

Mass-Spectrometric and GAUSSIAN2 Studies of the Diazene (HNNH) and Isodiazene (H₂NN) Molecules and Their Radical Cations[☆]

Norman Goldberg, Max C. Holthausen, Jan Hrušák*, Wolfram Koch*, and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin, Germany

Received, September 9, 1993

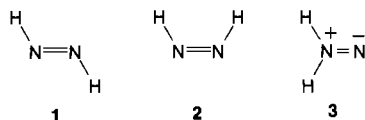
Key Words: Charge-transfer experiments / Tandem mass spectrometry / Diazene / Potential energy surface

Collision experiments demonstrate that isodiazene (H₂NN) and its radical cation are viable molecules in the gas phase. The mass-spectrometric experiments are complemented by

extensive ab-initio MO calculations using the GAUSSIAN-2 procedure in order to map out relevant parts of the potential energy surface of H₂N₂ (singlet) and H₂N₂⁺ (doublet).

I. Introduction

Among the H_xN_y compounds, the well-characterized^[1] diazene (HNNH) is widely used as a synthetic reagent for the stereospecific *cis*-hydrogenation of multiple bonds^[2]. Several experimental and theoretical^[3] studies have firmly established that diazene possesses a singlet ground state with C_{2h} symmetry [*trans*-diazene (**1**)]. Evidence for the existence of the energetically unfavored *cis* isomer **2** is, in comparison, quite scarce, and only a few vibrational absorption lines have been tentatively assigned to that isomer^[4]. Finally, relatively little is also known about the least stable isomer on the H₂N₂ surface, i.e. *iso*-diazene H₂NN (**3**), also referred to as aminonitrene. Already more than 90 years ago *iso*-diazene was predicted to play a key role as intermediates in the chemistry of azo compounds^[5]. However, until the work of Dervan et al.^[6] none of these compounds had been observed. These authors reported the first characterization of a substituted *iso*-diazene, the (2,2,6,6-tetramethylpiperidyl)nitrene in 1981, and three years later the same group described the generation and characterization of unsubstituted *iso*-diazene in a low-temperature matrix-isolation study^[7]. Their findings were supported by further studies of Teles et al.^[8] who reported *iso*-diazene to be available upon photolysis of amino isocyanates in an Argon matrix at 12 K.



However, until now no evidence for the existence of these species as *solitary* molecules in the gas phase has been reported. What is more, no experimental data for the corresponding radical cations of the H₂N₂⁺ isomers are available except for the ionization energy of *cis*- and *trans*-diazene obtained from appearance energy measurements^[9] using hydrazine as precursor, and photoelectron-spectroscopic studies^[10] of the neutral precursor molecules. The H₂N₂⁺ radical cations have been shown to be of considerable interest for the understanding of chemical processes taking place in the plasma environment surrounding spacecrafts in low earth orbit. H₂N₂⁺ ions are formed in these regions upon the reaction of uncombusted hydrazine (or its methyl derivatives which are used as rocket propellants) and the most abundant ionospheric species, the O⁺ radical cation^[11].

Theoretical work, dealing with the relative energies of the H₂N₂⁺ isomers is scattered in the literature^[12–15]. The first study was published as early as 1976^[12]. Employing a 4-31 G basis set and singles- and doubles-configuration wavefunction, neutral *trans*-diazene (**1**) was predicted to be 20.3 kcal mol⁻¹ more stable than the lowest lying singlet state of *iso*-diazene (**3**). On the cationic surface the reverse situation was found, and the stability of the H₂NN⁺ radical cation **3**⁺ was estimated to be 32.5 kcal mol⁻¹ more stable than *trans*-HNNH⁺ (**1**⁺). The same system was examined by Nguyen, Hegarty and Brint^[3] by using the semi-empirical MNDO method, and the authors, in contrast to the calculations by Baird and Wernette, predicted *trans*-HNNH⁺ to be the most stable cation lying 4.6 kcal mol⁻¹ and 4.9 kcal mol⁻¹ below the corresponding *cis*- and *iso*-diazene cations, respectively.

More recently, Pople and Curtiss^[15] have reexamined the energy of the neutral as well as the cationic H₂N₂ minima and related compounds by using the GAUSSIAN-2 (G2) theory. According to their calculations, *trans*-diazene is the most stable isomer on both the cationic as well as the neutral surface. The *trans*-HNNH⁺ cation (**1**⁺) was predicted to lie 6.2 kcal mol⁻¹ below the *cis*-isomer **2**⁺ and 3.5 kcal mol⁻¹ below the *iso*-diazene radical cation H₂NN⁺. On the corresponding neutral surface *cis*-diazene (**2**) was found to be 5.0 kcal mol⁻¹ less stable than the *trans* isomer **1**. Neutral *iso*-diazene **3** was shown to be energetically less favored by 24.1 kcal mol⁻¹ with respect to the global minimum **1**.

