A Theoretical Study of Thionitrosyl Azide ($N_3-N=S$), Thiazyl Azide ($N_3-S\equiv N$) and Nitrosyl Azide ($N_3-N=O$)

Minh Tho Nguyen*[a] and Robert Flammang[b]

Department of Chemistry, University of Leuven[a],
Celestijnenlaan 200 F, B-3001 Leuven, Belgium

Laboratory of Organic Chemistry, University of Mons-Hainaut[b],
Avenue Maistriau 19, B-7000 Mons, Belgium

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Stimulated by the recent detection of nitrosyl azide ($N_3-N=O$), we investigated the stability of the sulfur analogues thionitriosyl azide ($N_3-N=S$) and thiazyl azide ($N_3-S\equiv N$) by using ab initio MO calculations up to the QCISD(T)/6-311+G(d)//QCISD/6-311G(d) + ZPE level. Both azides have a similar energy content. While thionitrosyl azide is not stable with respect to N_2 elimination, thiazyl azide resists to this process by an energy barrier of about 110 kJ/mol. The NS and N_3 fragments resulting from homolytic cleavage lie about 100 kJ/mol above the azides. The five-membered ring is thermodynamically much more stable than both azides but kinetically unstable with respect to cheletropic decomposition yielding $N_2S + N_2$. Overall, *trans*-thiazyl azide is the most likely candidate for experimental observation of, for example, the reaction of NS^+ salts with the azide anion. IR wavenumbers of the azides were also predicted.

Since the discovery of azides in 1864, their chemistry has been attracting intense interest, owing to their widespread use as building blocks in organic and heterocyclic syntheses[1]. Nevertheless, up to now little is known about the azides containing nitrogen substituents[2]. In fact, an amino azide $(FSO_2)_2N-N_3$ has only recently been prepared[2]. While *C*-azido imines ($N_3-CR=NR_1$) are well-known compounds, their *N*-azido isomers ($RR_1C=N-N_3$) have not been prepared yet. Similarly, the acyclic pentazene forms ($N_3-N=NR$) have never been detected, whereas their cyclic pentazole isomers were prepared and characterized[3].

In 1955, nitrosyl azide ($N_3-N=O$) was shown to exist by isotopic labeling experiments[4], but it was also found to be unstable with respect to decomposition giving N_2O and N_2[5]. Subsequently, Lucien[6] attempted to identify nitrosyl azide for the first time by recording its IR spectrum at temperatures below −30 °C, but most of the assignments were not correct. Its vibrational spectrum was only recently established by Klapötke and coworkers[7] on the basis of Raman spectroscopy and ab initio molecular orbital calculations. It should be noted that nitro azide (N_3-NO_2) was also recently prepared by the same group[8].

Owing to the fact that azides and other nitrogen-containing compounds undergo unimolecular decomposition yielding molecular nitrogen with a considerable release of energy, they have in recent years attracted interest as potential environmentally friendly high-energy density materials[9]. Concerning our current interest in the chemistry of the thionitrosyl functional group ($R-N=S$)[10-12], we have asked the question whether thionitrosyl azide ($N_3-N=S$) is stable enough to be generated and characterized. As the azidyl group (N_3) often behaves as a pseudohalogen, the relative stability of the thiazyl isomer ($N_3-S\equiv N$) is also of interest. In the halogen series, a thiazyl form ($X-S\equiv N$) is consistently more stable than its thionitrosyl ($X-N=S$) counterpart.

In the present work, we have raised the question mentioned above making use of high-level ab-initio molecular orbital calculations. For the purpose of comparison, the stability of nitrosyl azide ($N_3-N=O$) was also examined. We hope that our theoretical results reported here will stimulate further experimental work to prepare these challenging compounds.

Details of Calculations

All molecular orbital calculations were carried out with the aid of a local version of the Gaussian 92 set of programs[13]. Geometry optimizations and harmonic vibrational analyses were conducted at both Hartree-Fock (HF) and second-order pertubation theory (MP2) levels with the polarized 6-31G(d) basis set. Improved geometrical parameters of the relevant stationary points were then obtained by using the quadratic configuration interaction method, the QCISD/6-31G(d) and MP2 method with the larger 6-311G(d) basis set.

