

Ab Initio and Density Functional Study of Thionitroso XNS and Thiazyl Isomers XSN, X = H, F, Cl, Br, OH, SH, NH₂, CH₃, CF₃, and SiF₃

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Standard enthalpies of formation of several thionitroso (XNS) and thiazyl (XSN) isomers, with X = H, F, Cl, Br, OH, SH, NH₂, CH₃, CF₃, and SiF₃, were determined using coupled cluster (CC) theory with Dunning's correlation consistent basis sets cc-pVXZ and aug-cc-pV(X+d)Z, G3 and CBS-QB3 model chemistries, as well as the B3LYP DFT method. The results support the idea that the electronegativity of the bonding atom in the substituent is correlated, albeit not perfectly, with the relative stability of the XNS over the XSN isomer. A detailed study was performed on the parent isomers HNS and HSN. They exhibit a singlet ¹A' ground state (as all the other molecules) at 5.4 and 9.4 kcal/mol below their first excited ³A'' state, respectively (CCSD(T)/CBS calculations). The enthalpies of formation of the isomers at the CCSD(T)/CBS limit, including core valence correlation, and spin-orbit splitting, are $\Delta_f H^\circ_{298}(\text{HNS}) = 55.3 \pm 1$ kcal/mol and $\Delta_f H^\circ_{298}(\text{HSN}) = 75.4 \pm 1$ kcal/mol. The activation energy at 0 K for the HNS \rightarrow HSN isomerization was determined as 63.0 and 64.2 kcal/mol at the CCSD(T)/CBS and B3LYP/6-311+G(3df,2p) levels of theory, respectively. Additional calculations were performed for the cationic isomeric pairs XNS⁺/XSN⁺ with the general result that ionization increases the relative stability of the thionitroso isomer with respect to the thiazyl isomer. In the cases of ClSN and BrSN, for which the thiazyl isomer is the most stable neutral species, the thionitroso isomer is more stable for the cations. The average deviation of the B3LYP/6-311+G(3df,2p) ionization potentials with respect to the G3 model chemistry is only 0.1 eV.

Introduction

Organic compounds containing nitrogen–sulfur multiple bonds have proved to be particularly elusive, in part because of their low thermodynamic stability.¹ Except for thionitrosoamines (R₂N–N=S) that could be prepared and isolated in pure form,² compounds featuring the N=S functionality could only be generated in situ and captured by diverse organic trapping agents^{3,4} and transition-metal fragments.⁴ Consequently, experimental information on basic thermochemical and spectroscopic properties of thionitroso compounds is rather scarce.¹ Experimental studies have demonstrated, however, that these transient species undergo a variety of reactions, particularly important in heterocycle syntheses.^{1–4} The doubly bonded N=S system can be used as a dienophile in Diels–Alder reactions⁵ and as a dipolarophile in 1,3-dipolar cycloadditions with diazoalkenes and azides.^{1–3}

Using a combination of collisional activation (CA) and neutralization–reionization (NR) mass spectrometric techniques,⁶ some of us recently have been able to generate—upon dissociative ionization of appropriate precursors—and to identify simple thionitroso compounds.^{6–9} Thus, the parent species (HN=S),⁶ its protonated form (H₂NS⁺) and corresponding radical (H₂NS),⁷ the thionitrosyl cyanide (NCNS),⁸ as well as the elusive chloro derivative (Cl–N=S)⁹ have been generated and unambiguously identified. Spectral data obtained during the experiments clearly demonstrated that these nitrogen–sulfur

molecules are stable gas-phase species. Nevertheless, besides this qualitative information on their existence, all other quantitative characterizations to date for the class of thionitroso compounds has been based on ab initio quantum chemical calculations.^{8–13}

A basic molecular property of importance to understand the characteristics of the thionitroso compounds is the standard enthalpy of formation of the parent thionitrosyl hydride (HN=S). Using perturbation theory calculations at the MP4SDTQ/6-311++G(3df,2p) level in conjunction with isodesmic reactions, one of us derived $\Delta_f H^\circ(\text{HN=S}) = 52.6 \pm 3$ kcal/mol at 0 K.⁹ In a subsequent article, Watts and Huang¹⁰ determined $\Delta_f H^\circ(\text{HN=S}) = 60.4$ kcal/mol at 0 K at the CCSD(T)/cc-pVQZ level of theory, without any attempt to extrapolate to the CBS limit. However, taking the expected errors of calculations into account, these authors¹⁰ suggested that the enthalpy of formation at 0 K of HN=S lies in the range 53–60 kcal/mol and should be closer to the lower limit if larger basis sets than cc-pVQZ are used. Although the lower limit of this error bar is close to our earlier estimate, an uncertainty of about 6⁹ or 7 kcal/mol¹⁰ on the enthalpy of formation of a triatomic molecule appears rather incongruous with regard to the performance of present day quantum chemical computations, although it is understandable because of the difficulty to converge dissociation energies with respect to basis set. Therefore, two motivations for the present work are, on one hand, to revisit the enthalpy of formation of the HN=S and HSN parent species employing coupled cluster (CC) theory and Dunning's correlation consistent