As we have recently demonstrated in a number of cases, the combined applications of G1- and G2-energy calculations^[16] with the technique of neutralization-reionization mass spectrometry (NRMS)^[17] offers a unique tool for the characterization of elusive solitary molecules in the gas phase. In addition the NRMS method can also provide valuable information on the structure (i.e. connectivities) of the corresponding ionic precursor molecules.

In the present study we will report the first gas-phase characterization of the neutral as well as the cationic *iso*-diazene species. The connectivities of the species were established by means of collisional activation (CA) and neutralization-reionization (NR) experiments. To support our conclusions, the diazene radical cation HNNH⁺ and its neutral analogue were studied by the same experimental techniques.

To supplement these experimental findings ab-initio MO calculations were performed by using the framework of the

G2 theory^[18]. In addition to the already known minima calculated by Curtiss and Pople^[15] we have investigated the transition structures (TS) for the possible unimolecular rearrangements and H[•] atom losses, that were found to be crucial for the interpretation of the mass spectra, on both the neutral and cationic energy surfaces, respectively.

II. Experimental Details

The collision experiments were performed on a large-scale four-sector tandem mass spectrometer having a *BEBE* configuration (*B* stands for magnetic and *E* for electrostatic sector). The design, properties and operation of the machine have been described in detail elsewhere^[19]. The corresponding H₂NN⁺⁺ as well as the D₂NN⁺⁺ cations were generated by electron bombardment (EI-source conditions: electron energy 30 eV; ion-trap current 100 μA; acceleration voltage 8 kV) of *N*-aminophthalimide or its *N,N*-deuterated isotopomer. This isotopomer was prepared by repeatedly dissolving undeuterated *N*-aminophthalimide in D₂O and removing the water after 3–4 h in vacuo; the sample was found to be sufficiently deuterated after this process had been repeated for three times. The HNNH⁺⁺ ions were produced from electron-impact ionization of hydrazine sulfate.

The ions of interest were mass-selected by means of *B*(1)*E*(1) at a resolution of $m/\Delta m = 3000$ (10% valley definition) and subjected to further collision experiments in the third field-free region of the mass spectrometer.

In the CA experiments the 8-keV ions were allowed to collide with helium [80% transmission (*T*) of the original ion beam, thus ensuring almost single collision conditions]^[20] in the second part of a differentially pumped tandem-collision cell. In the NRMS experiments the ions were neutralized in the first cell by allowing them to collide with xenon (80% *T*). Ions that did not undergo neutralization were deflected from the beam of neutral molecules by a voltage (1000 V) applied to a deflector electrode situated between the collision cells. In the second cell the beam of neutral molecules was reionized by allowing the neutrals to collide with oxygen (80% *T*). In all experiments the thus created ions were recorded by scanning *B*(2). The minimal lifetime *t* (derived from the transit time of the neutrals from the first to the second collision cell) is of the order of 4 μs. To improve the signal-to-noise-ratio 20–30 scans were accumulated and on-line-processed by means of the AMD Intetra data system.

III. Computational Details

Ab-initio molecular-orbital calculations were carried out by using the GAUSSIAN 92^[21a] program package and applying a slightly modified G2^[15,16,21b] procedure. Geometries were optimized at the MP2/6-31G(d) level and total energies obtained are *effectively* of QCISD(T)/6-311 + G(3df,2p) quality, assuming the validity of Pople's additivity approximations^[21b]. For details on Pople's G2 theory the reader is referred to the literature^[5,16,18,21]. This method has been shown to predict experimental thermochemical data with an average deviation of 1–2 kcal mol⁻¹^[15] and has been applied successfully to numerous systems of gas-phase chemistry^[15,16,18,21]. All calculations were performed on a cluster of IBM RISC RS/6000 workstations. In one case additional complete active-space self-consistent field (CASSCF)^[22] calculations using a 6-31G(d) basis set have been performed by employing the program package GAMESS^[23].

