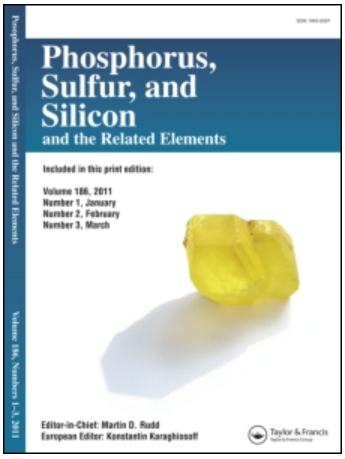

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THE ELECTRONIC STRUCTURE AND PHYSICAL PROPERTIES OF THIONITROSO COMPOUNDS—A QUANTUM CHEMICAL STUDY

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THE ELECTRONIC STRUCTURE AND PHYSICAL PROPERTIES OF THIONITROSO COMPOUNDS—A QUANTUM CHEMICAL STUDY

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Semiempirical and nonempirical quantum chemical methods have been used to describe the electronic structure and physical properties of thionitroso compounds unknown so far. Predictions on geometry, electron distribution, ionization potential, electron affinity, UV-VIS spectrum and the S_0-T_1-energy splitting of these compounds have been made. First experimental results on thionitroso compounds are critically examined.

1 INTRODUCTION

The thionitroso functional is one of the most poorly investigated groups in organic chemistry. Whereas various isoelectronic nitroso (R—N=O) and thiocarbonyl (R_1R_2C=S) compounds have been synthesized, knowledge on thionitroso compounds (R—N=S) is rather scanty.

In contrast to the oxygen analogue[1,2] thionitroxyl **1** seems to be unknown. Thionitrosomethane has been detected indirectly by cycloaddition but there is no direct evidence of its formation.[3] Also, attempts to prepare thionitrosobenzene **2** failed in spite of extensive experimental efforts.[4,5] Sulfurdiimides and persistent SN-radicals[6,7] rather than **2** are obtained from potential precursors of **2**, such as N,N-thiobisanilines and N,N-bisamino-sulfenylamines. N,N-dimethylthionitrosoamine **3** has been described by Middleton as a purple crystalline solid.[8] The same author, however, did not succeed in preparing *p*-N,N-dimethylaminothionitrosobenzene.

Recently, Petersen *et al.* subjected benzo[c]-1,2,5-thiadiazole-2-oxide to photolysis and found a transient which they assigned the structure **4**.[9,10] Formation and decay of the transient was recorded by flash photolysis. The main argument of the authors in favor of the thionitroso structure **4** is the reversibility of its formation, similar lifetimes of the transient in ethanol and cyclohexane and its formation even at 20 K.

Due to the lack of experimental results the characteristic properties of thionitroso compounds are unknown. Thionitroso compounds are even hardly studied theoretically. Collins *et al.* included thionitroxyl **1** into an ab initio study using a contracted Gaussian basis set. They found that the structure HNS is favored energetically over the isomeric structure NSH.[11]

The present paper aims to gather some more information about the molecular and electronic structure of thionitroso compounds by means of quantum chemical investigations.

Part XLV in a series "MO-LCAO-Calculations on Sulfur-containing π-Electron Systems" (for Part XLIV see J. Fabian, R. Mayer and S. Bleisch, *Phosphorus and Sulfur*, **7**, 61 (1979).

In detail, the following properties of thionitroso compounds will be briefly considered:

i) molecular geometries of simple thionitroso compounds

ii) charge distributions and dipole moments

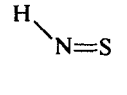
iii) ionization potentials and electron affinities

iv) UV-VIS spectra

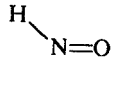
v) the singlet-triplet energy gap between the S_0 and T_1 states

In order to make predictions more reliable conclusions are drawn from a series of compounds which encompass the unknown compounds as well as related known ones. Approaching from known systems, theoretical results obtained on unknown systems can be more critically assessed and properties more reliably predicted.