Improved electronic energies were finally estimated from quadratic configuration interaction calculations including corrections for triple substitutions and an even larger basis set, QCISD(T)/6-311+G(d). For the nitrosyl azide system, calculations using the coupled-cluster method, CCSD(T), and the larger 6-311+G (3df) basis set were also performed. Vibrational wavenumbers of the azides were computed at the MP2/6-311G(d) level. Throughout this paper, bond

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lengths are given in Ångstrøms, bond angles in degrees, total energies in hartrees, and relative energies, unless stated otherwise, in kJ/mol.

Results and Discussion

Stability of Nitrosyl Azide (N_3–N=O)

The molecular structure, vibrational spectrum, and relative stability of nitrosyl azide as well as the N_4O potential energy surface were examined in two recent papers[14,15]. Accordingly, the *trans* chain of nitrosyl azide is more stable than the *cis* conformer by 3 kJ/mol; both forms are connected by a transition structure for rotation about the N–N bond, which lies 40 kJ/mol above the *trans* form. The latter turned out to be 76 and 350 kJ/mol less stable than the five-membered ring and the N_2O + N_2 fragments, respectively. Nevertheless, the ring isomer is not stable towards [3 + 2] cycloreversion giving N_2O + N_2; the corresponding energy barrier is, at most, 8 kJ/mol.

The electrocyclization connecting *cis*-nitrosyl azide and the five-membered ring could not be confirmed. Attempts to locate the transition structure (TS) for ring-chain isomerization failed, as the supermolecule tends to converge to the TS for 1,3-cycloreversion. In this context, the only thermochemical parameter which could indicate the kinetic stability of nitrosyl azide is the barrier height for N_2 elimination. Calculated values reported in previous papers[14,15] for this energy barrier are, however, not consistent, namely 100 kJ/mol obtained from MP2/6-31+G(d) + ZPE calculation in ref.[14] and 54 kJ/mol obtained from CCSD/DZP + ZPE calculations in ref.[15]. On the other hand, it was mentioned that N_2 elimination of *trans*-nitrosyl azide leads to the cyclic N_2O (C_{2v}) rather than the linear N_2O as a product[14]. This is surprising in view of the fact that the latter is much more stable than the former (>280 kJ/mol). Because nitrosyl azide will be served as a reference for the sulfur analogue, it is important to reexamine these two points. The results obtained in the present work by using different levels of theory are recorded in Figure 1 and Tables 1 and 2. As already shown in ref.[15], geometrical parameters of the N_4O species are extremely sensitive to the levels of theory employed. However, the various effects exerted on the barrier height turned out to be reasonable, the largest variation not exceeding 12 kJ/mol. It appears that the extension of the basis set and inclusion of triple substitutions in the wavefunctions tend to enlarge the barrier. Assuming a certain additivity of both effects, we could estimate a lower limit of 68 ± 10 kJ/mol for the energy barrier at an approximate QCISD(T)/6-311++G(3df,2p) + ZPE level. This value is consistent on the one hand with the CCSD value mentioned above and on the other hand with the experimental fact that nitrosyl azide can only be detected at low temperatures[6,7].

In order to establish the identity of the product of the decomposition of nitrosyl azide, namely linear versus cyclic N_2O, we calculated the corresponding intrinsic reaction coordinate (IRC) path. Starting from the TS for N_2 elimination, the geometry of the supersystem is optimized following the normal coordinate of its imaginary vibrational mode. The process ends up when both minima are reached. On the one hand, it was confirmed that the N^1–N^2–O bond angle is becoming smaller in going from nitrosyl azide to TS (from 7 to 10°) upon cleavage of the N^1–N^2 bond (Figure 1). On the other hand, IRC calculations show that when the TS is passed on the reaction coordinate, with the $N^1 \cdots N^2$ distance larger than 2 Å, the N^1–N^2–O angle widely opens, rapidly reaching a linear N=N=O structure. It can thus be concluded that N_2 elimination of *trans*-nitrosyl azide does not lead at all to cyclic N_2O, as suggested in earlier papers[14,15], but rather to linear N_2O.