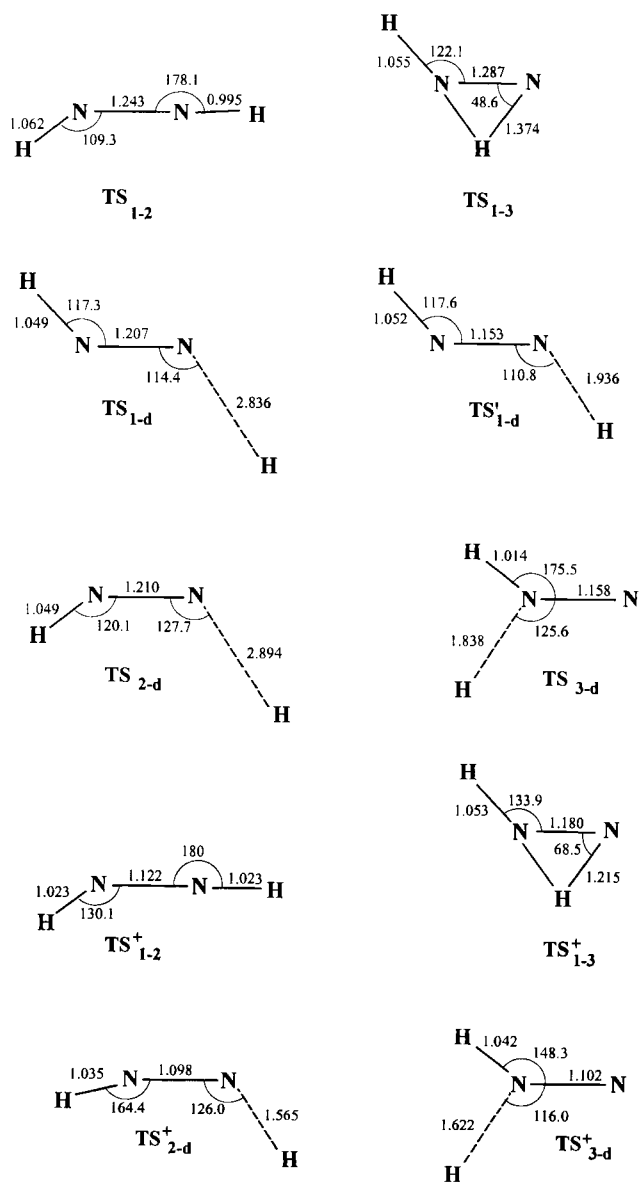
IV. Theoretical Results

The equilibrium structures and G2 energies of neutral and cationic *trans*- (**1** and **1**⁺), *cis*- (**2** and **2**⁺) and *iso*-diazene

(**3** and **3**⁺) have been taken from Pople and Curtiss' recent G2 study^[15] and are not reiterated here. The main thrust of the present calculations is to support and rationalize the experimental findings that two distinct [H₂N₂] species exist for the neutral as well as for the cationic case. Thus, in this section we will focus on the determination of transition structures and barrier heights related to intramolecular rearrangements, in particular for the interconversion of *trans*- or *cis*-diazene into *iso*-diazene, and dissociation reactions by hydrogen atom loss that were not investigated by Pople and Curtiss^[15].

However, part of the neutral [H₂N₂] surface formed the subject of a CASSCF study^[13]. The optimized geometries of the transition structures for rearrangements, obtained by distributing 8 electrons in 8 orbitals and employing a DZP one-particle basis set, are very similar to the saddle-point

Scheme 1. Geometrical data of the transition structures optimized at the MP2/6-31G(d) level of theory (the related minima are given in ref.^[15]; bond lengths [Å] and bond angles [°])



structures obtained in our MP2/6-31G*(d) optimizations (TS₁₋₂, TS₁₋₃) (Scheme 1). The barrier heights are overestimated by some 10–15 kcal/mol in the CASSCF scheme as compared to the G2 level. This is not unexpected, since, unlike the CASSCF results, the G2 calculations account for a large fraction of the dynamical electron correlation which typically reduces the activation barriers of intramolecular rearrangements.

In contrast, there are major discrepancies between the two sets of data for the homolytic N–H bond dissociation of **1** and **2** to generate HN₂ + H[•]. While Jørgen et al.^[14] did not find any saddle point for these reactions, genuine transition structures with one and only one negative eigenvalue and with a very large N–H distance of 2.836 Å (TS_{1-d}) and 2.894 Å (TS_{2-d}) are located at MG2/6-31G(d). However, their final G2 energies are lower than the sum energies of the fragments. An analysis of the RHF wavefunction, upon which the RMP2 treatment is based, indicated a substantial RHF/UHF instability^[24]. Upon reoptimization of the saddle point for the dissociation of **1** by using an unrestricted wavefunction, the UMP2 calculations again generate a transition structure, but with a considerably smaller N–H bond distance of 1.93 Å (TS'_{1-d}). The large $\langle S^2 \rangle$ expectation value of 1.052 (instead of the correct value of $\langle S^2 \rangle = 0$) indicates a large spin contamination of the wavefunction. Also for this transition structure the final G2 energy is lower than the energy of the homolytic bond cleavage products. All these inconsistencies point to a breakdown of the theoretical approach (RMP2(Full)/6-31G(d,p)) caused by the inadequate description of the homolytic bond rupture at the one-determinant level. To elucidate whether the H[•] loss saddle points are indeed artifacts of the method, we performed a set of full-valence (i.e. 12 electrons in 10 orbitals) CASSCF/6-31G(d) calculations monitoring the energy as a function of the N–H bond distance (all other parameters were fully optimized at each point of the scan). As shown in Figure 1, no saddle point could be located; rather, the energy rises steadily from the reactant molecule **1** to the products

