant activation barrier but in the former case no reaction is observed between **1** and C_6H_5CHO or $C_6H_4CH_2O^-$ and diazirine. This prevents any thermodynamic information from being deduced from these observations. In contrast, the reaction of **1** with nitric oxide slowly affords small amounts of HNO^-. Hydride transfer is not observed in the reverse direction so these results indicate that the hydride affinity of diazirine is ≤40.2 kcal mol^{-1}. This experimental assignment is in accord with the CBS/APNO prediction for this quantity of 27.9 kcal mol^{-1}. These results also further distinguish **1** from a ring-opened isomer because 3-methyl-1-azallyl anion does not react with N_2O and reacts with CS_2 to give SH^- and $CH_3CH{=}C(SH)S^-$ [26].

It is of interest to compare *N*-diaziridyl anion with the parent hydrazyl anion, NH_2NH^-. Deprotonation of hydrazine with strong bases in a flowing afterglow or FTMS, however, does not afford the target ion; instead only signal loss is observed [9]. Presumably, this occurs because the hydrazyl anion is unstable with respect to spontaneous electron detachment. Computational results therefore were used to obtain the relevant thermochemistry. CBS/APNO calculations reproduce the acidity and N–H bond energy of ammonia as well as the electron affinity of $^{\cdot}NH_2$ (Table 1). Equally impressive results for these three quantities (ΔH°_{acid}, BDE, and EA) on the diaziridine system were obtained, and the N–H bond dissociation energy of hydrazine is in excellent accord with Berkowitz's experimental determination [2a]. Based upon these comparisons and previous work in the literature [13a], it is reasonable to expect that the computed values for $\Delta H^{\circ}_{acid}(NH_2NH_2)$ and EA $(NH_2NH^{\cdot})$ are reliable and that the energetics given below probably are accurate to within 1–2 kcal mol^{-1}.

The N–H bond energies of diaziridine and hydrazine are within 4 kcal mol^{-1} of one another [Eq. (11)] and are considerably weaker than in ammonia (21.7 and 25.6 kcal mol^{-1}, respectively) because of the stability of the resulting delocalized radical. Both hydrazines have nearly equal bond energies because the greater electron affinity of **1R** relative to $NH_2NH^{\cdot}$

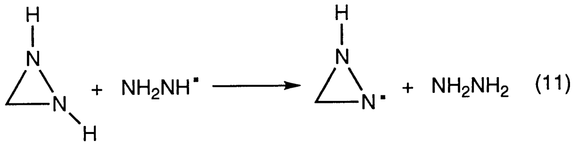


A = COS, CS_2, N_2O or NO

Table 1
Experimental and CBS/APNO acidities, bond dissociation energies, and electron affinities[a]

	ΔH°_{acid}(HX)[b]		EA(X)[c]		BDE(HX)[d]	
cmpd (HX)	Calc	Expt	Calc	Expt	Calc	Expt
NH_2–H	403.9	404.0 ± 0.4[e]	0.766	0.772 ± 0.003[e]	107.8 (106.4)	108.2 ± 0.3[e] (106.7 ± 0.3)[e]
NH_2NH–H	400.2		−0.179 (−0.173)		82.2 (80.8)	 (80.8 ± 0.3)[f]
2[g]	389.5	390 ± 3	0.449 (0.455)	0.50 ± 0.10	86.1 (84.6)	88 ± 4
$CH_2{=}NNH$–H	375.2[h]		1.50		96.1 (94.7)	

[a] Acidities and BDEs are in kcal mol^{-1}. Electron affinities are in eV.
[b] Acidities have been corrected to 298 K.
[c] Electron affinities are at 0 K and represent the direct energy difference between the anion and radical. Parenthetical values were obtained via an isogyric reaction such as in Eq. 8.
[d] Bond energies are at 298 K. Parenthetical values are at 0 K.
[e] J. Berkowitz, G.B. Ellison, D. Gutman, J. Phys. Chem. 98 (1994) 2744.
[f] See [2a].
[g] Values correspond to the N–H bond or the N-centered radical.
[h] ΔH°_{acid} = 369.5 for the isomeric diazene resulting from C-protonation of **3**.