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TABLE 1: Geometrical Parameters and Harmonic Vibrational Frequencies for the HSN and HNS Isomers^a

method	basis set	HSN							HNS						
		<i>r</i> (NS)	<i>r</i> (HS)	θ (HSN)	ZPE	w1	w2	w3	<i>r</i> (NS)	<i>r</i> (HN)	θ (HNS)	ZPE	w1	w2	w3
				¹ A'							¹ A'				
CCSD(T)	cc-pVDZ	1.526	1.440	110.2	5.96	1146	2019	1008	1.614	1.042	107.0	7.89	980	3293	1232
	cc-pVTZ	1.513	1.417	110.0	6.08	1152	2083	1021	1.590	1.028	107.9	7.99	1016	3341	1227
	cc-pVQZ	1.503	1.412	110.0					1.580	1.027	107.9				
	∞ (D,T)	1.508	1.407	110.1		1155	2110	1027	1.580	1.022	108.3		1031	3361	1225
	∞ (T,Q)	1.496	1.408	110.0					1.573	1.026	107.7				
	cc-pwCVDZ,Fc ^b	1.517	1.438	111.0					1.600	1.042	107.4				
	cc-pwCVDZ,Fu ^c	1.516	1.438	111.0					1.599	1.041	107.4				
	cc-pwCVTZ,Fc ^b	1.499	1.411	110.3					1.580	1.027	108.2				
	cc-pwCVTZ,Fu ^c	1.496	1.410	110.4					1.577	1.027	108.3				
	aug-cc-pV(D+d)Z	1.524	1.425	109.9	6.02	1125	2083	1002	1.601	1.039	108.2	7.87	985	3292	1229
	aug-cc-pV(T+d)Z	1.505	1.408	109.9	6.17	1162	2126	1025	1.582	1.029	108.7	7.98	1022	3340	1222
	∞	1.497	1.401	109.9		1178	2144	1035	1.574	1.025	108.9		1038	3360	1219
B3LYP	6-311+G(3df,2p)	1.492	1.417	109.9	6.17	1191	2095	1033	1.562	1.028	110.0	8.05	1081	3328	1225
				³ A''							³ A''				
CCSD(T)	cc-pVTZ	1.660	1.351	97.1	6.05	760	2611	859	1.563	1.014	123.9	7.74	773	3550	1088
	cc-pVQZ	1.643	1.350	97.6					1.553	1.014	124.8				
	∞	1.631	1.349	98.0					1.546	1.014	125.5				
	aug-cc-pv(D+d)Z	1.677	1.360	96.8		850	2611	736	1.578	1.026	123.0	7.65	1052	3499	799
	aug-cc-pV(T+d)Z	1.646	1.350	97.4	6.06	867	2604	767	1.555	1.015	124.7	7.81	1095	3542	783
	∞	1.633	1.346	97.7		874	2601	780	1.545	1.010	125.4		1113	3560	776
B3LYP	6-311+G(3df,2p)	1.631	1.356	98.5	6.02	877	2556	779	1.549	1.015	126.5	7.72	1098	3528	787

^a Bond lengths in Å, bond angles in degrees, frequencies in cm⁻¹. ^b Frozen core calculation. ^c Full calculation.

(cc) basis sets and to extrapolate to the CBS limit, and on the other hand, to determine reliable values for a series of simple thionitroso (R–N=S) and related nitrogen–sulfur compounds using appropriate ab initio and density functional methods.

Another interesting property of the nitrogen–sulfur multiple bond is the existence of both thionitroso (R–N=S) and thiazyl (N=S–R) isomers. While halogenated compounds (R=F, Cl, Br, and I) are well-established to exist mainly in thiazyl form,^{8–13} the parent (R=H) and alkyl, aryl, amino, and other substituted derivatives are known to exist in the thionitroso form.¹ In the case of the cyano derivative, both thiazyl (N≡C–S≡N) and thionitroso (N≡C–N=S) have been found to be stable species in the gas phase.⁸ On the other hand, experimental reports showed the exclusive generation of thiazyl derivatives for species such as F₃C–SN¹⁴ and SCN–SN.¹⁵ Recent density functional studies, namely B3LYP/6-31+G(d)¹¹ and B3LYP/6-311+G(d,p),¹² have been performed, aiming to find a systematic way to correlate the enthalpy difference between the RNS and NSR isomers with properties of the substituent R. The general conclusion was that the relative energies of the isomers is indeed correlated with the electronegativity of the bonding atom. This correlation is not perfect, however, because of other effects such as resonance (in the case of X = NH₂) and size of the substituent for which the bonding atom has similar electronegativity (CH₃ against PH₂). Since in this article we report the relative enthalpies of the isomers at a higher level of theory than used previously (G3 and CBS-QB3), it is interesting to investigate whether this conclusion is upheld at these theoretical levels.

Theoretical Methods

Enthalpies of formation of the simplest HSN and HNS isomers were determined using CC theory with single and double excitations and a quasi-perturbative treatment of triple excitations, CCSD(T).¹⁶ Additionally, we employed the full CCSDT method¹⁷ to estimate the contribution of complete triple excitations. The “T” correction was calculated as the difference between CCSD(T) and CCSDT estimated enthalpies of formation, both obtained with the same basis set, namely cc-pVDZ or cc-pVTZ. The basis sets employed for all the calculations

