Infrared Spectra and Photochemistry of Isodiazene and Its Deuterated Isotopomers

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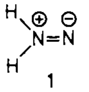
The matrix isolation of aminoisocyanate opens a new efficient route for the preparation of isodiazene (aminonitrene). Its infrared spectrum can now, with the help of ab initio calculations, be interpreted, and its photochemistry can be studied.

Infrarot-Spektren und Photochemie von Isodiazen und seinen deuterierten Isotopomeren

Die Matrixisolation von Aminoisocyanat eröffnet einen neuen ergiebigen Weg zur Darstellung von Isodiazen (Aminonitren). Damit ist es möglich geworden, nicht nur sein IR-Spektrum eindeutig festzulegen und mit Hilfe von ab-initio-Rechnungen zu interpretieren, sondern auch seine Photochemie zu untersuchen.

Isodiazene (**1**), also known as aminonitrene, is the parent compound of the family of isodiazenes and the least stable of all isomers of the formula N_2H_2. Isodiazenes were first proposed, as intermediates, by Angeli[1] at the turn of this century. Since then much work has been done on isodiazenes and their conjugate acids[2], but it took till 1978 to achieve the isolation and characterization of an isodiazene, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene, by Dervan and co-workers[3]. This long search for isodiazenes attained its climax with the isolation of **1** (1984) in an argon matrix, also by Dervan[4].



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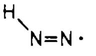

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Following the interest of the experimentalists, theoreticians also gave much attention to isodiazene[5]. The earlier work dealt mainly with the problem of establishing the nature of its ground state[6], which was shown to be a singlet by configuration interaction calculations. However, the best value for the singlet/triplet separation in **1** is only about 10.5 kcal/mol[7].

Another problem, which has been at the center of later theoretical work, concerns the reactivity of isodiazene, since similar activation energies have been predicted for its isomerization into *trans*-diazene[7,8] and for its cleavage into the diazenyl radical **2** and a hydrogen atom[9]. The predicted kinetic instability of the diazenyl radical makes this problem particularly difficult. Recent calculations by Pople[10] predict **2** to have a half-life of only 5×10^{-11} s at 30 K because of proton tunneling. This would hardly allow the experimental observation of **2** under matrix isolation conditions.

The Infrared Spectrum of Isodiazene

The H_2, HD and D_2 isotopomeric isodiazenes were produced by the 313-nm or 254-nm photolysis of the corresponding aminoisocyanates[11], isolated in an argon matrix at 12 K (matrix ratio ca. 1:6000). This method affords amounts of **1** about an order of magnitude larger than those of Dervan[4] and also gives samples with sharper bands and better optical quality. This largely compensates for the extra experimental effort of preparing the isocyanates.

Curiously, although Dervan[4] reports the spectrum of deuterated samples of **1**, he mentions only the dideuterated isomer but makes no reference to the monodeuterated **[D$_1$]1**, and he makes no vibrational assignments other than the N=N stretch. We found that, as correctly predicted by Jacox[12], the band at 1863 cm^{-1} does not belong to **1** as proposed by Dervan, but to the formyl radical, $H\dot{C}O$. All this prompted us to reexamine the infrared spectrum of **1** and of its deuterated counterparts.

For this purpose, spectra of samples containing about 0, 50, and 90% of deuterium were measured. This allowed us to distinguish bands of **[D$_1$]1** from those of **[D$_2$]1**. The observed spectra and the assignments, made by comparison with theoretical (MP2/6-31G**) spectra, are shown in Tables 1–3 and also in Figures 1 and 2.

Table 1. Observed and calculated IR spectra for H_2NN (**[H$_2$]1**)

Vibration		Symmetry	Observed $\tilde{\nu}[cm^{-1}]$	Observed Rel. Int.	Calculated $\tilde{\nu}[cm^{-1}]$	Calculated Rel. Int.
1	$\nu^{s}_{NH_2}$	A_1	2862.0	0.75	3221	0.729
2	δ_{NH_2}	A_1	1644.7	0.021	1784	0.025
3	ν_{NN}	A_1	1574.2	0.31	1666	0.267
4	$\nu^{as}_{NH_2}$	B_1	2804.6	0.33	3181	0.507
5	ϱ_{NH_2}	B_1	1287.5	0.008	1364	0.050
6	γ	B_2	1002.7	1.00	1059	1.000
6+6		A_1	2012.3	0.014		