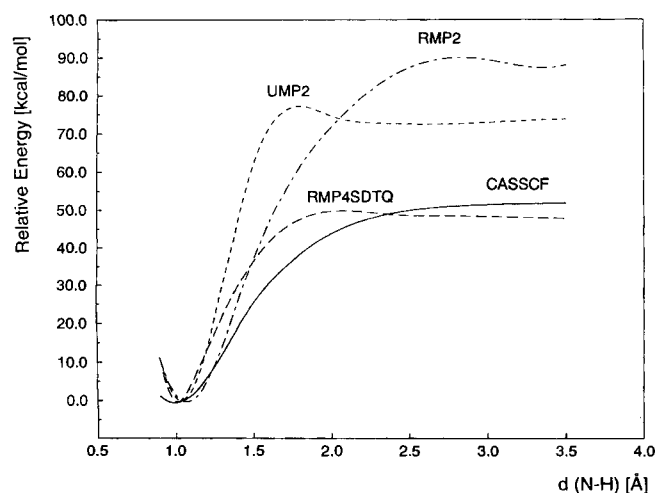


Figure 1. Potential energy curves (scanning the N–H distance) for the H[•] loss channel from **1** at various levels of theory; all other geometrical parameters of the incipient (N₂H[•]) fragment were completely optimized

HN₂ + H[•]. The results of the MP4SDTQ/6-311G* calculations based on the restricted wavefunction are close to the CASSCF energy profile. However, the MP4 calculations also reveal a local maximum of the energy profile along the N–H cleavage reaction coordinate. We have not performed a complete G2 energy scan, but it can be expected from the few G2 calculated points that the H[•] loss is a barrierless process at this level, too.

Structural data of all transition structures are given in Scheme 1. The potential energy surfaces are shown in Figures 2 and 3. In contrast to the H[•] elimination from *cis*-

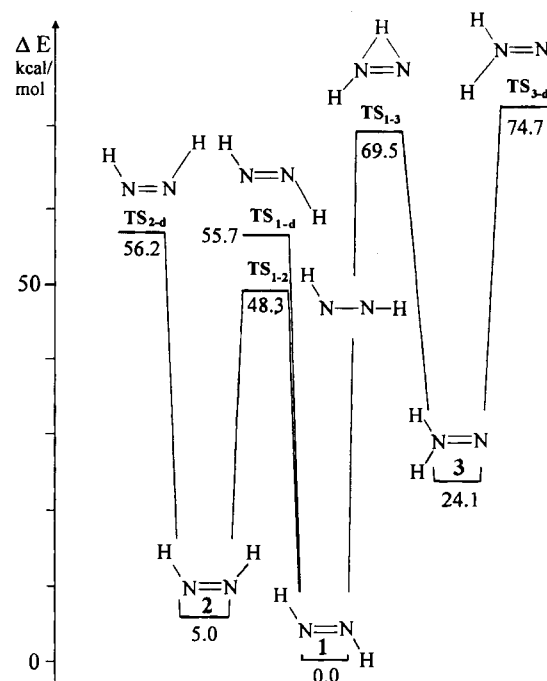


Figure 2. Potential energy surface of neutral H₂N₂ as calculated at the G2 level of theory; relative stabilities (ΔE [kcal/mol]) are related to the most stable isomer **1**

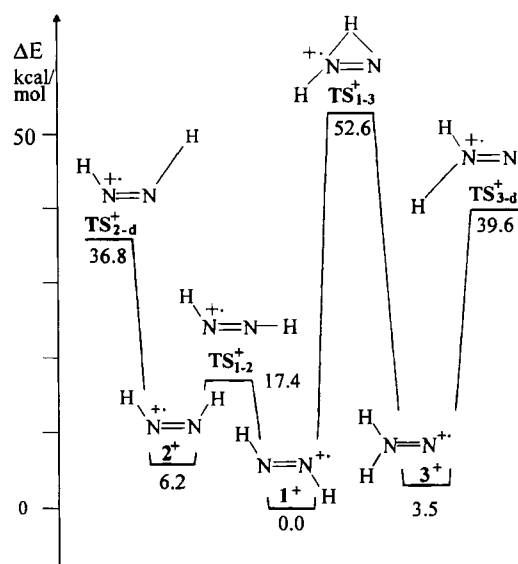


Figure 3. Potential energy surface of H₂N₂^{+•} as calculated at the G2 level of theory; relative stabilities (ΔE [kcal/mol]) are related to the most stable isomer **1**⁺

and *trans*-diazene for which *no* real transition states can be located as discussed above, the H[•] loss from *iso*-diazene (3) proceeds via a genuine transition state, i.e. TS_{3-d}. The G2 energy for this transition structure is 7.3 kcal/mol *higher* in energy than the separated HNN[•] and H[•] products, and the geometrical parameters are very similar to the previously reported transition structure^[14]. We believe that TS_{2-d} is indeed a "true" transition structure.