$$\Delta H^\circ_{rxn} = \text{BDE}(\mathbf{2}) - \text{BDE}(NH_2NH\text{–}H)$$
$$= +3.9 \text{ kcal/mol (CBS/APNO)}$$

(ΔEA = 14.5 kcal mol^{-1}) is nearly canceled by the increased acidity of **2** compared to NH_2NH_2 ($\Delta\Delta H^\circ_{acid}$ = −10.7 kcal mol^{-1}). These acidity and electron affinity differences can be largely attributed to the stabilization of the diaziridyl anion; incorporation of the hydrazine moiety into a three-membered ring changes the hybridization such that the lone pairs of electrons in **1** are in orbitals with increased *s* character. Radicals show the opposite trend with respect to hybridization, so **1R** is destabilized relative to $NH_2NH^\bullet$ and this accounts for why ΔEA is somewhat greater than $\Delta\Delta H^\circ_{acid}$. The analogous hydrocarbons also display similar behavior [22].

Geometric constraints in *trans*-diaziridine force the nitrogen lone-pair electrons into a *trans* or *anti* orientation. This geometry is atypical in that most hydrazines adopt a gauche conformation [30]. Nevertheless, the same trends are observed upon deprotonation and the removal of a hydrogen atom in both *trans*-diaziridine and hydrazine. That is, the N–N bond elongates in the anion and contracts in the radical; full geometrical data are given in the Appendix. These structural effects and the differences between the cyclic and acyclic substrates also must affect the thermodynamic properties of these species.

Hydrazine is computed to be 3.7 kcal mol^{-1} more acidic than ammonia. This small difference is not surprising because replacing a hydrogen at a charged carbon center by a σ-withdrawing and π-donating substituent such as NH_2, OH, or even F often has little effect on the proton affinity of the carbanion [26]. [Interestingly, the same changes at an oxygen center have a large impact on the acidity (i.e. $\Delta H^\circ_{acid}(H_2O)$ = 390.7, $\Delta H^\circ_{acid}(Et_2NOH)$ = 370.6, ΔH°_{acid}(HOOH) = 375.9, and ΔH°_{acid}(HOF) = 367.3.] In contrast, the electron affinity of $^\bullet NH_2$ and $^\bullet NHNH_2$ differs by 0.95 eV. This large variance is a result of the extra stabilization in the hydrazyl radical and leads to a predicted electron affinity of −0.17 eV. This means that the radical is more stable than its corresponding anion and accounts for why efforts to produce the conjugate base of hydrazine and *N*,*N*-dimethylhydrazine have met with failure, even when the deprotonation was carried out in our flowing afterglow at subambient temperatures under conditions that enable us to detect weakly bound ions such as the conjugate base of cyclohexene and NO^- [9].

4. Conclusions

N-Diaziridyl anion, the first conjugate base of an aliphatic hydrazine to be observed in the gas phase, has been prepared. By measuring the acidity of its conjugate acid and the electron affinity of its corresponding radical, we were able to derive the N–H bond dissociation energy for *trans*-diaziridine via a thermodynamic cycle. Our results are in excellent accord with high-level CBS/APNO calculations and provide strong support for Berkowitz's determination of the N–H bond energy for hydrazine.

Acknowledgements

Support from the National Science Foundation, the donors of the Petroleum Research Foundation as administered by the American Chemical Society, the Minnesota Supercomputer Institute, and the University of Minnesota—IBM Shared Research Project are gratefully acknowledged.

Appendix

Absolute energies and calculated structures (*xyz* coordinates) are provided for all of the computed species in this article. All structures were optimized at the QCISD/6-311G(d,p) level. CBS-QCI/APNO energies are at 0 K.

trans-Diaziridine (**2**)

	x	*y*	*z*
C	0.000000	0.000000	0.797350
N	0.000000	0.748122	−0.443499
N	0.000000	−0.748122	−0.443499
H	0.915672	−0.076640	1.379671
H	−0.915672	0.076640	1.379671
H	0.965080	0.987525	−0.667229
H	−0.965080	−0.987525	−0.667229