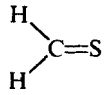
If we consider thionitroso compounds as heteroanalogous carbonyl compounds, **1**, **2** and **3** are members of the following iso-π-electronic series:



1



1a



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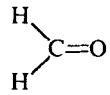
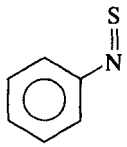


1c



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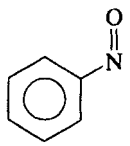
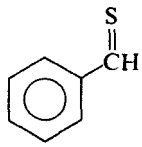


2a



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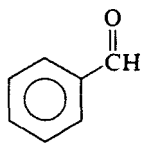

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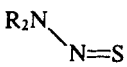

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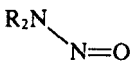
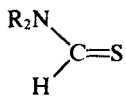
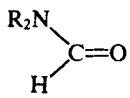


3a

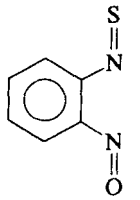


3b



3c

In connection with the synthesis of **4** by Petersen *et al.*[9,10] the following series was investigated in addition.



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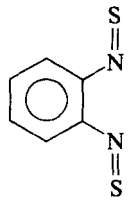
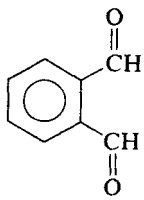


4a



4b

2 QUANTUM CHEMICAL METHODS

Different quantum chemical methods, nonempirical and semiempirical ones, have been used in order to describe the aforementioned properties of the different-sized molecules **1–4** and their iso-π-electronic analoga.

The total energy of the lowest energy singlet and triplet states of **1** and of the tri-

plet state of **1a** have been calculated by an ab initio SCF-method using the 3-21 G basis set.[12] The calculations included the optimization of the molecular geometry.

Simultaneously, geometry optimization for **1**, **1a** and **3a** have been carried out by INDO-calculations using Gordon's parametrization.[13,14]

The frontier orbital energies, the charge distributions, the dipole moments and the $n\pi^*$ transition energies reported were obtained from CNDO/S calculations.[15] In order to improve the energies of the $n\pi^*$ states some slight variations of the standard parameters[16] had to be made. Thus, the κ-factor, which scales the π-resonance integrals, was increased to 0.7. The parameters β_N^0 and γ_{00} were set to −22.0 eV and 13.0 eV, respectively. The reduction of the γ_{00}-integral corresponds to a recent proposal made by Ridley and Zerner.[17] The parameters for sulfur were those applied by Pfister-Guillouzo *et al.*[18] The matrix of singly excited configurations was restricted to 49 configurations. As assured for **2a**, enlargement of the configurational basis up to 100 singly excited configurations does not markedly change the results.

In addition, PPP calculations[19] have been carried out to estimate the positions of the $\pi\pi^*$ transitions, especially for the benzenoid compounds. The complete set of singly excited configurations was taken into account.

3 RESULTS AND DISCUSSION

Geometry

The distances of the bond N=X obtained by ab initio and INDO energy minimization for aliphatic thionitroso and nitroso compounds are collected in Table I. As far as available experimental results are included. The experimental NO bond length for **1a** is excellently reproduced by the ab initio calculations. The lowest energy triplet state for **1** and **1a** is characterized by a considerable widening of the N=X double bond relative to that in the S_0 ground state. The HNX bond angles for both compounds in both states are predicted between 109 and 116 degrees.

The INDO method provides bond lengths which are somewhat too short in comparison to both the ab initio and the experimental results. However, their sequences

TABLE I

Theoretical and experimental lengths of the bond N=X in simple nitroso and thionitroso compounds.

Compound	State	N=X distance in Å		
		ab initio	INDO	exp.
HNS	S_0	1.618 (1.5499)[a]	1.552	—
HNS	T_1	1.717	—	—
HNO	S_0	1.217 (1.191 . . . 1.239)[b]	1.178	1.211[c]
HNO	T_1	1.349 (1.358)[d]	—	—
Me_2NNS	S_0	—	1.582	—
Me_2NNO	S_0	—	1.197	1.233[e]

[a] Ref. 11.
[b] Ref. 20.
[c] Ref. 2.
[d] Ref. 21.
[e] Ref. 22.

on going from **1** to **1a**, from **1** to **3** and from **1a** to **3a** are predicted in accordance to the *ab initio* results.

The results show that the N=S double bond is comparable in length to the C=S double bond. Thioformaldehyd **1c**, for example, shows a C=S distance of 1.611 Å,[23] the lengths for larger thiocarbonyl compounds increase up to 1.65 Å.[24] In thionitrosamine **3** the effect of the donor group on the N=S distance is similar but weaker than in thioamides (C=S bond length in thioacetamide amounts 1.713 ± 0.006 Å[25]). The methyl groups for **3** and **3a** are found to be inclined to the NNX plane by 10–30 degrees.