Due to the open-shell character of the N₂H₂⁺ species no problems concerning the G2 calculations, neither with the electronic state nor the wavefunction are expected for the cationic dublet surface (Figure 3). Both transition structures for the H[•] elimination can be characterized by similar N–H distances for the leaving hydrogen radical ($d_{\text{N-H}} = 1.565 \text{ \AA}$ for TS_{2-d} and 1.622 Å for TS_{3-d}). Due to some symmetry-breaking problems the transition structure (TS_{1-d}) for the H[•] loss of the *trans*-diazene cation could not be located.

V. Mass-Spectrometric Results

The experimentally generated H₂NN⁺ ions were subjected to a collisional activation (CA) experiment, and the resulting CA mass spectrum is shown in Figure 4a.

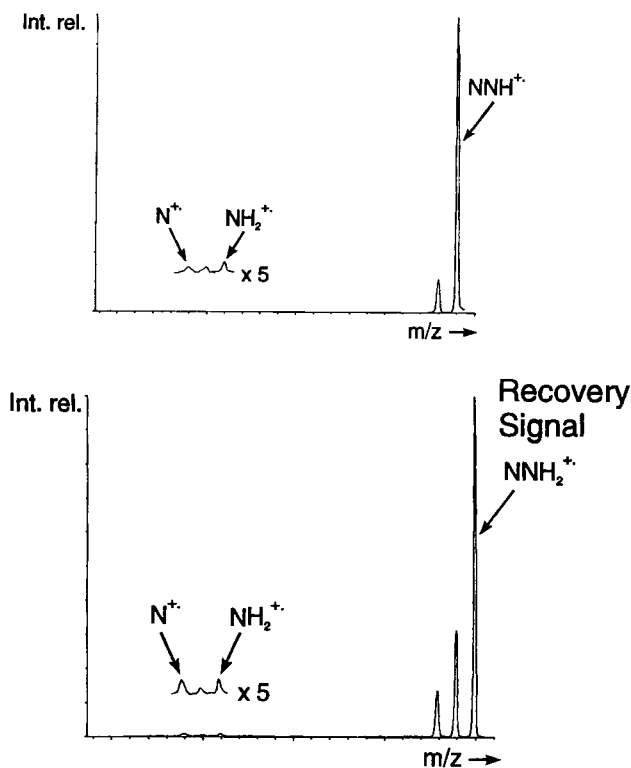


Figure 4. a) Collisional activation mass spectrum of H₂NN⁺ (collision gas: helium, 80% T) (top); b) neutralization-reionization mass spectrum of H₂NN⁺ (collision gases: xenon, 80% T//oxygen, 80% T) (bottom)

The base peak of the spectrum corresponds to H[•] loss resulting in the formation of the HNN⁺ ion. A further hydrogen loss gives rise to N₂⁺ (m/z 28). This process can also be viewed upon as a [1,1]-H₂ elimination. The lower mass

region of the spectrum shows weak signals at m/z 16, 15 and 14. The structure-indicative NH₂⁺ signal dominates the NH_x⁺ signals ($x = 0-2$) clearly.

In order to support the view that we are dealing with the *iso*-diazene cation the ion beam was subjected to a neutralization-reionization experiment. This was brought about by two consecutive collisions in the course of which the ions first were neutralized with xenon and then reionized with oxygen.

The result of the NRMS experiment is shown in Figure 4b. The reduction of H₂NN⁺ gives rise to an intense recovery signal. This observation points to stability of the neutral H₂NN molecule as well as favorable Franck-Condon factors in the vertical electron-transfer processes^[25]. The two signals at m/z 29 and 28 represent the H[•] and H₂ losses. At m/z 16 the structure-indicative NH₂⁺ signal appears. Furthermore, a much weaker signal for the NH⁺ ions can be seen, whereas the N⁺ ions at m/z 14 appear stronger again.

In order to further assess the structure of the ions the dideuterated *iso*-diazene was generated from the corresponding *N*(dideuterio-amino)phthalimide. The collision spectra of D₂NN⁺, given in Figure 5a is dominated by the N₂D⁺ signal.