were Dunning’s correlation consistent,¹⁸ cc-pVXZ, X = D, T, Q, 5 and the recently developed cc-pV(X+d)Z X = T, Q and aug-cc-pV(X+d)Z, X = D, T, Q, 5 basis sets.¹⁹ Correlation contributions were extrapolated with the aid of the two-parameter equation²⁰ $A = B + C/X^3$, where X = 2, 3, 4, 5 for the cc-pVXZ or aug-cc-pV(X+d)Z basis sets used. The effect of core correlation was estimated employing the cc-pwCVXZ, X = T, Q basis sets.²¹ This contribution to the enthalpy of formation was calculated as the difference between the frozen-core (FC) and full CCSD(T) results, both obtained using the same cc-pwCVXZ, X = T, Q basis set. The core valence contributions to the binding energy were extrapolated to the complete basis set limit using the cc-pwCVTZ and cc-pwCVQZ results. Zero-point energies (ZPE) were obtained at the CCSD(T)/aug-cc-pV(X+d)Z level of theory. We did not correct for anharmonic contributions to the ZPE energies but considered them in the error bars instead. Scalar relativistic effects were not estimated but were also considered in the error bars. Spin–orbit splitting has been considered only for atoms³⁸ since the ground states of HSN and HNS are closed shell singlets. The adiabatically coupled B3LYP DFT method, which includes Becke 1988 exchange²² and Lee–Yang–Parr correlation²³ potential, was used in conjunction with Pople’s 6-311+(3df,2p) basis set.³⁷ The enthalpies of formation of the remaining members in the XSN/XNS series considered, X = F, Cl, Br, OH, SH, NH₂, CH₃, CF₃, and SiF₃, were estimated using DFT and the standard model chemistries G3²⁴ and CBS-QB3.²⁵ DFT, G3, and CBS-QB3 calculations were performed using the Gaussian 98²⁶ code. Coupled cluster calculations were performed using the ACESII^{27,28} computer program.

Results and Discussion

Characterization of HSN and HNS. Geometrical parameters and vibrational frequencies of the HSN and HNS species for the ¹A' and ³A'' lowest electronic states are reported in Table 1. The singlet–triplet (S–T) energy gap is reported in Table 2. At the CCSD(T)/CBS level of theory the singlet states are predicted to be the ground states. For HSN the S–T gap is estimated as 9.4 kcal/mol, almost twice the value recommended by Watts and Huang,¹⁰ while for HNS the S–T gap obtained is

TABLE 2: Energy Gap between the $^1A'$ and the $^3A''$ States of HNS and HNS Corrected by ZPE^a

method	basis set	HNS	HSN
CCSD(T)	cc-pVTZ	6.0	4.9
	cc-pVQZ	5.6	7.2
	∞	5.3	8.9
	aug-cc-pV(T+d)Z	5.2	7.3
	aug-cc-pV(Q+d)Z	5.3	8.5
	∞	5.4	9.4
	cc-pwCVTZ, Fc ^b	5.5	7.4
CCSDT	cc-pwCVTZ, Fu ^c	5.5	7.4
	cc-pVTZ	5.6	4.5
G3		5.0	10.2
CBS-QB3		4.8	11.1
B3LYP	6-311+G(3df,2p)	-1.2	5.0

^a In kcal/mol. ^b Frozen core calculation. ^c Full calculation.

5.4 kcal/mol, this one in good agreement with the Watts–Huang¹⁰ result. The inclusion of full triple excitations with the cc-pVTZ basis set has a minor effect, lowering the S–T gap by 0.4 kcal/mol for both isomers. The CCSD(T)/cc-pVTZ and CCSDT/cc-pVTZ calculations predict that the S–T splitting is larger for the HNS isomer than for the HSN isomer. However, this situation is reversed after extrapolation to the CBS limit, and the S–T gap is larger for HSN. In fact, the basis set effect observed in the S–T splitting of HSN is much larger than that in HNS, a result connected with the higher valence state of the S atom in HSN than in HNS. This effect can be also appreciated in the extrapolated results with the two families of basis set considered. In the case of HNS, the cc-pVXZ and aug-cc-pV(X+d)Z extrapolated results are identical. For HSN instead, the S–T splitting is 0.5 kcal/mol larger when tight d functions are added. Notice also that the G3 and CBS-CB3 estimations for the S–T gap are in reasonable agreement with the CCSD(T)/CBS results. They are, respectively, 0.8 and 1.7 kcal/mol larger than the CCSD(T)/CBS S–T gap in HSN and 0.4 and 0.6 kcal/mol lower than the CCSD(T)/CBS S–T gap in HNS. It is possible that this difference may be reduced for HSN if calculations with the aug-cc-pV(5+d)Z basis set could be performed at the CCSD(T) level (this is beyond our computational possibilities).

Contrary to the ab initio results, B3LYP predicts that the triplet state is the ground state for HNS. This drawback is probably connected to the multiconfigurational ground state of this molecule. It is well-known⁶ that the UHF method predicts the same wrong ordering of the triplet and singlet state. The closed-shell singlet is unstable at both UHF and DFT levels, leading to a spin-contaminated solution lower in energy. This singlet wave function is still less stable than the triplet at the UHF level, but the order is reversed at the DFT level. A simple CAS(2,2)/6-311++G(3df,2pd) calculation is able to restore the correct ordering of the triplet and singlet states and gives an S–T gap of the same order of the CCSD(T) calculations. The situation is not completely clear at the DFT level, and it is under study in our labs.

Structure of HNS and HSN Singlet States. As expected, the nitrogen–sulfur distance is larger in HNS than in HSN by about 0.1 Å. This is due to the N sharing its electrons with H and S in HNS, whereas N shares the electrons only with sulfur in HSN. This effect translates also in a larger S–N stretching frequency in HSN than in HNS, 1178 cm⁻¹ in HSN and 1038 cm⁻¹ in HNS, both values obtained at the CCSD(T)/CBS level of theory. The angle has a similar value, about 110°, in both isomers. Finally, the SH distance is somewhat larger than in normal S–H bonds because of the shorter S–N distance in HSN, while the H–N distance is normal for this type of bond. The cc-pVXZ

optimum geometries are in reasonable agreement with those obtained with the aug-cc-pV(X+d)Z basis set. The largest discrepancy is near 0.1 Å for the SH bond in HSN. The inclusion of core correlation has a minor effect in geometries at the CCSD(T)/cc-pwCVDZ level of theory. However, enlarging the basis set up to cc-pwCVTZ shortens the sulfur nitrogen bond by 0.003 Å for HSN and HNS.