Electronic Structure and Dipole Moment

Table II contains the gross charges of the $\diagdown$N=X and, for sake of comparison, those of the $\diagup$C=X group in dependence on the substituents H, NMe_2 and Ph (structures **1–3** and **1a–3c**). Like the thiocarbonyl group, N=S is a polar and easily polarizable acceptor group with both σ and π excess charge. The distribution of charge excess among the atoms N and S depends largely on the adjacent substituents of the thionitroso group. Bonded at a hydrogen or a carbon atom in the molecules **1**, **2**, **4** and **4a** the nitrogen atom carries a higher negative charge than the sulfur atom. Hence, the N=S group is polarized according to the mesomeric structure $\overset{\delta-}{N}=\overset{\delta+}{S}$. However, introduction of the amino group in **3** increases the weight of the zwitterionic structure $\overset{\oplus}{N}R_2=N-\overset{\ominus}{\underline{S}}|$ and the negative charge on the sulfur atom now exceeds that of the nitrogen.

The dipole moments obtained by CNDO/S are obviously overestimated compared with the experimental values. Therefore the calculated differences in dipole moments between $\diagdown$N=S (—CH=S) and $\diagdown$N=O (—CH=O) compounds only allow qualitative conclusions. Along these lines, thionitroso compounds (except **1**) are predicted to be stronger polar than nitroso compounds.

Ionization Potentials and Electron Affinities

The energies of the frontier orbitals of different thionitroso compounds are compared to those of related compounds in Figure 1. The HOMO has *n* character for

TABLE II

Gross charges and differences of dipole moments for nitroso and thionitroso compounds obtained by CNDO/S. The adequate values for carbonyl- and thiocarbonyl compounds are given for the sake of comparison.

Y	Y$\diagdown$N=S		Y$\diagdown$N=O		$\mu_{N=S} - \mu_{N=O}$ [D]
H	−0.1510	+0.0312	+0.2032	−0.3467	−0.91
Ph	−0.1199	−0.1094	+0.1886	−0.4020	0.18
NR_2	−0.0606	−0.3025	+0.2499	−0.4715	1.24
Y	Y$\diagdown$CH=S		Y$\diagdown$C=O		$\mu_{C=S} - \mu_{C=O}$
H	+0.0901	−0.2222	+0.3423	−0.4844	0.03
Ph	+0.0967	−0.3161	+0.3503	−0.5463	0.82
NR_2	+0.0891	−0.3277	+0.4253	−0.5659	0.77

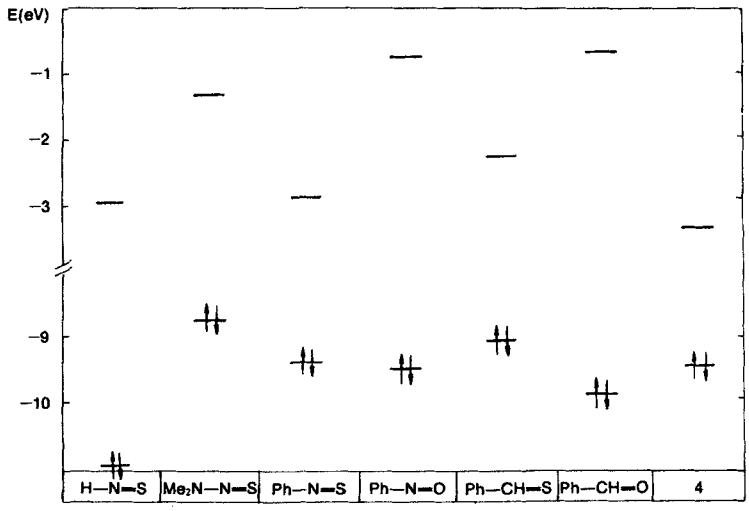


FIGURE 1 CNDO/S Energies of the frontier orbitals for thionitroso compounds and analoga.

the aliphatic but π character for the aromatic thionitroso compounds. The LUMO is of the π^* type in all cases.

The HOMO energies of the benzenoid types **2**, **2a-2c** and **4** are very similar and constant within a range of 1 eV. Consequently, aromatic thionitroso compounds should have similar ionization potentials as nitroso compounds.

