200. Gas-Phase Generation and Characterization of Nitrileimine, HCNNH: A New, Stable Isomer of Diazomethane

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A new isomer of diazomethane **1**, the nitrile imine, HCNNH (**2**) is reported to be a stable molecule in the gas phase. Upon neutralizing the α-distonic $HCNNH^{+\cdot}$ cation in a beam experiment, this long-time predicted ylide can be generated. The experiments are supported by theoretical calculations (DFT/HF hybride method) on the neutral and cationic diazomethane **1**, nitrile imine **2**, and *N*-isocyano amine **3** as well as the transition states for their interconversion.

In a recent study, we have been able to demonstrate that hydrogen cyanide *N*-methylide $HCNCH_2$, the isoelectronic analogue of fulmic acid HCNO, is a stable molecule in the gas phase [1]. The characterization of this species by mass-spectrometric experiments succeeded only shortly after *Maier et al.* [2] had reported its matrix isolation. One member of the intriguing family of HCNR ylides (R = O, NH, CH_2) that still lacks compelling evidence for its existence is the nitrile imine molecule HCNNH **2** (hydrogen cyanide-*N*-imide).

$$H_2\overset{-}{C}-\overset{+}{N}\equiv N \qquad H\overset{-}{C}=\overset{+}{N}=NH \qquad \overset{-}{C}\equiv\overset{+}{N}-NH_2$$

1 **2** **3**

Already 40 years ago, the title compound **2** was suggested to be viable through hydrolysis of the metalated diazomethane LiHCNN [3]. However, as was demonstrated later [4], the $[H_2,C,N_2]$ molecule generated was not **2**; instead another isomer of diazomethane (**1**), the *N*-isocyano amine $CN-NH_2$ (**3**) had been obtained. There have been a number of further unsuccessful attempts to generate **2** which are scattered throughout the literature, and which have been covered by the recent review article of *Bertrand* and *Wentrup* [5]. HCNNH (**2**) represents the parent species of the nitril imines RCNNR′, molecules that, until recently, were believed to be reactive intermediates. In the last decade, however, a large number of substituted nitrile imines have been characterized and shown to be stable species, even at room temperature¹). That the unsubstituted molecule **2** should be a stable, accessible species, at least in the gas phase or in matrices, has been proposed in a number of theoretical studies dealing with the stabilities of the various possible $[H_2,C,N_2]$ isomers [6]. In a recent theoretical study, *Schubert et al.* [7] predicted the nitrile imine **2** to lie only 26 kcal/mol higher in energy than neutral diazomethane **1**.

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¹) For a recent exhaustive review covering most aspects of the generation, characterization, and chemistry of substituted nitrile imines, see [5].

Here, we report the gas-phase characterization of this as yet unknown species by neutralization-reionization mass spectrometry (NRMS; for reviews, see [8]) of the corresponding α-distonic cation²)³) $\mathbf{2}^{+\cdot}$. In addition, the results from density functional theory/*Hartree-Fock* calculations (B3LYP hybride method) will be reported that have been carried out in order to establish the heigths of the barriers for interconversion of the neutral and ionic isomers **1**, **2**, and **3**.

It is well known that the neutralization of distonic ions leads to the corresponding diradicals or, when α-distonic ions are used as precursor molecules, to ylides [11]. The ionization of 1,2,4-triazol⁴) under electron-impact conditions⁵) [12] gives rise to a strong signal for a cation at *m/z* 42 having an elemental composition $[H_2,C,N_2]^{+\cdot}$. The collisional activation (CA) [13] mass spectrum of this ion is shown in *Fig. 1*.