E = −149.87417 hartrees

N-Diaziridyl anion (**1**)

	x	*y*	*z*
C	0.686425	−0.284289	0.008886
N	−0.768593	−0.387848	−0.169663
N	−0.002177	0.927446	0.041377
H	1.092305	−0.777250	0.939522
H	1.296639	−0.619404	−0.863724
H	−1.112109	−0.674801	0.768886

E = −149.25581 hartrees

N-Diaziridyl radical (**1R**)

	x	*y*	*z*
C	0.778584	−0.151184	0.019714
N	−0.611304	−0.508156	−0.151081
N	−0.282309	0.844533	0.023022
H	1.277410	−0.303091	0.976086
H	1.394344	−0.264761	−0.868276
H	−1.087964	−0.879686	0.670315

E = −149.23931 hartrees

Hydrazine

	x	*y*	*z*
N	−0.710901	0.102627	−0.078913
N	0.710901	−0.102614	−0.078930
H	−1.043770	0.371879	0.843874
H	−1.131937	−0.794100	−0.291457
H	1.043770	−0.372015	0.843814
H	1.131937	0.794147	−0.291330

E = −111.81444 hartrees

Hydrazyl anion

	x	*y*	*z*
N	0.008854	−0.684250	0.000000
N	0.008854	0.821772	0.000000
H	−0.576724	−0.972123	0.792707
H	−0.576724	−0.972123	−0.792707
H	1.029488	0.981594	0.000000

E = −111.17910 hartrees

Hydrazyl radical

	x	*y*	*z*
N	−0.602002	0.025591	−0.089899
N	0.743254	−0.151587	0.029720
H	−1.006869	0.884269	0.266740
H	−1.115739	−0.795467	0.195627
H	1.133842	0.793165	−0.041119

E = −111.18567 hartrees

Ammonia

	x	*y*	*z*
N	0.000000	0.000000	0.118726
H	0.000000	0.935231	−0.277028
H	0.809934	−0.467615	−0.277028
H	−0.809934	−0.467615	−0.277028

E = −56.52590 hartrees

Amide (anion)

	x	*y*	*z*
N	0.000000	0.000000	0.153918
H	0.000000	0.780302	−0.538713
H	0.000000	−0.780302	−0.538713

E = −55.88455 hartrees

Amide (neutral)

	x	*y*	*z*
N	0.000000	0.000000	0.144401
H	0.000000	0.798475	−0.505405
H	0.000000	−0.798475	−0.505405

E = −55.85641 hartrees

Diazirine

	x	*y*	*z*
C	0.000000	0.000000	0.806356
N	0.000000	−0.614805	−0.538783
N	0.000000	0.614805	−0.538783
H	−0.935272	0.000000	1.352417
H	0.935272	0.000000	1.352417

E = −148.68348 hartrees

C-Deprotonated *trans*-diaziridine

	x	*y*	*z*
C	−0.477632	−0.776140	−0.201517
N	−0.375505	0.747649	−0.158140
N	0.816593	−0.074872	0.201524
H	−0.901236	−1.072703	0.802728
H	−0.678718	1.071880	0.766451
H	1.358129	−0.051771	−0.663762

E = −149.22960 hartrees

C-Deprotonated *cis*-diaziridine (C lone pair anti to N lone pairs)

	x	*y*	*z*
C	−0.037665	0.925993	0.000000
N	−0.037665	−0.407493	0.746467
N	−0.037665	−0.407493	−0.746467
H	−1.129072	1.189348	0.000000
H	0.941188	−0.520204	1.026921
H	0.941188	−0.520204	−1.026921

E = −149.22842 hartrees

C-Deprotonated *cis*-diaziridine (C and N lone pairs syn)

	x	*y*	*z*
C	0.131280	0.927763	0.000000
H	−0.948460	1.273888	0.000000
N	0.131280	−0.398801	0.751242
N	0.131280	−0.398801	−0.751242
H	−0.838568	−0.628630	1.011933
H	−0.838568	−0.628630	−1.011933

E = −149.21868 hartrees

CH_3NNH

	x	*y*	*z*
N	−0.194633	−0.554239	0.000013
C	1.101324	0.142872	−0.000013
H	1.658021	−0.174246	0.887328
H	0.975678	1.237873	−0.000752
H	1.658629	−0.175409	−0.886546
N	−1.222732	0.139525	−0.000021
H	−0.978717	1.157550	0.000103