Figure 1. Geometrical parameters of nitrosyl azide (NA) and the transition structure (TS) for N_2 elimination calculated at two different levels of theory: MP2/6-31G(d) and QCISD/6-31G(d) (values in parentheses)

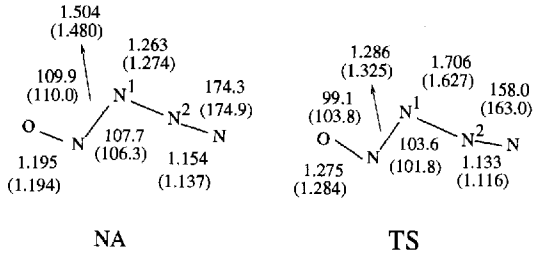


Table 1. Calculated total energies and energy barrier to decomposition of nitrosylazide using different levels of theory

Method	Geometry[b]	Nitrosyl azide	Transition structure	Energy barrier[c]
MP2(F)/6-31G(d)	MP2/6-31G(d)	-293.32542	-293.28100	108
QCISD/6-31G(d)	QCISD/6-31G(d)	-293.30541	-293.28190	53
QCISD/6-311+G(d)	„	-293.43274	-293.40828	55
QCISD(T)/6-311+G(d)	„	-293.47991	-293.45309	62
CCSD/6-311+G(d)	„	-293.42706	-293.40039	61
CCSD(T)/6-311+G(d)	„	-293.47699	-293.44906	64
QCISD/6-311+G(3df)	„	-293.59116	-293.56425	62
ZPE[a]	MP2/6-31G(d)	45	36	

[a] Zero-point energies at the indicated level and scaled by 0.95, in kJ/mol. – [b] Geometrical parameters are given in Figure 1. – [c] Including corrections for ZPE.

Table 2. Calculated harmonic vibrational wavenumbers of *trans*-nitrosyl azide; experimental fundamental Raman wavenumbers taken from ref.[7]

Mode	MP2/6-31G(d)	MP2/6-311G(d)	Expl.[b]	Description
a' ω_1	2339	2330	2207	N=N=N asym. stret.
ω_2	1595	1652	1485	N=O stret
ω_3	1180	1204	1095	N=N=N sym. stret.
ω_4	820	799	784	bend.
ω_5	615	618	566	N_3–NO bend.
ω_6	376	270	415	N_3–NO stret.
ω_7	185	174	-	bend.
a'' ω_8	559	548	484	N_3 torsion
ω_9	168	166	162	torsion

Table 2 lists the calculated and experimental vibrational wavenumbers of nitrosyl azide; these will be employed as references to derive corrected values for sulfur analogues.

Thionitrosyl Azide (N_3–N=S) and Thiazyl Azide (N_3–S≡N)

Calculated total and relative energies of the N_4S structures are summarized in Table 3, whereas their geometrical parameters will be discussed within the text. The structures

Table 3. Calculated total and relative energies of the N_4S structures[a]