The performance of B3LYP in the calculation of the structural parameters of the isomers is remarkable. The largest deviation between B3LYP/6-311+G(3df,2p) and CCSD(T)/CBS occurs for the N–S bond in HNS, for which B3LYP/6-311+G(3df,2p) predicts $r_{S-N} = 1.562$ Å vs 1.574 Å for CCSD(T)/CBS. It is possible that CCSD(T) predicts a longer bond distance because the basis sets employed are not complete enough to describe this S–N bond. The correction of the CCSD(T)/CBS results for core correlation improves the agreement between B3LYP/6-311+G(3df,2p) and CCSD(T). The differences between CCSD(T) and B3LYP/6-311+G(3df,2p) calculations may also be related to the instability of the B3LYP solution, but this fact cannot be assessed yet.

Structure of HNS and HSN Triplet States. The sulfur nitrogen bond and the hydrogen nitrogen bond in the triplet state of HNS are shortened by 0.029 Å and 0.015 Å, respectively, at the CCSD(T)/CBS(aug-cc-pV(X+d)Z) level of theory. The reduction of the bond distances increases the electronic repulsion, increasing the H–N–S angle from 108.0° for the singlet state to 125.4° for the triplet state. The situation is quite different for HSN. The sulfur nitrogen equilibrium bond distance increases by 0.136 Å, and the sulfur hydrogen decreases in 0.055 Å. The new H–S–N bond angle is reduced to 97.7° because of the elongation of the S–N bond.

The agreement between the B3LYP/6-311+G(3df,2p) and the CCSD(T)/CBS(aug-cc-pV(X+d)Z) results is excellent, the same that was observed with the singlet states. The largest difference is observed for the sulfur hydrogen bond length, 0.01 Å.

Thermochemistry. The thermochemical data obtained at different levels for HSN and HNS isomers are collected in Tables 3 and 4, respectively. An interesting fact observed in those data is that HSN and HNS do not exhibit a very strong basis set dependence as was observed instead in other sulfur molecules, such as SO₂ and SO₃.^{19,29,30} It was essential in those molecules to include tight d functions to converge the SCF and correlation energies values to the proper limits.

The SCF contribution to $\Delta_f H^\circ_{298}$ is fully converged for both isomers with the aug-cc-pV(5+d)Z basis set. Thus, it is not necessary to extrapolate this contribution to the CBS limit. However, the SCF results are not converged for the cc-pVXZ family of basis sets. Even when using the cc-pV6Z basis set, the results are slightly worse than those obtained with the aug-cc-pV(5+d)Z basis set, showing the importance of this tight d function for converging the SCF binding energies when second-row atoms are present. At any rate, the SCF contribution to the enthalpy of formation with the cc-pVXZ family of basis sets was not extrapolated because Halkier, Helgaker, Jorgensen, Klopper, and Olsen³¹ showed that the error introduced by extrapolation is larger than that introduced by basis set incompleteness. The HF–SD difference (i.e., the effect of including the correlation energy due to single and double excitations) is the only one component for which extrapolation is important, exhibiting an increase of about 2 to 3 kcal/mol. The extrapolated singles and doubles contributions is identical with both families of basis sets for HNS and HSN. The (T) contribution (quasiperturbative calculation of correlation energy due to the triplet excitations) is almost converged within both

TABLE 3: Estimated Enthalpies of Formation of HSN at 298 K and Correlation Contributions at Different Theoretical Levels^a

basis set	$\Delta_f H^\circ_{298}$ CCSDT	$\Delta_f H^\circ_{298}$ CCSD(T)	$\Delta_f H^\circ_{298}$ CCSD	$\Delta_f H^\circ_{298}$ HF	SD	(T)	T
cc-pVDZ		113.9	121.4	199.1	-77.7	-7.5	
cc-pVTZ	92.0	91.7	100.8	186.5	-85.7	-9.1	0.3
cc-pVQZ		82.8	92.3	183.5	-91.2	-9.5	
cc-pV5Z		78.2	87.9	181.0	-93.1	-9.7	
cc-pV6Z				180.5			
aug-cc-pV(D+d)Z		99.5	105.3	182.0	-79.6	-8.1	
aug-cc-pV(T+d)Z		84.3	93.6	181.5	-87.9	-9.3	
aug-cc-pV(Q+d)Z		78.9	88.6	180.6	-92.0	-9.7	
aug-cc-pV(5+d)Z				180.4			
cc-pwCVDZ,Fc ^b		108.1					
cc-pwCVDZ,Fu ^c		107.6					
cc-pwCVTZ,Fc ^b		87.1					
cc-pwCVTZ,Fu ^c		86.4					
cc-pwCVQZ,Fc ^b		80.0					
cc-pwCVQZ,Fu ^c		79.2					
∞ -cc-pVXZ X = Q, T					-95.2	-9.8	
∞ -cc-pVXZ X = 5, Q					-95.0	-9.7	
∞ -aug-cc-pV(X+d)Z X = Q, T					-95.0	-9.7	

^a In kcal/mol. ^b Frozen core calculation. ^c Full calculation.