E = −149.89126 hartrees

CH_2NNH_2

	x	*y*	*z*
N	0.085568	−0.534000	0.007801
N	−1.116529	0.151146	−0.108311
C	1.148476	0.176173	0.008397
H	2.102887	−0.340037	0.039525
H	1.140456	1.272471	−0.030372
H	−1.081122	1.084503	0.298083
H	−1.836350	−0.394002	0.345947

E = −149.90049 hartrees

CH_2NNH (**3**)

	x	*y*	*z*
N	−0.038200	−0.502117	0.000000
C	1.105518	0.161775	−0.000001
H	2.041019	−0.395396	0.000003
H	1.127249	1.266857	0.000003
N	−1.214479	0.079434	0.000001
H	−1.032621	1.116666	−0.000002

E = −149.30468 hartrees

CH_2NNH (**3R**)

	x	*y*	*z*
N	0.036504	−0.548254	0.000000
C	−1.074039	0.178927	0.000000
H	−2.027746	−0.338404	0.000000
H	−1.041409	1.275229	0.000000
N	1.182322	0.100491	0.000000
H	0.981611	1.123952	0.000000

E = −149.24959 hartrees

References

[1] (a) E.W. Schmidt, Hydrazines and its Derivatives: Preparation, Properties, Applications, Wiley, New York, 1984; (b) J.-M. Kim, S.E. Hoegy, P.S. Mariano, J. Am. Chem. Soc. 117 (1995) 100; (c) J. Wang, M. Chicharro, G. Rivas, X. Cai, N. Dontha, P.A.M. Fanas, H. Shiraishi, Anal. Chem. 68 (1996) 2251; (d) K. Shyamik, P.G. Penketh, R.H. Loomis, W.C. Rose, A.C. Sartorelli, J. Med. Chem. 39 (1996) 796; (e) A. Chomiakow, Zesz. Nauk. Politech Slask. Chem. 127 (1993) 9; (f) S. Veda, J. Propul. Power 10 (1994) 1646.

[2] (a) B. Ruscic, J. Berkowitz, J. Chem. Phys. 95 (1991) 4378; (b) M.A. Grela, A.J. Colussi, Int. J. Chem. Kinet. 20 (1988) 713; (c) M. Meot-Ner, S.F. Nelsen, M.R. Willi, T.B. Frigo, J. Am. Chem. Soc. 106 (1984) 7384; (d) P. Gray, J.C.J. Thynne, Trans. Faraday Soc. 60 (1964) 1047; (e) I.P. Fisher, G.A. Heath, Nature, 208 (1965) 1199; (f) I.J. Eberstein, The Gas-Phase Decomposition of Hydrazine Propellants, Prince-

ton University, Department of Aerospace and Mechanical Science, Technical Report 708, Contract AD 49(638)1268 1964; (g) V.H. Diebler, J.L. Franklin, R.M. Reese, Adv. Mass Spectrom. 1 (1959) 443; (h) S.N. Foner, R.L. Hudson, J. Chem. Phys. 29 (1958) 442.

[3] S.T. Gibson, J.P. Greene, J. Berkowitz, J. Chem. Phys. 83 (1985) 4319.

[4] Y. Zhao, F.G. Bordwell, J.-P. Cheng, D. Wang, J. Am. Chem. Soc. 119 (1997) 9125.

[5] (a) D.A. Armstrong, D. Yu, A. Rauk, J. Phys. Chem. A 101 (1997) 4761; (b) J.A. Pople, L.A. Curtiss, J. Chem. Phys. 95 (1991) 4385.

[6] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 77th Ed, CRC Press, Boca Raton, FL, 1996, pp. 9–65.

[7] (a) S.N. Foner, R.L. Hudson, J. Chem. Phys. 53 (1970) 4377; (b) V.H. Dibeler, J.L. Franklin, R.M. Reese, J. Am. Chem. Soc. 81 (1959) 68.

[8] S. Ingeman, R.H. Fokkens, N.M.M. Nibbering, J. Org. Chem. 56 (1991) 607.

[9] G.D. Dahlke, S.R. Kass, unpublished results.