Structure	MP2/6-31G(d)[b]	MP2/6-311G(d)[c]	QCISD(T)/6-311G(d)[c]	QCISD/6-31G(d)[d]	QCISD(T)6-311+G(d)[d]	ZPE[e]
Thionitrosyl	-615.94380	-615.21986	-616.06899	-615.92276	-616.08419	42
azide (**1**)	(0)	(0)	(0)	(0)	(0)	
Thiazyl	- 615.94117	-615.21724	-616.06415	-615.91888	-616.08174	41
azide (**2**)	(6)	(6)	(12)	(9)	(6)	
Cycle (**3**)	-615.00366	-616.27541	-616.12227	-615.98035	-616.13748	44
	(-155)	(-144)	(-138)	(-149)	(-137)	
N=N=S +	-616.11019	-616.38899	-616.23042	-616.08820	-616.24300	33
N_2 (**4**)	(-446)	(-453)	(-432)	(-443)	(-426)	
N=S–N +	-616.03809	-616.31430	-616.16763	-616.02687	-616.018019	28
N_2 (**5**)	(-261)	(-262)	(-279)	(-287)	(-266)	
NS + N_3 (**6**)	-615.84778	-616.12470	-616.01781	-615.89014	-616.04084	31
	(241)	(239)	(123)	(75)	(103)	
TS (**3/4**)	-615.99436	-616.26654	-616.12000	-615.97326	-616.13350	37
	(-138)	(-128)	(-139)	(-138)	(-134)	
TS (**1/4**)	-615.92275	-616.19904	-616.05901	-615.91416	-616.07378	32
	(45)	(45)	(16)	(13)	(18)	
TS (**2/5**)	-615.85000	-615.12618	-616.02408	-615.87005	-616.03452	31
	(235)	(235)	(129)	(127)	(119)	

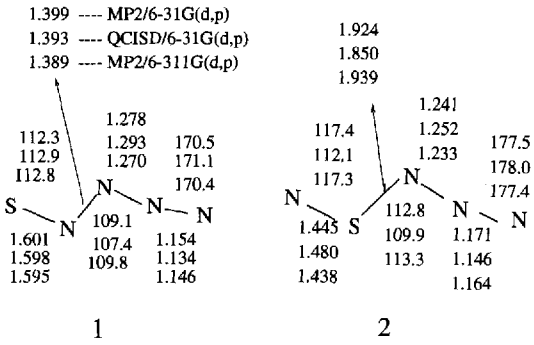
[a] Relative energies given in parentheses include ZPE corrections; MP2 calculations employ full sets of MOs; core orbitals are kept frozen in QCI calculations. – [b] Using MP2/6-31G(d) geometries. – [c] Using MP2/6-311G(d) geometries. – [d] Using QCISD/6-31G(d) geometries. – [e] Zero-point energies obtained from MP2/6-31G(d) wavenumbers and scaled by 0.95 to account for systematic overestimation.

considered include three molecules, thionitrosyl azide (**1**), thiazyl azide (**2**), the five-membered ring **3** (tetraazathiophene), and three fragments, N=N=S + N_2 (**4**), N=S=N + N_2 (**5**), and NS + N_3 (**6**) as well as various transition structures (TS) linking them. As for a notation, **X/Y** denotes a TS connecting both equilibrium structures **X** and **Y**. We note again that while the relative energies are rather sensitive to the methods employed, the energy order remains unchanged. Unless stated otherwise, the values quoted in the following refer to our best estimates obtained from QCISD(T)/6-311+G(d) calculations based on QCISD/6-31G(d) geometries and corrected for zero-point energies.

For both acyclic forms, only the *trans* conformers are given. The *cis* conformers were calculated to be less stable than the *trans* conformers by 2 kJ/mol in the case of thionitrosyl azide and by 4 kJ/mol in the case of thiazyl azide. Of the two azide forms, the thionyl **1** is slightly more stable (6 kJ/mol) than the thiazyl **2**. Such an energy oder is similar to that in the parent HN=S/HS≡N system[10], but in contrast to that in halogenated species where the thiazyl XSN isomer is markedly more stable than the thionitrosyl XNS. In fact, FSN was calculated to lie 95 kJ/mol below FNS and ClSN 53 kJ/mol below ClNS, at a similar level of theory. Geometries of the azidyl group in both forms are also different. While the N=N=N distance remains comparable, the central nitrogen in **2** seems to be displaced slightly away from the terminal nirogen; the azidyl group is also closer to linearity in **2** than in **1**. A remarkable difference between thionitrosyl azide (**1**) and nitrosyl azide concerns the N^1-N^2 distance whose value in the latter is in fact significantly larger (0.1 Å) than that in **1**.