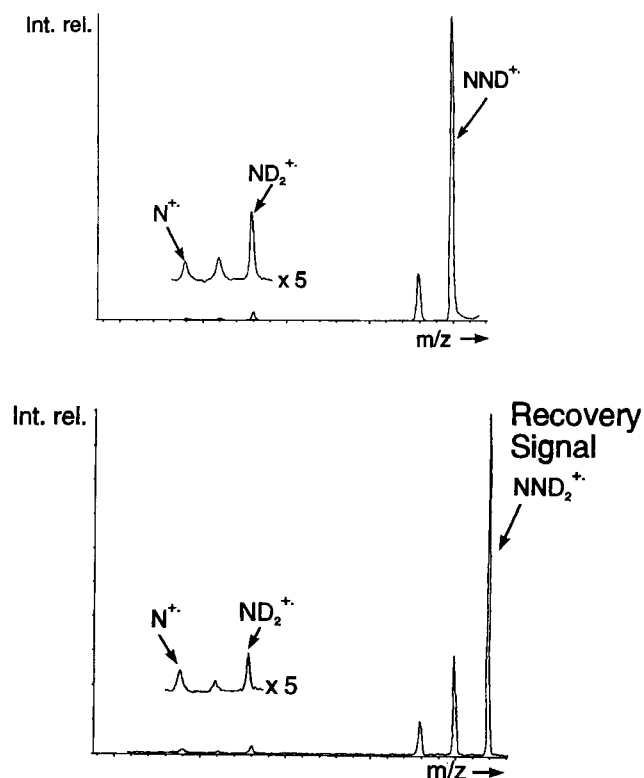


Figure 5. a) Collisional activation mass spectrum of D₂NN⁺ (collision gas: helium, 80% T) (top); b) neutralization-reionization mass spectrum of D₂NN⁺ (collision gases: xenon, 80% T//oxygen 80% T) (bottom)

Further signals for the structure-indicative ND₂⁺ (m/z 18) cation as well as the ND⁺ and N⁺ cations are observed. This ion was subsequently submitted to an NRMS experi-

ment (Figure 5b). The survivor signal forms the base peak in the spectrum, followed in intensity by the D⁺ and D₂ loss channels. The structure-indicative mass region shows the ND₂⁺ ion as the strongest signal, but also fragmentation of the ion to ND⁺ and N⁺ can be seen.

Formation of the diazene radical cation from hydrazine sulfate under EI conditions was attempted. Upon collision with helium (CA spectra given in Figure 6a) this ion was found to fragment into N₂H⁺ and N₂⁺ predominantly.

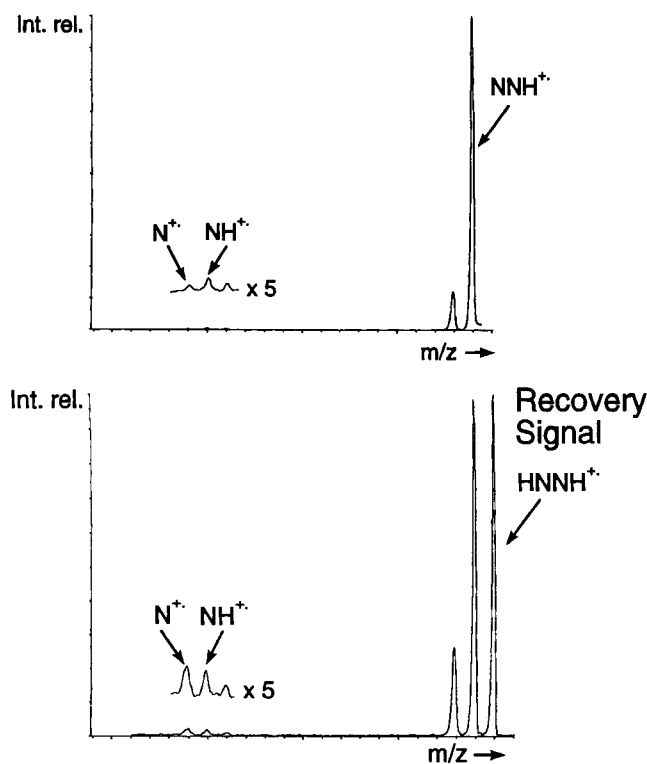


Figure 6. a) Collisional activation mass spectrum of HNNH⁺• (collision gas: helium, 80% T) (top); b) neutralization-reionization mass spectrum of HNNH⁺• (collision gases: xenon, 80% T//oxygen, 80% T) (bottom)

In the structure-indicative region weak signals for NH₂⁺ and N⁺ are observed, and the NH⁺ cation forms the dominant fragment. In the NR experiment (Figure 6b) HNNH⁺• was found to give a recovery signal at *m/z* 30. Interestingly, the HNN⁺ ion corresponding to the H[•] loss was found to be of comparable intensity. Also the fragments that require the breaking of the N–N bond can be detected. In this lower part of the spectrum the NH⁺ and N⁺ signals are, again, the dominant fragments.