As can be seen from Figures 1 and 2, there is good agreement between predicted and observed spectra of **1** and **[D$_2$]1**. It is interesting to note that the overtone 2γ in **1** appears at a frequency that is more than twice the frequency

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Table 2. Observed and calculated IR spectra for HDNN (**[D$_1$]1**)

Vibration		Symmetry	Observed $\tilde{\nu}$[cm^{-1}]	Observed Rel. Int.	Calculated $\tilde{\nu}$[cm^{-1}]	Calculated Rel. Int.
1	ν_{NH}	A'			3202	0.024
2	ν_{ND}	A'			2333	1.000
3	ν_{NN}	A'	1587.2	0.18	1684	0.225
4	δ_{NHD}	A'	1507.6[a] 1498.9[a]	0.16 0.17	1612	0.162
5	ϱ_{NHD}	A'			1127	0.007
6	γ	A''	913.5[a] 899.5[a]	0.39 0.61	956	1.000

[a] Splitting caused by complexation with CO.

Table 3. Observed and calculated IR spectra for D_2NN (**[D$_2$]1**)

Vibration		Symmetry	Observed $\tilde{\nu}$[cm^{-1}]	Observed Rel. Int.	Calculated $\tilde{\nu}$[cm^{-1}]	Calculated Rel. Int.
1	$\nu^{s}_{ND_2}$	A_1	2140.2	1.0	2392	1.000
2	ν_{NH}	A_1	1599.0	0.11	1672	0.572
3	δ_{ND_2}	A_1			1285	0.002
4	$\nu^{as}_{ND_2}$	B_1	2107.0	0.62	2276	0.674
5	ϱ_{ND_2}	B_1			1066	0.007
6	γ	B_2	793.5	0.52	840	0.922
6+6		A_1	1570.8	0.07		

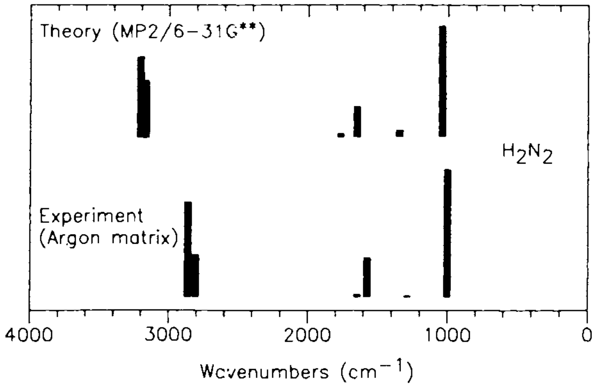


Figure 1. Observed and calculated IR spectra for **[H$_2$]1**

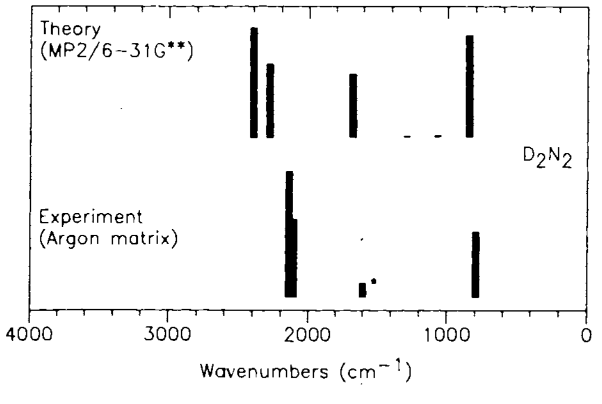


Figure 2. Observed and calculated IR spectra for **[D$_2$]1**

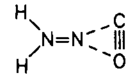
of the fundamental. This overtone is quite intense for **[D$_2$]1** because of Fermi resonance with the N=N stretch, which in turn is found to be weaker than predicted.

The experimental frequency and intensity given in Table 3 for $\nu^{s}_{ND_2}$ have a much larger uncertainty than the values given for other bands since it is severely overlapped by the band of CO. Only in a difference spectrum before and after photolysis of a sample of **[D$_2$]1**, which has already been photolyzed until it no longer contains aminoisocyanate, can it be recognized that the observed absorption cannot be due only to CO.