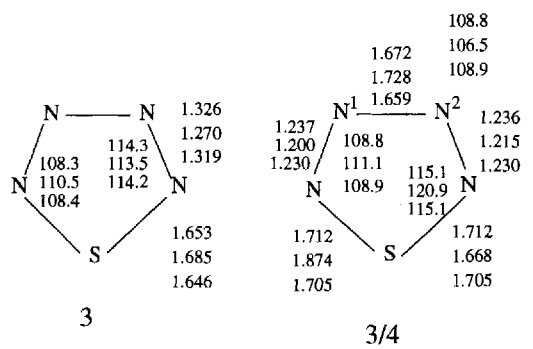
Compared with the parent HNS/HSN species, while the N=S bond length in **1** remains unchanged upon azidyl substitution [1.596 Å in HN=S at MP2/6-31G(d,p)], the S≡N bond length in **2** becomes shorter than that in HS≡N [1.494 Å at the MP2/6-31G(d,p) level[10]].

As expected, both azide forms lie higher in energy than the cyclic **3** and both fragments **4** and **5**. Compound **1** was



1 2

found to be 137 and 426 kJ/mol above **3** and **4**, respectively. Decomposition of **2** into fragments **5** is also largely an exothermic process (−272 kJ/mol). With respect to the oxygen analogues, there is an apparent destabilization of the azide form toward cyclization and fragmentation. In spite of extensive attempts, we are again not able to locate the TS for 1,5-electrocyclization connecting *cis*-thionitrosyl azide and **3**. As in the oxygen case mentioned above, the supersystem was optimized to the TS **3/4** for [3 + 2] cycloreversion of the five-membered ring **3**. Because both TS differ from each other mainly by the N^1-N^2 distance which should be shorter in the hypothetical TS **1cis/3** for cyclization.

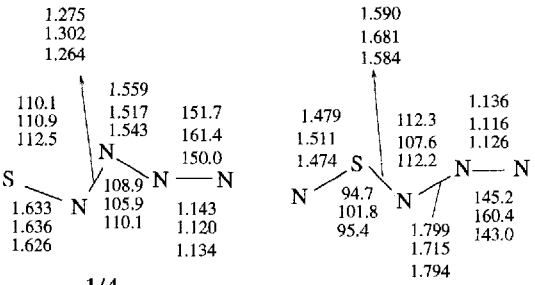


3 3/4

Because **3/4** lies much lower in energy than the latter, the supermolecule tends to go downhill reaching **3/4**. As seen

in Table 3, **3/4** lies only a few kJ/mol above **3** implying that **3** is not at all stable with respect to a cheletropic reaction.

We now turn to the stability of both azides **1** and **2** relative to direct decomposition. While they are rather resistant to simple bond cleavage giving NS + N_3 radicals, both tend to undergo readily N_2 elimination affording the neutral fragments **4** and **5**. In fact, **1** was calculated to lie 103 kJ/mol below the limit of dissociation into **6** (NS + N_3), but only 18 kJ/mol below TS **1/4** connecting it to N_2S + N_2. Separate calculations indicate that at the QCISD(T)/6-311+G(3df) level the barrier height increases slightly up to 22 kJ/mol. An energy barrier of this size suggests that it should be difficult to detect thionitrosyl azide using conventional techniques.



In contrast, thiazyl azide (**2**) appears to be substantially more stable toward N_2 elimination. As a matter of fact, the TS **2/5** is calculated to lie 113 kJ/mol above **2**. Such an energy barrier to dissociation can be accounted for by the lower stability of the NSN product whose cyclic form is 160 kJ/mol less stable than N=N=S. Intrinsic reaction coordinate (IRC) calculations confirmed that the NSN ring is the product of decomposition of **2** via **2/5**.