VI. Discussion

According to the G2 calculations the neutral as well as the cation *iso*-diazenes are separated from the corresponding *trans*-diazenes by substantial barriers (45.1 kcal mol⁻¹ and 49.1 kcal mol⁻¹ for the neutral and cationic surface, respectively). Thus, the *iso*-diazene and the diazene connectivities should be distinguishable in the collision experiments. The

observed structure-indicative fragments in both the CA as well as the NR spectra of 3⁺ at *m/z* 16 (NH₂⁺) and *m/z* 18 (ND₂⁺) for the deuterated *iso*-diazene confirm this prediction. With regard to the stereoisomers 1 and 2, a differentiation based on the collision mass spectra should be rather difficult if not impossible, as the expected fragments are identical. However, this latter aspect did not form the purpose of our study.

The strong recovery signals for the NNH₂⁺• and NND₂⁺• ions give evidence that *iso*-diazene (and, of course, its isotopomer) are stable species in the gas phase. The fact that the HNNH⁺• ion, which was examined in order to make a meaningful comparison with the obtained data for 3⁺, gives rise to comparatively small but noticeable NH₂⁺• fragments points towards a considerable contribution of NNH₂⁺• to the ion beam of the HNNH⁺•. All attempts to generate pure HNNH⁺• cations from other precursor molecules failed. Obviously, electron-impact ionization of hydrazines produces H₂N₂⁺• cations that can either result from a [1,1]- or a [1,2]-H₂ elimination. Even though these isomeric "impurities" were not avoidable, the differences in the fragmentation pattern of the species are obvious. Not only the notable differences in the CA and NRMS fragmentation pattern but also the remarkably less intense recovery signal for the HNNH⁺• species point to the observation of two different isomers. Thus, Franck-Condon factors for the electron-transfer processes, in line with the computed geometry differences^[15] between the neutral and cationic molecules, which are significantly larger for 1/1⁺ and 2/2⁺ than for 3/3⁺, seem to differ substantially. In conclusion, the information obtained from the experiments, combined with the theoretical results, strongly suggest that the cationic as well as the neutral *iso*-diazene molecule are distinct species in the gas phase, an observation that should certainly be considered in the evaluation of data concerning the ion-molecule reactions of hydrazine and related compounds in the atmosphere. These furthermore point towards the necessity of a careful analysis of information on N₂X₂⁺• cations obtained from mass spectrometric studies.

We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Gesellschaft von Freunden der Technischen Universität Berlin* for financial support. A. Fiedler is to be thanked for helpful discussions and M. Schmidt for providing the GAMESS program.

* Dedicated to Professor Werner Schroth on the occasion of his 65th birthday.

[1] [1a] L. Trombetti, *Can. J. Phys.* **1968**, *46*, 1005. — [1b] S. Hünig, R. Müller, W. Thier, *Angew. Chem.* **1965**, *77*, 368; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 271.

[2] For a review of hydrogenation with diazene, see: C. E. Miller, *J. Chem. Educ.* **1965**, *42*, 254.

[3] A. P. Sylwester, P. B. Dervan, *J. Am. Chem. Soc.* **1984**, *106*, 4648.

[4] K. Rosengren, G. C. Pimentel, *J. Chem. Phys.* **1965**, *43*, 507.

[5] A. Angeli, *Chem. Zentralbl. II* **1900**, *71*, 857.

[6] P. B. Dervan, M. E. Squillacote, P. M. Lahti, A. P. Sylwester, J. D. Roberts, *J. Am. Chem. Soc.* **1981**, *103*, 1120.

[7] A. P. Sylwester, P. B. Dervan, *J. Am. Chem. Soc.* **1984**, *106*, 4648.

[8] J. H. Teles, G. Maier, A. Hess, L. Schaad, *Chem. Ber.* **1989**, *122*, 749.