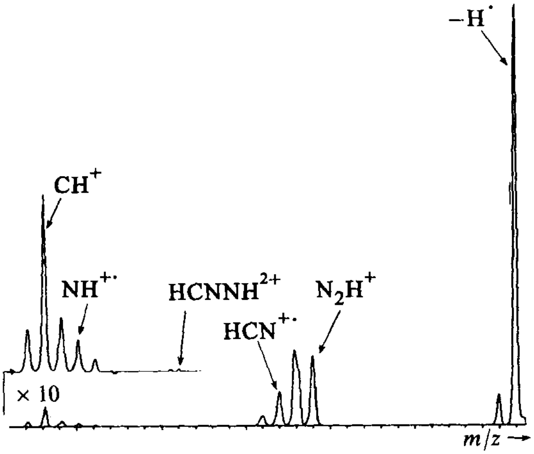

Fig. 1. *Collisional activation mass spectrum of* $HCNNH^{+\cdot}$ (He, 80% T)

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²) In 1984, the term *distonic ion* was introduced by *Radom* and coworkers for ions that formally possess spatially separated charge and spin sites [9].

³) For reviews on the generation and unique chemistry of distonic ions, see [10].

⁴) It should be noted that also 1,2-triazoles give rise to the cyanoimine ions $\mathbf{2}^{+\cdot}$ upon electron-impact ionization; however, here isobaric interferences due to the largely abundant $H_3\,^{13}CCN^{+\cdot}$ ions do not permit further collision experiments.

⁵) The experiments were performed on a modified *ZAB-HF* machine [12] of *BEBE* configuration (*B* stands for magnetic and *E* for electrostatic analyzer) (ion-source conditions: temperature, 200°; ionization energy, 70 eV; trap current, 100 μA; repeller voltage, 30 V; acceleration voltage, 8 kV). The ions of interest were mass-selected (mass resolution $m/\Delta m \approx 2000$) by means of the first magnetic (*B*1) and electrostatic analyzer (*E*1). The experiments were performed at a transmittance (*T*) of 80% of the ion beam. Collisional-activation mass spectra were obtained by colliding the cations with He in the second part of a tandem-collision cell. For the neutralization-reionization experiments, Xe (80% T) was used in the neutralization and O_2 in the reionization step. In the case of the $^+NR^+$ experiments, the combination Xe (80% T)//O_2 (80% T) was employed. In both NR experiments, remaining ions were deflected from the beam by means of a voltage (1000 V) applied to the deflector electrode which is situated between the two differentially pumped collision cells. The neutral molecules were reionized to the corresponding species by colliding them with O_2; in the case of the $^-NR^-$ experiments, Xe was used as second collision gas. For a particle *m/z* 42, having been accelerated to 8 keV kinetic energy, it takes *ca.* 4 μs to travel from the first part of the collision cell to the entrance of the second chamber. This value defines a lower bound for the lifetime of the neutral molecules. The mass spectra were obtained by scanning the second magnetic analyzer (*B*2). To improve the signal-to-noise-ratio, 10–30 scans were accumulated and on-line processed with an *AMD Intectra* data system.

The interpretation of the experimental results is straightforward. The base peak in the spectrum corresponds to the loss of a hydrogen radical. The abundant structure-diagnostic at m/z 29 (N_2H^+) and that at m/z 15 ($NH^{+\cdot}$) together with the absence of a signal for $N_2H_2^{+\cdot}$ indicate that the ion possesses an N–NH subunit[6]). Furthermore, the strong signal for the CH^+ fragment gives evidence that the investigated ions is in fact the distonic radical cation of the nitrileimine $\mathbf{2}^{+\cdot}$. To probe the possible existence and stability of the neutral nitrileimine **2**, these $HCNNH^{+\cdot}$ cations were subjected to a NR experiment (*Fig. 2*).