Attempts to locate a TS connecting **1** and **2** by a 1,2-migration of the azidyl group failed. It seems that both azides are linked together simply by the NS + N_3 fragments **6**. Thus, thiazyl azide (**2**) can be regarded as a kinetically stable and isolable species. At this stage, it seems to be useful to predict the IR spectra of the azides. For this purpose, harmonic vibrational wavenumbers were computed at the same levels of theory used for nitrosyl azide (Table 2). Knowledge of the experimental fundamentals of the latter allows us to obtain an appropriate scaling factor at each level for every normal mode. We then applied these scaling factors to the calculated values for the corresponding modes in sulfur analogues **1** and **2**. The best estimated wavenumbers were taken as the averages of the scaled values. The results are summarized in Table 4. Compared with nitrosyl azide, the asymmetric azide stretching mode represents a downward shift of 70–80 cm^{-1} in both forms **1** and **2**. The IR absorption due to this mode is consistently the most intense one. The S≡N stretching mode in **2** is associated with a higher wavenumber than that of the N=S stretching in **1**; the difference in corresponding calculated wavenumbers amounts up to 450 cm^{-1}.

Now a question of interest is: how might **1** and/or **2** be prepared? A seemingly reasonable procedure for **2** is that similar to the preparation of nitrosyl azide (equation 1). Due to the high tendency of NSCl to form the trimer $(NSCl)_3$ in solution, this reaction may be best carried out in the gas phase; the product could be then detected by, for example, mass, infrared, or photoelectron spectrometry.

$$NSCl + NaN_3 \rightarrow NS{-}N_3\,(\mathbf{2}) + NaCl \qquad (1)$$

Use of salts containing the NS^+ ion as starting materials (equation 2) is another possibility, but in this case the identity of the product could not be predicted.

$$NS^+\,(AsF_6)^- + N_3^- \rightarrow N_4S\,(\mathbf{1}\text{ or }\mathbf{2}) + AsF_6^- \qquad (2)$$

In summary, portion of the N_4S potential energy surface was investigated by using ab initio molecular orbital methods. The most chemically interesting result concerns the stability of the possible isomers. The five-membered ring compound is the more stable isomer but it is not stable with respect to a cheletropic reaction. Both acyclic azides have similar energy contents. While thionitrosyl azide (N_3–N=S) readily undergoes decomposition, thiazyl azide (N_3–S≡N) is more stable towards N_2 elimination and relatively stable towards homolytic dissociation. Therefore, the latter appears to be the most realistic N_4S target for a laboratory preparation.

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Table 4. Calculated fundamental vibrational wavenumbers [cm^{-1}] of both azides considered; IR intensities [km/mol] are given in parentheses

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8 (a'')	ω_9 (a'')
Nitrosyl azide (N_3–N=O)									
MP2/6-31G(d)	2282	1125	1083	949	604	425	176	524	132
Corrected[a]	2153	1044	1029	902	555	420	170	453	127
MP2/6-311G(d)	2267	1140	1088	954	604	430	177	503	128
	(414)	(398)	(34)	(94)	(52)	(0)	(0)	(5)	(1)
Corrected[a]	2147	1038	1030	905	553	420	170	445	125
Predicted[b]	2150	1039	1030	904	554	420	170	449	126
Description	N=N=N asym. stret.	N=N=N sym. stret.	N=S stret.	bend	bend	bend	bend	torsion	torsion
Thiazyl azide (N_3–S≡N)									
MP2/6-31G(d)	2276	1572	1261	675	406	250	112	568	87
Corrected[a]	2147	1493	1170	645	373	238	110	493	85
MP2/6-31G(d)	2256	1588	1264	659	395	237	112	562	87
	(1003)	(170)	(179)	(26)	(202)	(139)	(4)	(5)	(9)
Corrected[a]	2137	1508	1150	646	362	230	110	495	85
Predicted[b]	2144	1501	1160	645	367	234	110	494	85
Description	N=N=N asym. stret.	N≡S stret.	N=N=N stret.	bend	bend	bend	bend	torsion	torsion

[a] Corrected values using scaling factors obtained from calculated and experimental values for N_3–N=O (Table 2); when appropriate factors are not available, 0.95 was used. – [b] Average of two corrected values.

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