TABLE 4: Estimated Enthalpies of Formation of HNS at 298 K and Correlation Contributions at Different Theoretical Levels^a

basis set	$\Delta_f H^\circ_{298}$ CCSDT	$\Delta_f H^\circ_{298}$ CCSD(T)	$\Delta_f H^\circ_{298}$ CCSD	$\Delta_f H^\circ_{298}$ HF	SD	(T)	T
cc-pVDZ		87.4	94.9	179.4	-84.5	-7.5	
cc-pVTZ	68.4	68.1	77.5	169.1	-91.6	-9.4	0.3
cc-pVQZ		61.0	70.7	166.9	-96.2	-9.7	
cc-pV5Z		57.9	67.8	165.7	-97.9	-9.9	
cc-pV6Z				165.4			
aug-cc-pV(D+d)Z		77.9	86.0	171.2	-85.2	-8.1	
aug-cc-pV(T+d)Z		63.5	73.0	166.1	-93.1	-9.5	
aug-cc-pV(Q+d)Z		58.7	68.5	165.4	-96.9	-9.8	
aug-cc-pV(5+d)Z				165.3			
cc-pwCVDZ,Fc ^b		84.8					
cc-pwCVDZ,Fu ^c		84.2					
cc-pwCVTZ,Fc ^b		66.0					
cc-pwCVTZ,Fu ^c		65.3					
cc-pwCVQZ,Fc ^b		59.8					
cc-pwCVQZ,Fu ^c		59.0					
∞ -cc-pVXZ X = Q, T					-99.6	-9.9	
∞ -cc-pVXZ X = 5, Q					-99.7	-10.1	
∞ -aug-cc-pV(X+d)Z X = Q, T					-99.7	-10.0	

^a In kcal/mol. ^b Frozen core calculation. ^c Full calculation.

families of basis sets and again there is almost no difference between the (T) contribution determined with both families of basis sets. Thus, in this case at least, tight d functions seem not to be an important factor for correlation energy convergence. Indeed, the difference between SD results extrapolated using the cc-pVTZ and cc-pVQZ basis sets and those extrapolated using the cc-pV5Z and cc-pVQZ basis sets is only 0.2 kcal/mol for HSN and 0.1 kcal/mol for HNS, showing that the convergence of the correlation energy with the cc-pVXZ family of basis sets does not present any problem. On the basis of this evidence, only minor changes are expected in the SD and (T) components if correlated calculations are performed with the aug-cc-pV(5+d)Z basis set. The effect of full triple excitations, calculated as the difference between the CCSDT and CCSD(T) values using the cc-pVTZ basis set. It was only 0.3 for both isomers. This contribution will not be considered to estimate the enthalpies of formation because in two recent articles^{32,33} it was observed that generally, CCSD(T) outperforms CCSDT in the determination of enthalpies of formation. The exceptions found to this empirical rule are some molecules with large multiconfigurational character such as CH₂³² or FOO.³⁴

All the CC calculations referred to above were performed within the FC approximation. The contribution of the core

electrons to the binding energy was calculated extrapolating the cc-pwCVXZ, X = T, Q results to the CBS limit. The value obtained is -0.9 kcal/mol for both isomers, showing that this is not a large component in the relative stability of the isomers.

Finally, if a precise evaluation of the enthalpies of formation is to be calculated using the atomization reactions, it is necessary to consider the relativistic effects. Since both isomers are closed-shell species, spin-orbit splitting should be included only for the atoms. These values were taken from the literature.³⁸ Scalar relativistic effects were not calculated, but considered instead to be included into the estimated uncertainty, since the effect of this contribution should be small.

Using now all the previously estimated contributions, plus a calculated thermal and ZPE correction of 4.04 kcal/mol at the CCSD(T)/aug-cc-pV(T+d)Z level, one obtains $\Delta_f H^\circ_{298}$ (HSN) = 75.4 ± 1 kcal/mol. Doing the same for HNS, now with a thermal and ZPE correction of 5.95 kcal/mol at the same level as before, one obtains $\Delta_f H^\circ_{298}$ (HNS) = 55.3 ± 1 kcal/mol.

Enthalpies of formation of these species were also evaluated using the standard model chemistries G3 and CBS-QB3. The former predicted $\Delta_f H^\circ_{298}$ (HSN) = 75.6 kcal/mol and CBS-QB3 predicted $\Delta_f H^\circ_{298}$ (HSN) = 74.0 kcal/mol in good agreement with the result obtained from the atomization

TABLE 5: Geometrical Parameters, Harmonic Vibrational Frequencies, and Isomerization Barrier at 0 K for the Transition State of the Reaction HNS \rightarrow HSN at Different Levels of Theory^a

method	basis set	r(SH)	r(SN)	θ (HSN)	ν_1	ν_2	ν_3	Zpe	E_{act} 0 K
CCSD(T)	aug-cc-pV(D+d)Z	1.413	1.675	58.4	1782i	823	2398	4.61	62.4
	aug-cc-pV(T+d)Z	1.401	1.646	58.6	1848i	865	2435	4.72	62.8
	aug-cc-pV(Q+d)Z								63.0
	∞	1.396	1.634	58.5	1875i	883	2451		63.2
B3LYP	6-311+G(3df,2p)	1.403	1.625	57.9	1945i	905	2429	4.76	64.2

^a Barriers in kcal/mol, bond lengths in Å, bond angles in degrees, and frequencies in cm^{-1} .