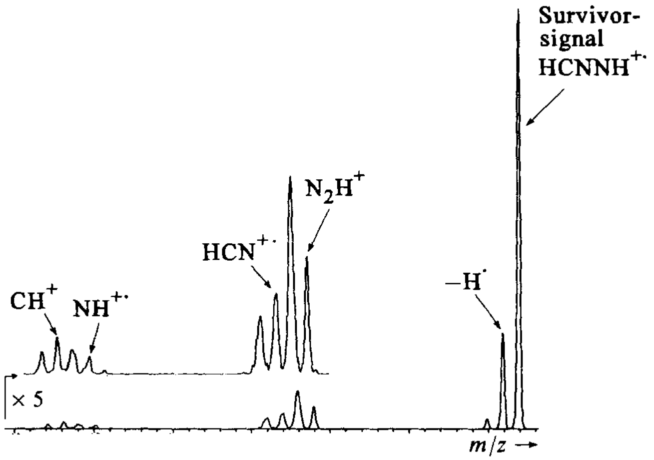

Fig. 2. *Neutralization-reionization mass spectrum of HCNNH*$^{+\cdot}$ (Xe, 80% T // O_2, 80% T)

The base peak in the NR spectrum corresponds to the survivor signal for the reionized $HCNNH^{+\cdot}$ cations. The structure-diagnostic signals for the ions N_2H^+ (m/z 29), $HCN^{+\cdot}$ (m/z 27), $NH^{+\cdot}$ (m/z 15), and CH^+ (m/z 13) indicate a HCNNH connectivity of the neutralized cation, thus, strongly suggesting that the neutral molecule generated in the course of the collision events is nitrileimine **2**. The strong ion flux permitted a further investigation of the reionized survivor ions $\mathbf{2}^{+\cdot}$ by means of an MS/MS/MS experiment. This NR-CA spectrum was obtained upon colliding the beam of survivor ions with He (*Fig. 3*).

The gross features in this MS/MS/MS spectrum are practically identical with the fragmentation pattern obtained in the CA experiment of source-generated ions $\mathbf{2}^{+\cdot}$ and render further evidence for a preservation of the structure of the ions in the course of the multiple collision events[7]). To gain further consolidation of the structural assignment, the

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[6]) In principle it could also be argued that the isomeric $HCN(H)N^{+\cdot}$ species may be formed to some extent upon ionization of the triazole. This, however, is discarded as the distonic cation of such a nitrene diradical HCN(H)N, if stable at all, is expected to lie significantly higher in energy.

[7]) The similarity of the CA and NR-CA spectra gives additional evidence for the purity of the ion beam, thus, ruling out a major contribution of isomeric $HCN(H)N^{+\cdot}$ cations. If the beam contains a mixture of two or more isomers the two spectra are expected to vary significantly as the different cross sections for the electron-transfer processes is expected to lead to an enrichment of one isomer in the reionized beam.

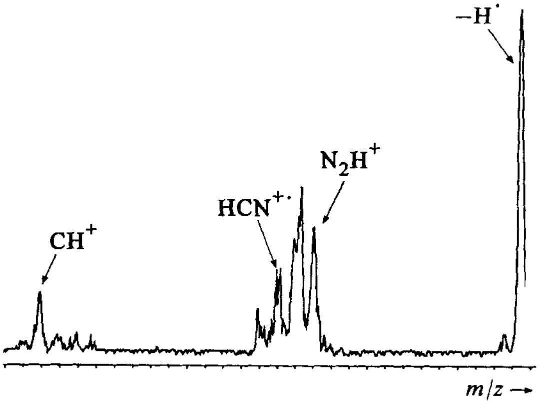

Fig. 3. *NR-CA Mass spectrum of HCNNH*$^{+\cdot}$ (Xe, 80% T//O_2, 80% T//He, 80% T)

isomeric diazomethane $H_2CN_2^{+\cdot}$ ($\mathbf{1}^{+\cdot}$) cation was investigated under the same experimental conditions[8]). The ions show an overall different fragmentation behavior in the CA experiment (*Fig. 4*) when compared to $\mathbf{2}^{+\cdot}$.