For **[D$_1$]1**, which has only C_s symmetry, while **1** and **[D$_2$]1** have C_{2v} symmetry, the δ_{NHD} and γ fundamentals appear as doublets of peaks with comparable intensities. These doublets retain their original shape on annealing the matrix to 30 K for 15 minutes, meaning they are not caused by a matrix effect or by quantized rotation. The splitting in these doublets depends on the matrix material. It is smaller in nitrogen than in argon and disappears almost completely in carbon monoxide (Table 4). In view of these data it must be admitted that the splittings observed for **[D$_1$]1** are due to complexation with carbon monoxide, which is present as a byproduct in the photolysis of aminoisocyanate. The incompleteness of the IR spectrum of **[D$_1$]1** does not allow the definite establishment of a structure for this complex, but **3** and **4** seem reasonable and are not contradicted by the observed spectrum.

Table 4. Frequencies of the δ_{NHD} and γ fundamentals for **[D$_1$]1** in several matrices [cm^{-1}]

Matrix	δ_{NHD}	γ
Ar	1507.6 1498.9	913.5 899.5
N_2	1505.8 1500.8	921.6 912.4
CO	1495.5	923.9 921.2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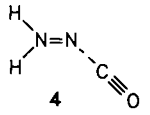
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The Ultraviolet Spectrum of Isodiazene

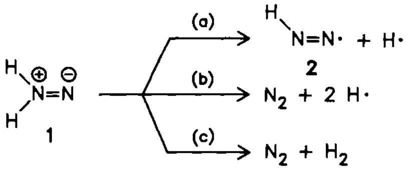
To understand the photochemistry of isodiazene, some preliminary comments about its ultraviolet spectrum and the nature of the excited states are necessary. Besides the low-lying triplet state mentioned before (the T_1 state with $^3A_2$ symmetry), **1** is predicted[6] to have two other excited states, both singlets, with energies less than the ionization potential. These are the S_1 state, with symmetry $^1A_2$, 2.22 eV above S_0, and the S_2 state with symmetry $^1A_1$, 7.08 eV above S_0. The ground state S_0 has the symmetry $^1A_1$ in the point group C_{2v}. Although only **1** and **[D$_2$]1** have C_{2v} symmetry, **[D$_1$]1** can be considered to have a quasi-C_{2v} symmetry since substitution of hydrogen by deuterium has only a negligible effect on the electronic structure. Further, the excited states that are important for the following discussion, S_1 and S_2, involve $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions and should be particularly insensitive to the exchange of hydrogen by deuterium. According to this, isodiazene should have two transitions in the near ultraviolet and visible spectra: a weak, symmetry-forbidden $S_1(^1A_2) \leftarrow S_0(^1A_1)$ at 2.22 eV or 558 nm, and a strong, symmetry-allowed $S_2(^1A_1) \leftarrow S_0(^1A_1)$ at 7.08 eV or 175 nm.

Dervan[4)] reports for isodiazene a structured absorption between 500 and 720 nm, with resolved vibrational structure due to the N–N stretch in S_1, in a 2-methyltetrahydrofuran glass at 80 K. In our matrix experiments with typical concentrations of 2×10^{-4} mol of **1**/mol of Ar and path lengths of less than 1 mm, this band was too weak to be observed, but its existence could be deduced from the fact that **1** is photoreactive when irradiated through an OG 570 filter ($\lambda > 570$ nm). Indeed, for a substituted isodiazene, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene, a molar extinction of only 18 ± 3 was reported[13)], which is a reasonable value for a symmetry-forbidden band. The second transition has never been directly measured, although this should be possible, but once again its existence can be shown indirectly. Irradiation of **1** at 313 or 366 nm gives no reaction although this should be energetically possible, but irradiation at 254 nm does, meaning that the onset of the absorption is somewhere between 313 and 254 nm. This is somewhat less than predicted, but it must be taken into account that large errors are involved in the calculation of the energy of electronically excited states.

The Photochemistry of Isodiazene

Dervan[4)] reports N_2 and H_2 to be the only products from the photolysis of isodiazene. In this work we were able to demonstrate, through the formation of the formly radical, that, at least when the irradiation is carried out at 254 nm, hydrogen atoms are produced. The situation is not so clear-cut when light of wavelengths > 570 nm is used. At these wavelengths the formyl radical splits back to carbon monoxide and a hydrogen atom and cannot be used as a probe for the formation of atomic hydrogen in the photolysis of **1**.