TABLE 6: Relative Enthalpies at 298 K and SN Bond Length for the XSN and XNS Isomers^a

R	δ^b	B3LYP/6-311+G(3df,2p) NS bond length		relative enthalpies ^c			ref 37
		XSN	XNS	B3LYP ^d	G3	CBS-QB3	
F	4.0	1.439	1.537	-36.5	-38.2	-37.4	-26.2
OH	3.5	1.451	1.584	-20.3	-23.0	-22.5	-7.8
Cl	3.0	1.447	1.540	-21.9	-20.9	-21.8	-14.3
Br	2.8	1.450	1.528	-18.9			-13.7
SH	2.5	1.462	1.581	2.1	-1.1	-0.9	5.6
NH ₂	3.0	1.461	1.573	5.2	1.0	1.6	18.1
PH ₂	2.1	1.481	1.573	11.3	11.1	11.4	16.1
CH ₃	2.5	1.487	1.562	12.6	11.6	11.7	17.9
H	2.1	1.492	1.562	17.4	19.6	19.0	24.7
CF ₃		1.478	1.553	17.5			
SiF ₃		1.508	1.555	28.4			

^a Bond lengths in Å, relative enthalpies in kcal/mol. ^b Mulliken scale electronegativity value. ^c $\Delta_f H^\circ(\text{XSN}) - \Delta_f H^\circ(\text{XNS})$. ^d Obtained with the 6-311+G(3df,2p) basis set.

reactions using the CCSD(T)/CBS method. The same is true in the case of HNS, for which G3 predicts $\Delta_f H^\circ_{298}(\text{HNS}) = 56.0 \pm 1$ kcal/mol and CBS-QB3 predicts $\Delta_f H^\circ_{298}(\text{HNS}) = 55.0 \pm 1$ kcal/mol. One should not expect large accuracy from DFT calculations of the enthalpy of formation using atomization reactions in the general case. However, the B3LYP/6-311+G(3df,2p) enthalpy of formation of the HSN and HNS isomers were obtained as 74.1 and 56.0 kcal/mol, respectively, in excellent agreement with the CC, G3, and CBS-QB3 results.

Isomerization Reaction. The transition state for the HNS \rightarrow HSN conversion was located using the CCSD(T) and B3LYP methodologies. The results are presented in Table 5. The agreement between both methodologies is remarkable, both for the structure of the transition state and the isomerization barrier. This was expected since we have found a similar performance of the B3LYP for the HSO-SOH isomerization.²⁹ The activation energy at 0 K is very large—63.2 kcal/mol at the CCSD(T)/CBS limit, 64.2 kcal/mol with B3LYP/6-311+G(3df,2p)—a reasonable result for a three-member transition state. Our best estimation of this barrier is 5 kcal/mol lower than the previous determination of Watts and Huang,¹⁰ also using the CC theory.

Relative Stabilities of the XSN-XNS Isomers. Relative enthalpies of the isomers for all the species considered in this work, namely X = H, F, Cl, Br, OH, SH, NH₂, CH₃, CF₃, SiF₃, at the DFT level and, in most cases, also at the G3 and CBS-QB3 levels, are listed in Table 6 (for X = CF₃ and SiF₃ we did not performed G3 and CBS calculations because of the computational cost of these calculations). The enthalpies of formation of the isomers, necessary for calculating the values in Table 6, are collected in Table 7. Since the performance of G3 for the S-T energy gap of HNS and HSN was as good as that of CCSD(T), the former can be used to estimate the S-T gap for all the substituents considered here. In all cases, the singlet ¹A' is the ground state. The S-T splitting for all the XSN considered is larger than that observed for HSN. However, this is not true for CH₃ and PH₂ in the case of the XNS isomers. The S-T splitting at the G3 level of theory is 3 kcal/mol for X = PH₂ and 5.3 kcal/mol for X = CH₃. The DFT S-N distances for both isomers of each species are also included in

TABLE 7: Enthalpies of Formation for Some XSN and XNS Species, Calculated at the G3 and CBS-QB3 Levels^a

X	$\Delta_f H^\circ_{298}$ G3		$\Delta_f H^\circ_{298}$ CBS	
	XSN	XNS	XSN	XNS
H	75.6	56.0	74.0	55.0
F	-1.0	37.2	-1.3	-36.1
Cl	42.3	63.2	-38.9	-61.7
OH	8.4	31.4	7.2	29.7
SH	61.6	62.7	59.0	59.9
NH ₂	-52.3	-53.5	-53.3	-55.1
PH ₂	74.9	63.3	71.5	59.8
CH ₃	62.8	51.7	62.1	50.8

^a In kcal/mol.

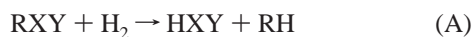
Table 6. As discussed for the parent species, the S-N bond is always larger in the thionitroso form. The largest difference of about 0.13 Å is observed for X = OH.

From the energetic point of view, one can observe a reasonable agreement between the values obtained with different methods. The species have been arranged in decreasing order of stability of the thionitroso isomer with respect to the thiacyl one. One can see that this ordering is largely unaltered, considering either the DFT, G3, or CBS-QB3 values, except in the case of the OH and Cl substituents, for which the DFT ordering is inverse to that of G3 and CBS-QB3. These two pairs were further studied using CCSD(T) and the cc-pV(X+d)Z X = T, Q basis sets, followed by extrapolation to the CBS limit. The CCSD(T)/CBS relative enthalpies at 298 K are -24.4 for X = OH and -23.1 kcal/mol for X = Cl. Thus, the CCSD(T)/CBS ordering of these two pairs is in agreement with the G3 and CBS-QB3 ordering. It is important to notice that if zero-point energies and thermal corrections are not included, these two pairs have nearly the same stabilization energy at the CCSD(T)/CBS level of theory: -23.8 and -23.5 kcal/mol for X = Cl and X = OH, respectively.