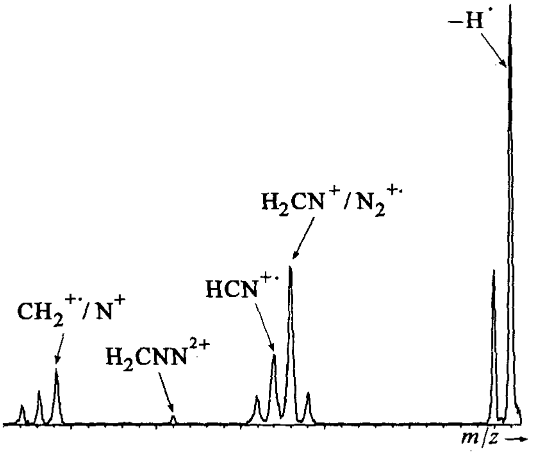

Fig. 4. *Collisional activation mass spectrum of H*$_2$*CN*$_2^{+\cdot}$ (He, 80% T)

Strong fragments at *m/z* 28 ($N_2^{+\cdot}$ and H_2CN^+) are obtained indicating that the ion has preserved the structure of the neutral diazomethane precursor. In the low-mass region, the expected $CH_x^{+\cdot}$ ($x = 0–2$) cations are observed and in line with the connectivity of H_2CNN no NH_x ions ($x = 0–2$) can be detected. For a meaningful comparison, the NR spectrum of the isomeric diazomethane cation $\mathbf{1}^{+\cdot}$ was recorded (*Fig. 5*). It displays a considerably stronger survivor signal indicative of rather different *Franck-Condon* factors in the electron-transfer processes. Indicative for H_2CNN (**1**) and in sharp contrast to the NR spectrum of nitrileimine (**2**), strong signals can be seen at *m/z* 28 ($N_2^{+\cdot}$ and H_2CN^+) and *m/z* 16 (N^+ and $H_2C^{+\cdot}$) which establish H_2CN and N_2 subunits of the molecule.

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[8]) Gaseous diazomethane was generated directly in the ion source by gently heating a mixture of wet NaOH and *N*-nitroso-4-toluenesulfomethylamide. The sample was inserted into the ion-source *via* a solid-probe inlet system.

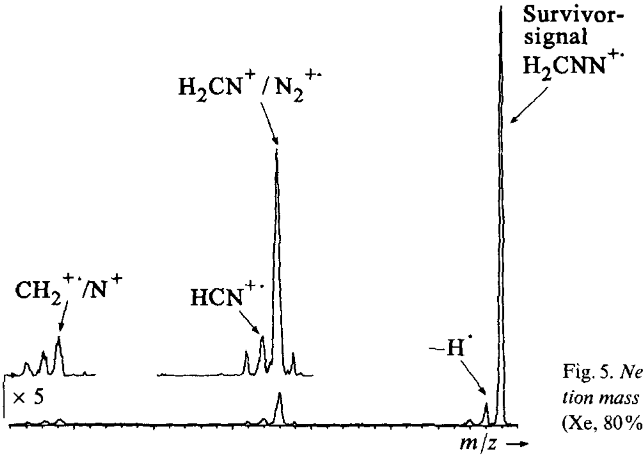

Fig. 5. *Neutralization-reionization mass spectrum of* $H_2CN_2^{+\cdot}$ (Xe, 80% T//O_2, 80% T)

Further support for the experimental findings was obtained from theoretical calculations[9]). The neutral HCNNH (**2**) as well as its cation are found to correspond to stable species which can be well distinguished from other possible isomers (*Fig. 6*). The quality