- ^[9] ^[9a] S. N. Foner, R. L. Hudson, *J. Chem. Phys.* **1958**, *29*, 442. — ^[9b] D. C. Frost, S. T. Lee, C. A. McDowell, N. P. C. Westwood, *J. Chem. Phys.* **1976**, *64*, 4719.
- ^[10] B. Ruscic, J. Berkowitz, *J. Chem. Phys.* **1991**, *95*, 4378.
- ^[11] J. A. Gardner, R. A. Dressler, R. H. Salter, E. Murad, *J. Phys. Chem.* **1992**, *96*, 4210.
- ^[12] N. C. Baird, D. A. Wernette, *Can. J. Chem.* **1977**, *55*, 350.
- ^[13] M. T. Nguyen, A. F. Hegarty, P. Brint, *J. Chem. Soc., Dalton Trans.* **1985**, 1915.
- ^[14] H. J. Jørgen, A. Jensen, P. Jørgensen, T. Helgaker, *J. Am. Chem. Soc.* **1987**, *107*, 2859.
- ^[15] J. A. Pople, L. A. Curtiss, *J. Chem. Phys.* **1991**, *95*, 4385.
- ^[16] ^[16a] F. Grandinetti, J. Hrušák, D. Schröder, S. Karrass, H. Schwarz, *J. Am. Chem. Soc.* **1992**, *114*, 2806. — ^[16b] F. Grandinetti, J. Hrušák, D. Schröder, H. Schwarz, *J. Phys. Chem.* **1992**, *96*, 2100. — ^[16c] N. Goldberg, M. Iraqi, J. Hrušák, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, 267. — ^[16d] J. Hrušák, H. Schwarz, *J. Phys. Chem.* **1993**, *97*, 4659. — ^[16e] F. Grandinetti, J. Hrušák, H. Schwarz, *Chem. Phys. Lett.* **1993**, *204*, 53. — ^[16f] N. Goldberg, M. Iraqi, J. Hrušák, H. Schwarz, *J. Phys. Chem.*, in press. — For excellent review articles on the application of G(1)/G(2) calculations for the study of solitary molecules in the gas phase, see: ^[16g] L. Radom, *Org. Mass Spectrom.* **1991**, *26*, 359. — ^[16h] L. Radom, *Int. J. Mass Spectrom. Ion Processes* **1992**, *118/119*, 339.
- ^[17] ^[17a] J. K. Terlouw, P. C. Burgers, B. L. M. van Baar, T. Weiske, H. Schwarz, *Chimia* **1986**, *40*, 357. — ^[17b] C. Wesdemiotis, F. W. McLafferty, *Chem. Rev.* **1987**, *87*, 485. — ^[17c] J. K. Terlouw, H. Schwarz, *Angew. Chem.* **1987**, *99*, 829; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 805. — ^[17d] H. Schwarz, *Pure Appl. Chem.* **1989**, *61*, 685. — ^[17e] J. L. Holmes, *Mass Spectrom. Rev.* **1989**, *8*, 513. — ^[17f] J. K. Terlouw, *Adv. Mass Spectrom.* **1989**, *11*, 984. — ^[17g] F. W. McLafferty, *Science* **1990**, *247*, 925. — ^[17h] F. W. McLafferty, *Int. J. Mass Spectrom. Ion Processes* **1992**, *118/119*, 221.
- ^[18] L. A. Curtiss, K. Raghavachari, G. W. Trucks, *J. Chem. Phys.* **1991**, *94*, 7221.
- ^[19] ^[19a] R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1990**, *107*, 369. — ^[19b] R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 5970. — ^[19c] R. Srinivas, D. K. Böhme, D. Sülzle, H. Schwarz, *J. Phys. Chem.* **1991**, *95*, 9836.
- ^[20] J. L. Holmes, *Org. Mass Spectrom.* **1985**, *20*, 169.
- ^[21] ^[21a] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, L. A. Curtiss, *J. Chem. Phys.* **1989**, *90*, 5622. — ^[21b] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, *GAUSSIAN 92*, Revision B, Gaussian Inc., Pittsburgh, PA., **1992**.
- ^[22] B. O. Roos, in *Ab initio Methods in Quantum Chemistry*, Part II (Ed.: K. P. Lawley), Wiley, New York, NY, **1987**.
- ^[23] M. W. Schmidt, K. K. Balridge, J. A. Boatz, J. H. Jensen, M. S. Gordon, K. A. Nguyen, T. L. Windus, S. T. Elbert, *QCPE Bull.* **1990**, *10*, 52.
- ^[24] For a similar case, see: T. Weiske, W. Koch, H. Schwarz, *J. Am. Chem. Soc.* **1993**, *115*, 6312.
- ^[25] ^[25a] P. Fourier, J. Appell, F. C. Fehsenfeld, J. Durup, *J. Phys. B: At. Mol. Phys.* **1972**, *5*, L 58. — ^[25b] F. C. Fehsenfeld, J. Appell, P. Fournier, J. Durup, *J. Phys. B: At. Mol. Phys.* **1973**, *6*, L 268. — ^[25c] J. C. Lorquet, B. Leyh-Nihaut and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 465.

[306/93]