The cleavage of isodiazene can in principle occur by three different mechanisms, for which we will only discuss the first step. Mechanism (a) demands as the first step the cleavage into the diazenyl radical and a hydrogen atom, mechanism (b) involves the direct cleavage of **1** into molecular nitrogen and two hydrogen atoms, and finally mechanism (c) postulates the concerted cleavage of **1** into molecular nitrogen and molecular hydrogen.



Due to symmetry considerations, none of these mechanisms is allowed from the S_1, but all are allowed from the S_0 or S_2 state, a situation which is analogous to that which is found for formaldehyde[14)] (formaldehyde and **1** are isoelectronic). It is also known from the work on substituted isodiazenes that both, the rate of intersystem crossing[15)] and the rate of fluorescence[16)], are much smaller than the rate of internal conversion. This means that excitation of **1** to the S_1 state (with light of $\lambda > 570$ nm) will give rise to a "hot ground state" reaction. In such a "thermal reaction" the determination of deuterium isotope effects in the photodecomposition of **1** could provide some insight into the reaction mechanism. The measured isotope effects are collected in Table 5.

Table 5. Isotope effects measured in the photolysis of deuterium-substituted isodiazenes at two wavelengths[17)]

	$S_2 \leftarrow S_0$ $\lambda = 254$ nm	$S_1 \leftarrow S_0$ $\lambda > 570$ nm
$k(H_2NN)/k(HDNN)$	1.0 ± 0.2	1.4 ± 0.2
$k(H_2NN)/k(D_2NN)$	1.8 ± 0.3	4.2 ± 0.8

The isotope effects which are measured when S_1 is excited are not compatible with mechanism (b) since in this case $k(H_2NN)/k(HDNN)$ should be about half of $k(H_2NN)/k(D_2NN)$. On the other hand, since mechanism (a) is still more endothermic than (b) by about 14 kcal/mol[10)], it is not very likely that mechanism (a) will be operating[18)]. In other words, the reaction path via S_1 is governed by internal conversion to S_0 followed by a thermal formation of molecular nitrogen and molecular hydrogen according to mechanism (c). This situation is similar to that of formaldehyde where the reaction path with the lowest activation energy is the one leading to carbon monoxide and molecular hydrogen[14)].

The situation is completely different if one excites the S_2 level, since in this case all three mechanisms (a), (b), and (c) are symmetry-allowed. It was somewhat surprising to find that **[D$_2$]1** – contrary to **[D$_1$]1** – shows quite a significant deuterium isotope effect. However, this observation does not allow any insight into the decay mechanism due to the fact that we are no longer dealing with a "hot ground state" reaction. It is nevertheless certain that either mechanism (a) or (b) will have to be operating since, when S_2 is excited, hydrogen atoms are a major reaction product.

Theoretical Vibrational Spectra

These were computed by the MP2 method using GAUSSIAN 86[19)] with the 6-31G** basis set. The structure was initially optimized with a C_{2v} symmetry constraint to give $R_{N=N} = 1.221$ Å, $R_{N-H} = 1.0371$ Å, $\measuredangle$ HNN = 124.1° and $E_{MP2} = -110.293496$ a.u. MP2 frequencies and intensities were obtained with analytical first and numerical second derivatives. Since all frequencies were found to be real, the C_{2v} structure does correspond to an energy minimum. Frequencies and intensities of the isotopomers of aminonitrene were calculated with a program written by us, which makes use of the GAUSSIAN 86 force-constant matrix and dipole-moment derivatives. Spectra in Figures 1 and 2 show intensities relative to the strongest band in each case.

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[15] Work on substituted isodiazenes[16] has shown that the role of intersystem crossing ($S_1 \rightarrow T_1$) must be negligible in comparison with the rate of cleavage, as would be expected for a molecule where the gap $S_1 \rightarrow T_1$ has about the same energy as the gap $S_1 \rightarrow S_0$.

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[17] The rate measurements were made by interrupting the photolysis at regular time intervals and measuring the integrated intensity of the vibration for the three isotopomers in the infrared spectrum. A Bruker IFS 85 FT-IR was used to take the spectra. These had a resolution of 0.5 cm^{-1}, and each was the average of 300 individual scans.

[18] The reaction enthalpies for (a), (b), and (c) were estimated (using our own MP2/6-31G** results, the data of ref.[10], and the experimental dissociation energy of H_2) to be: (a) + 42 kcal/mol, (b) + 28 kcal/mol, (c) − 78 kcal/mol. S_1 lies about 40 kcal/mol above S_0.

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