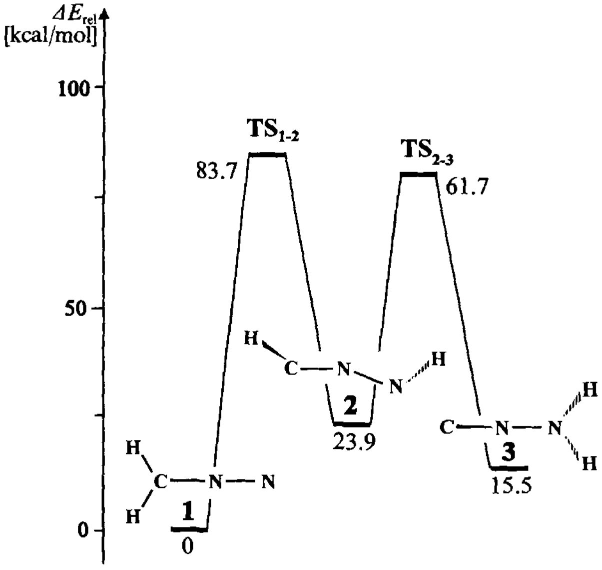

Fig. 6. *Relative energies* [kcal/mol] *of neutral diazomethane* (**1**), *nitrileimine* (**2**), N-*iso-cyanoamine* (**3**), *and the transition states for interconversion* (B3LYP/6-311+G(d,p) level of theory)

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[9]) The calculations of the structures, energetics, and frequencies have been performed using a hybrid method of *Hartree-Fock* (*HF*) and Density Functional Theory (DFT) [14]. We have used the local exchange-correlation functional of *Vosko et al.* [15] along with the non-local corrections for exchange as introduced by *Becke* [16], and the non-local *Lee-Yang-Parr* correlation function [17]. *Becke*'s empirical three-parameter fit [18] for mixing HF and DFT exchange-energy terms and the correlation-energy terms were further applied. The standard 6-311+G(d,p) basis set was used. The relative energies were corrected for zero-point vibrational energies (ZPVE). All calculations were performed with the GAUSSIAN92/DFT program package [19] on *IBM/RS6000* workstations.

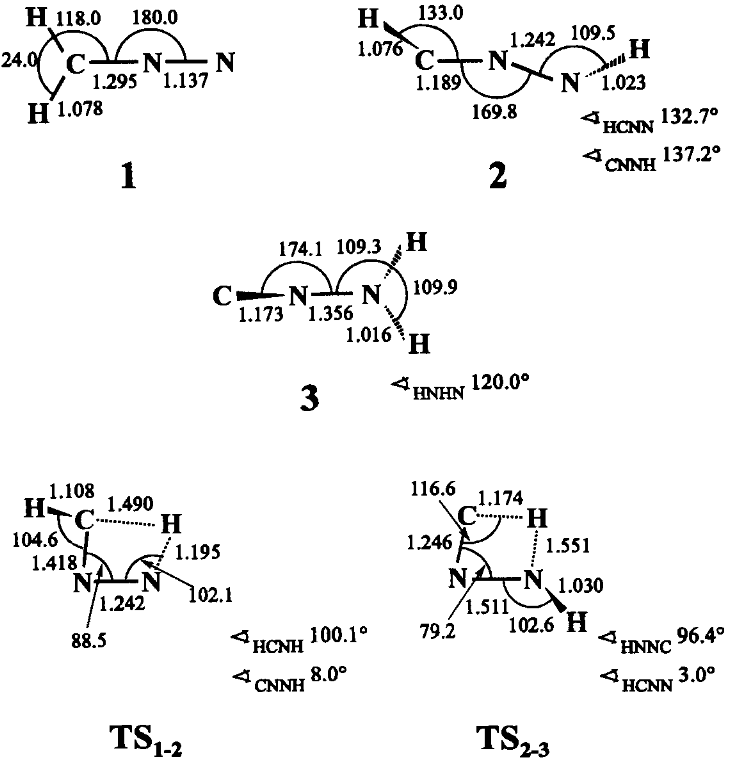


Fig. 7. *Structures of neutral diazomethane* (**1**), *nitrileimine* (**2**), N-*isocyanoamine* (**3**), *and the transition states* (B3LYP/6-311+G(d,p) level of theory; bond lengths are given in Å, angles in degrees)

of these B3LYP results can be verified by comparing them with the results of QCISD(T) calculations of the minimum structures that have recently been published by *Schubert et al.* [7]. These authors reported the nitrileimine (**2**) to lie 26.2 kcal/mol higher in energy than diazomethane (**1**). The DFT calculations arrive at a similar energy difference (23.9 kcal/mol).