It is not straightforward to predict which isomer is the most stable in each case. The thiacyl isomer is the most stable when the substituent is a halogen, OH or SH, but in the cases of NH₂, CH₃, CF₃, SiF₃, and the parent species, the thionitroso isomer

is more stable. SH and NH₂ are somewhat borderline cases; one cannot be completely sure about which is the most stable form, and both of them may eventually coexist. Reed and Zhang¹¹ have recently explored this same problem of the stability of thionitroso and thiazyl isomers of several species at the DFT level (B3LYP/6-31G*). They concluded that there is a correlation between the isomerization energy and the electronegativity of the bonding atom in the substituent, as expressed by the Mulliken electronegativity scale value, which we have also included in Table 6. The results of Reed and Zhang¹¹ have also been included in Table 6 for comparison purposes. We can see that their hypothesis is not fully obeyed by their own energy values, mostly because the level of theory employed is very low, and consequently the energy differences exhibit a large error. Using the enthalpy values reported in this article, we see that the relation holds up to SH, while it fails in the case of NH₂, holds again for PH₂, and fails again for CH₃ and H. These exceptions may be rationalized in terms of the size of substituents for which the bonding atom have more or less the same electronegativity (i.e., PH₂ against CH₃) or in terms of the resonance contributions of the NH₂ substituent, as was done by Reed and Zhang.¹¹

Young, Thomas, and Zhang¹² later expanded the study of Reed and Zhang¹¹ to include the nitrosyl compounds and the NS, PO, and PS isovalent analogues, performing calculations at the B3LYP/6-311+G(d,p) level. They used the reaction A:



which reaction energy they took as a measure of the size of the interaction between the R and XY groups (XY = NO, NS, PO, and PS). The authors claimed that the latter reaction is isodesmic. However, a careful inspection reveals that the broken bond is not similar to the formed ones. Therefore, some error is expected at the B3LYP/6-311+G(d,p) level of theory. They plotted the hydrogenation energy obtained against the withdrawing activity of the substituents, obtaining a reasonably consistent pattern. The larger the withdrawing activity of the substituent, the less stable the RNS species results. Comparing the data in their Figure 1, regarding the hydrogenation reaction, and the present data in Table 6 regarding isomerization, one observes the same pattern. In fact, the present data fit even better, because the CH₃ group follows the same pattern as the rest of the substituent groups, contrary to what is shown in Figure 1 of the article by Young et al.¹² According to the data in Table 6, the stability of X-NS decreases as CH₃ > NH₂ > OH > F, for first-row substituents, and SiF₃ > PH₂ > SH > Cl, for substituents containing second-row atoms.

A final point to consider is the differences observed between the DFT relative enthalpies in Table 6 on one hand and those obtained at the G3 or CBS-QB3 on the other. To check the reliability of the DFT, G3, and CBS-QB3 relative enthalpies of XSN and XNS, additional calculations were performed. The enthalpy of formation of CH₃SN was computed in the first place applying DFT methods to the isodesmic reaction



The standard enthalpies of formation taken from the NIST Thermochemical Data Tables website,³⁵ -5.46 and -4.9 kcal/mol, were employed of CH₃SH and SH₂. The previously calculated limit value of 75.4 ± 1 kcal/mol was used for HSN. The enthalpy change for reaction 1 was calculated at the B3LYP/6-311+G(3df,2p) level as -11.3 kcal/mol. Thus, the enthalpy of formation obtained was Δ_fH^o₂₉₈(CH₃SN) = 63.5 kcal/mol,

TABLE 8: Relative Enthalpies at 298 K of the Cations XSN⁺ and XNS⁺^a

X	B3LYP/6-311+G(3df,2p) NS bond length		relative enthalpies		
	XSN ⁺	XNS ⁺	B3LYP ^b	G3	CBS-QB3
H	1.520	1.468	34.1	34.2	31.3
F	1.510	1.497	-11.2	-13.7	-12.7
Cl	1.509	1.495	11.0	8.1	7.3
Br	1.500	1.495	11.2		
OH	1.513	1.511	1.2	-4.0	-2.0
CF ₃	1.466	1.473	22.1		
CH ₃	1.503	1.477	26.8		
SH	1.506	1.506	27.8	22.5	23.5
NH ₂	1.521	1.529	27.8	23.9	23.5
PH ₂	1.487	1.494	40.0		

^a Bond lengths in Å, relative enthalpies in kcal/mol. ^b Obtained with the 6-311+G(3df,2p) basis set.

in perfect agreement with the CBS-QB3 result of 62.8 kcal/mol reported in Table 7.

Second, the same procedure was applied to the HSSN species, using the isodesmic reaction:



Regretfully, the HSSH standard enthalpy of formation is not available in the NIST Thermochemical Data Tables website.³⁵ The value of 3.8 kcal/mol, recommended by Benson in an classical review article³⁶ was adopted. The predicted Δ_fH^o₂₉₈(HSSN) was then 64.1 kcal/mol, in fair agreement with the CBS-QB3 result, 59.0 kcal/mol. Two reasons may cause in this case a larger discrepancy between the B3LYP and CBS-QB3 results than in the case of CH₃SN. On one hand, the Δ_fH^o₂₉₈ of HSSH is not precisely determined. Therefore, an error may exist in the experimental value. On the second hand, while reaction 2 is formally isodesmic, there is a second-order effect connected to the difference of the SS bonds in HSSN and in HSSH.

On the basis of the previous calculations and the CCSD(T) for X = OH and CL, one can say that the G3 estimated enthalpies of formation for the XSN and XNS isomers (X different from H) reported in this article are correct by about ±2 kcal/mol. The discrepancies observed for some of the DFT values are due to the fact that the XSN → XNS isomerization reactions considered are not isodesmic.