[10] M.T.H. Liu, Chemistry of Diazirines, CRC Press, Boca Raton, FL, 1987.

[11] K.K. Anderson, S.R. Kass, Tetrahedron Lett. 30 (1989) 3045.

[12] (a) R.L. Kroeker, S.R. Kass, J. Am. Chem. Soc. 112 (1990) 9024; (b) K.M. Broadus, S.R. Kass, unpublished results.

[13] (a) J.A. Montgomery Jr., J.W. Ochtersk, G.A. Petersson, J. Chem. Phys. 101 (1994) 5900; (b) G.A. Petersson, T.G. Tensfeldt, J.A. Montgomery Jr., J. Chem. Phys. 94 (1991) 6091; (c) G.A. Petersson, M.A. Al-Laham, J. Chem. Phys. 94 (1991) 6081; (d) G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J. Mantzaris, J. Chem. Phys. 89 (1988) 2193.

[14] R. Ohme, E. Schmitz, Chem. Ber. 97 (1964) 297.

[15] (a) J.E. Wollrab, L.H. Scharpen, D.P. Ames, J.A. Merritt, J. Chem. Phys. 49 (1968) 2405; (b) E. Schmitz, R. Ohme, Tetrahedron Lett. (1961) 612.

[16] T.C.L. Wang, T.L. Ricca, A.G. Marshall, Anal. Chem. 58 (1986) 2938.

[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, R.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Gaussian, Inc., Pittsburgh, PA, 1995.

[18] (a) E.P. Clifford, P.G. Wenthold, W.C. Lineberger, G.A. Petersson, G.B. Ellison, J. Phys. Chem. A 101 (1997) 4338; (b) E.P. Clifford, P.G. Wenthold, W.C. Lineberger, G.A. Petersson, K.M. Broadus, S.R. Kass, S. Kato, C.H. DePuy, V.M. Bierbaum, G.B. Ellison, J. Phys. Chem. A 102 (1998) 7100.

[19] J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.

[20] (a) D. McQuarrie, Statistical Mechanics, Harper and Row, New York, 1976; (b) J.A. Pople, A.P. Scott, M.W. Wong, L. Radom, Israeli J. Chem. 33 (1993) 345.

[21] R.K. Sachs, Ph.D. Thesis, University of Minnesota, 1993.

[22] All acidities and electron affinities, unless otherwise noted, are taken from: S.G. Lias, J.E. Bartmess, J.F. Liebmann, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) Suppl 1 [or the slightly updated form available on a personal computer, NIST Negative Ion Energetics Database (Version 3.00, 1993); NIST Standard Reference Database 19B].

[23] R.R. Squires, V.M. Bierbaum, J.J. Grabowski, C.H. DePuy, J. Am. Chem. Soc. 105 (1983) 5185.

[24] S.E. Barlow, T.T. Dang, V.M. Bierbaum, J. Am. Chem. Soc. 112 (1990) 6832.

[25] R.L. Kroeker, S.M. Bachrach, S.R. Kass, J. Org. Chem. 56 (1991) 4062.

[26] G.D. Dahlke, S.R. Kass, J. Am. Chem. Soc. 113 (1991) 5566.

[27] (a) K.B. Wiberg, C.M. Breneman, T.J. LePage, J. Am. Chem. Soc. 112 (1990) 61; (b) S.R. Kass, C.H. DePuy, J. Org. Chem. 50 (1985) 2874.

[28] (a) P.K. Chou, S.R. Kass, Org. Mass Spectrom. 26 (1991) 1039; (b) P.K. Chou, G.D. Dahlke, S.R. Kass, J. Am. Chem. Soc. 115 (1993) 315.

[29] (a) Hydride affinities taken from: P. Ausloos, S.G. Lias (Eds.), Structure/Reactivity and Thermochemistry of Ions, Dordrecht, Boston, 1986, p. 373; (b) HA of HN_2O^- from S.R. Kass, H. Guo, G.D. Dahlke, J. Am. Soc. Mass Spectrom. 1 (1990) 366.

[30] B. Ma, J.-H. Lii, K. Chen, N.L. Allinger, J. Phys. Chem. 100 (1996) 11297.