Interestingly, a value of 133° is found for the HCN bond angle in species **2**. This feature together with the relative short CN as well as NN bond lengths in this molecule (1.189 and 1.242 Å, respectively) indicate that the ylide form **2a** is favored over **2b**. A similar observation has already been reported for the isoelectronic molecule $HCNCH_2$ [2]. This interpretation is further supported by a calculated dihedral angle (HCNH) of 90.1°; this value is expected for such a cumulenic structure. However, a population analysis of the atomic charges reveals that the terminal N-atom is negatively polarized, and thus the mesomeric structure **2b** also contributes significantly to the wave function.

$$\mathrm{H\overset{-}{C}{=}\overset{+}{N}{=}NH} \qquad \mathrm{HC{\equiv}\overset{+}{N}{-}\overset{-}{N}H}$$

2a **2b**

N-Isocyanoamine (**3**) was found to be 15.5 kcal/mol less stable than diazomethane, also in good agreement with the earlier calculations [7] that arrived at a relative energy value of 11.9 kcal/mol in favor of diazomethane. As indicated by our calculations, the three neutral isomers lie in deep potential wells. The transitions states for the two consecutive 1,3-H shifts **1**$\rightleftarrows$**2**$\rightleftarrows$**3** are found to be 83.7 kcal/mol (TS_{1-2}; freq = i1108 cm^{-1}) and 61.7 kcal/mol (TS_{2-3}; freq = i1043 cm^{-1}) higher in energy than the global minimum **1**. Frequency analysis furthermore reveals that they both possess imaginary frequencies in the order of 1000 cm^{-1} typical for such 1,3-H migrations. The first transition state for the hydrogen shift which results in the formation of **2** from diazomethane (TS_{1-2}) is found to be rather 'late' with respect to the geometry of the neutral diazomethane: the migrating hydrogen is located closer to the terminal N-atom than to the C-center. The second consecutive TS_{2-3} resembles far more the nitrileimine (**2**).

On the ionic $[H_2,C,N_2]^{+\cdot}$ surface (*Fig. 8*), the diazomethane cation $\mathbf{1}^{+\cdot}$ is also found to be the most stable isomer. However, the energetic situation for the nitrileimine cation ($\mathbf{2}^{+\cdot}$) and *N*-isocyanoamine cation ($\mathbf{3}^{+\cdot}$) is reversed when compared with the neutral surface.

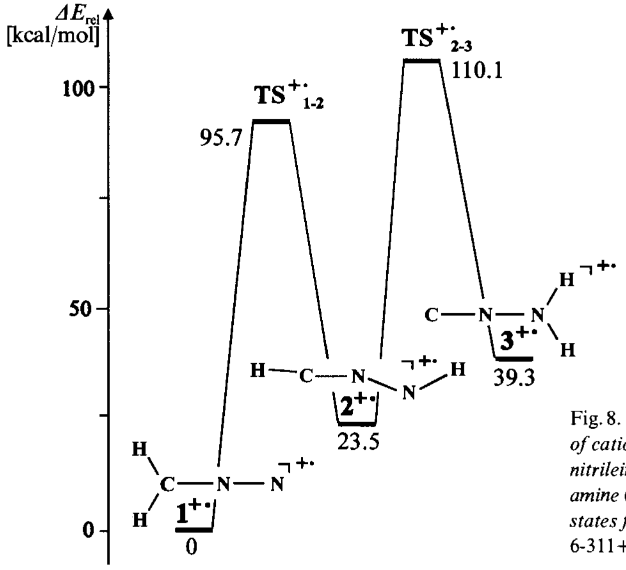
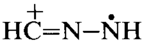
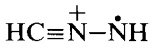