Ionization Potentials. The structure of the monocations of the above referred species was also determined to estimate the adiabatic ionization potentials at different levels of theory. The relative energies of the isomers calculated at the G3, CBS-QB3, and B3LYP/6-311+G(3df,2p) levels of theory, as well as SN bond lengths of the optimum B3LYP structures, are included in Table 8. Removal of an electron changes the stability pattern of the neutral molecules. While in the latter the NS bond distance was always shorter in the thiazyl isomer than in the thionitroso one, the opposite is true for most of the cations, with the exceptions X = NH₂, PH₂, and CF₃.

From the energetic point of view, the agreement between the DFT results and those obtained at the G3 and CBS-QB3 is somewhat disappointing (up to 4 kcal/mol difference in some cases) although they are qualitatively in agreement, except in the case of the OH substituent. Some independent assessment of the quality of the results can be done in the case of the HSN⁺/HNS⁺ pair, because there is a recent detailed study of Yaghlane et al.¹³ done at the CCSD(T)/cc-pV5Z level, in which the isomerization energy is determined as 34.9 kcal/mol. This result is fully in agreement with the 34.1 kcal/mol and the 34.2 kcal/mol found in this work at the B3LYP and G3 levels, respectively

TABLE 9: Estimated Adiabatic Ionization Potentials for the XSN and XNS Isomers^a

X	B3LYP 6-311+G(3df,2p)		G3		CBS-QB3	
	XSN	XNS	XSN	XNS	XSN	XNS
H	9.6	8.9	9.6	9.0	9.5	9.0
F	11.5	10.5	11.6	10.6	11.6	10.5
Cl	10.7	9.3	10.7	9.5	10.7	9.4
Br	10.4	9.1				
OH	10.4	9.5	10.5	9.7	10.5	9.6
SH	9.5	8.4	9.7	8.7	9.6	8.6
NH ₂	9.4	8.4	9.5	8.5	9.5	8.5
CH ₃	8.9	8.2	9.0	8.4		8.4
CF ₃	9.6	9.4				
PH ₂	8.7	7.9	8.9	8.3		8.1

^a In eV.

(see Table 9). The estimated adiabatic ionization potentials (IP) are presented in Table 9. The IP values calculated at the B3LYP/6-311+G(3df,2p) level are in good agreement with the G3 and CBS-QB3 results, with an average deviation of less than 0.1 eV. The relative stability of the isomers does keep a certain correlation with the electronegativity and size of the substituent atoms. In the case of the halogen-substituted neutral molecules, the XSN isomer is more stable by 36.5, 21.9, and 18.9 kcal/mol for F, Cl, and Br, respectively, at the DFT level. The isomerization energy of the cations is shifted toward an increased stability of the XNS form. FSN⁺ is still more stable than FNS⁺ by 11.2 kcal/mol, but the ordering of the isomers is reversed for Cl and Br. ClSN⁺ and BrSN⁺ are less stable than their XNS isomers by 11.0 and 11.2 kcal/mol, respectively.

Conclusions

An extensive characterization of the HSN and HNS isomers has been performed with the aid of coupled cluster theory. The singlet triplet energy gap is predicted to be 9.4 and 5.4 kcal/mol for HSN and HNS, respectively, at the CCSD(T)/CBS level of theory. The B3LYP functional fails, predicting that the ground state of HNS is triplet ³A'', 1.2 kcal/mol below the singlet state. The standard enthalpies of formation at 298 K of both HSN and HNS were determined as 75.4 ± 1 kcal/mol and 55.3 ± 1 kcal/mol, respectively, using the atomization reactions. The frozen-core CCSD(T) method, with an extrapolation to the complete basis set limit, inclusion of the core correlation energy, and correction for the spin-orbit splitting, was used for the purpose. The error bars were chosen to include any remaining errors, such as relativistic effects, Born-Oppenheimer diagonal corrections, and anharmonic contributions to ZPE. The enthalpy of formation of HNS is reasonably in agreement with our own previous, less accurate estimation of 52.5 kcal/mol, obtained at the MP4SDTQ/6-311++G(3df,2p) level in conjunction with isodesmic reactions. It is smaller than the value obtained by Watts and Huang,¹⁰ but still within their error range. The activation energy for the HNS → HSN isomerization has been determined as 63.0 kcal/mol at the CCSD(T)/CBS limit. The B3LYP/6-311+G(3df,2p) result for this barrier, 64.2 kcal/mol, is in fair agreement with the CCSD(T)/CBS value.

The relative enthalpies of the thionitroso and thiazyl isomers of several substituted XNS species were also obtained in this work. Values were obtained at the G3 and CBS-QB3 levels and believed to be accurate to ±2 kcal/mol. Indeed, the CCSD(T)/CBS relative enthalpies for X = OH and X = Cl, especially for difficult cases, are very close to the G3 and CBS-QB3 values. The hypothesis that there is a correlation between the isomerization energies (enthalpies in this work) and the electronegativity of the bonding atom in the substituent, due to Reed and

Zhang,^{11,12} was tested and shown to hold, better than with the data of those authors but yet not perfectly. Therefore, other factors must be taken into account to predict which isomer will be observed experimentally. A comparison with the calculations by Young et al.¹³ shows a strong correlation between the stability of the XNS isomer and the electron-withdrawing ability of the substituent group. The DFT results were proven to be reasonably accurate, except in the case of nearly isoenergetic isomeric pairs. More accurate methods, CBS-QB3 and G3 for instance, are necessary in this situation.

The structures of the cations of the above-referred species were also studied. Ionization reduces, and in some cases inverts, the stability of the thiazyl isomer with respect to the thionitroso one. DFT results are in reasonable agreement with the G3 and CBS-QB3 values, with errors a little larger than those noticed in the case of the neutral molecules. The calculation of the ionization potentials, however, shows a remarkable agreement between all methods, including DFT, with average discrepancies below 0.1 eV.

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