Fig. 8. *Relative energies* [kcal/mol] *of cationic diazomethane* ($\mathbf{1}^{+\cdot}$), *nitrileimine* ($\mathbf{2}^{+\cdot}$), N-*isocyanoamine* ($\mathbf{3}^{+\cdot}$), *and the transition states for interconversion* (B3LYP/6-311+G(d,p) level of theory)

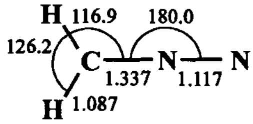
The nitrileimine cation ($\mathbf{2}^{+\cdot}$) lies 23.5 kcal/mol higher than $\mathbf{1}^{+\cdot}$ and is well separated by a large barrier of 72.2 kcal/mol for the 1,3-H shift connecting $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ ($TS^{+\cdot}_{1-2}$; freq = i1228 cm^{-1}). The results of the calculations further indicate that conversion of the nitrileimine cation to the energetically by 15.8 kcal/mol less favored *N*-isocyanoamine cation ($\mathbf{3}^{+\cdot}$) is even more unlikely, as the transition state for this rearrangement requires 86.6 kcal/mol ($TS^{+\cdot}_{2-3}$; freq = i1459 cm^{-1}). As in the neutral case, both transition states are found to resemble the nitrileimine cation ($\mathbf{2}^{+\cdot}$) with regards to the bonds lengths (*Fig. 9*). All three minima possess planar geometries. However, in contrast to the neutral nitrileimine (**2**), the HCN subunit in the cation $\mathbf{2}^{+\cdot}$ is found to be practically linear ($\sphericalangle$ HNC = 178.1°). This can be rationalized by the resonance structures $\mathbf{2a}^{+\cdot}$ and $\mathbf{2b}^{+\cdot}$.


$H\overset{+}{C}{=}N{-}\overset{\bullet}{N}H$

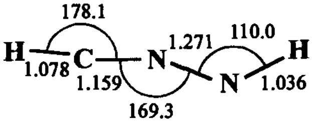
$\mathbf{2a}^{+\cdot}$


$HC{\equiv}\overset{+}{N}{-}\overset{\bullet}{N}H$

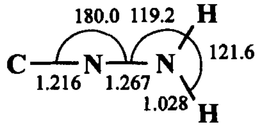
$\mathbf{2b}^{+\cdot}$



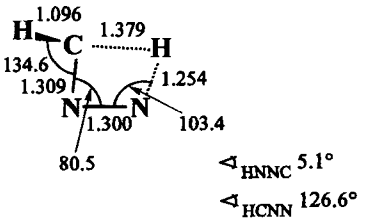
$\mathbf{1}^{+\cdot}$



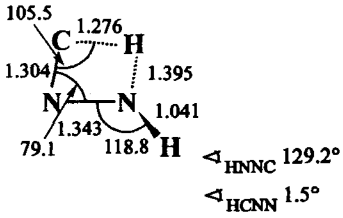
$\mathbf{2}^{+\cdot}$



$\mathbf{3}^{+\cdot}$



$\mathbf{TS}^{+\cdot}_{\mathbf{1\text{-}2}}$



$\mathbf{TS}^{+\cdot}_{\mathbf{2\text{-}3}}$

Fig. 9. *Structures of cationic diazomethane* ($\mathbf{1}^{+\cdot}$), *nitrileimine* ($\mathbf{2}^{+\cdot}$), N-*isocyanoamine* ($\mathbf{3}^{+\cdot}$), *and the transition states* (B3LYP/6-311+G(d,p) level of theory; bond lengths are given in Å, angles in degrees)

The population analysis shows that the unpaired electron is located mainly at the terminal N-atom. The atomic-charge analysis is slightly more in accord with structure $\mathbf{2a}^{+\cdot}$, where the positive charge is stronger located on the C-atom.

In conclusion, the theoretical results lend further support to our experimental observation that both species, the cationic as well as the neutral nitrile imine HCNNH (**2**), are in fact distinct species on the hypersurfaces which are well separated from the isomeric diazomethane (**1**) and *N*-isocyanoamine (**3**).

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