A different situation emerges in comparing the LUMO energies, which should reflect the change in the electron affinities. Thionitroso compounds are sharply distinguished from their iso-π-electronic counterparts by a very low-energetic antibonding MO. Thus, electron capture should easily occur resulting in thionitroso radical anions in the primary reduction step. This should drastically diminish the chance of isolating these compounds in presence of electron donor compounds.

Donor substituents on the N=S group decrease the electron affinity. This may explain both the existence of **3** and the stabilization of thionitroso groups as ligands of certain transition metal complexes.[26]

UV-VIS Spectra

Due to the mixing of the lone pair AO's of N and X[27-30] the UV-VIS spectrum of systems containing the group N=X is characterized by the weakly intensive $n\pi^*$ absorption. The coupling results in two $n\pi^*$ states ($n_+\pi^*$ and $n_-\pi^*$ [30]) the energy of which depends strongly on the atom X.

In Figure 2 the calculated $n\pi^*$ energies of the parent N=X systems **1** and **1a** are compared with those of the corresponding C=X compounds **1b** and **1c**, respectively. The strong coupling between the oxygen and the nitrogen lone pair in **1a** results in a considerable energy splitting of the two $n\pi^*$ states. The low-energy $n\pi^*$ state of **1a** is 254 kJ mol^{-1} more stable than that of **1c** and accounts for the bright green color of nitroso compounds. The second $n\pi^*$ state is positioned in the far ultraviolet region.

For the thionitroso compound **1** the splitting of the $n\pi^*$ states is predicted to be much smaller than for **1a**. However, due to the low ionization energy of the sulfur lone pair the low-energy $n\pi^*$-transition appears in the near infrared region. Thioni-

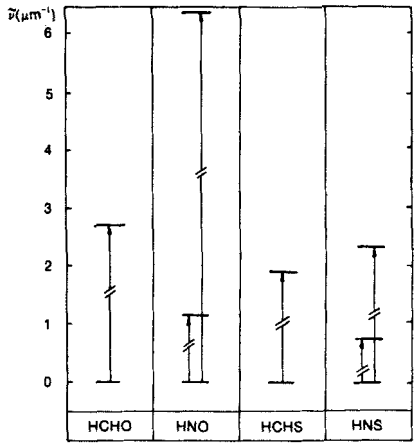


FIGURE 2 Theoretical $n\pi^*$ transitions of the N=X and C=X groups.

troso compounds are predicted to show weak absorptions between 1000 and 1400 nm which cannot contribute to their color. The color of thionitroso compounds should be originated, therefore, from the second $n\pi^*$ transition which is situated at about 500 nm. This is the same absorption region as for thiocarbonyl compounds. According to the theory the color of thionitroso compounds is of the second order.[31]

Table III contains the calculated $n\pi^*$ transition energies for all the compounds studied in comparison to experimental absorption maxima of the weak $n\pi^*$ band.

In the case of donor substitution a strong blue shift is predicted for the $n\pi^*$ absorption in thionitroso compounds. This has been actually found in passing from nitroso compounds to nitrosoamines.[37] Taking into account an underestimation of this blue shift in CNDO/S calculations, the theoretical results for **3** are compatible with the spectral data given by Middleton.[8]

The intensive $\pi\pi^*$ transitions obtained for **2**, **4** and **4a** by PPP calculations resemble those of other monosubstituted and ortho-disubstituted benzene derivatives. The CNDO/S method provides questionable results indicating deficiencies in the parametrization. Whereas the $\pi\pi^*$ transitions for sulfur-containing compounds are too low in energy, the opposite is true for oxygen and nitrogen-containing compounds. Therefore, PPP calculations have been carried out. The results are in very good accordance with the experimental spectra of **2a–2c** and **4b**. Figure 3 shows that a combination of the PPP results for the $\pi\pi^*$ transitions and the CNDO/S values for the $n\pi^*$ transitions permits a satisfactory reproduction of the UV spectra of the mono- and disubstituted benzenes studied. Consequently, the prediction of the excitation energies of the thionitroso compounds **2**, **4** and **4a** should be credible.

It must be noted, however, that the theoretical transition energies obtained for ortho-nitroso-thionitrosobenzene **4** are not in agreement with the flash spectrum for the photo-transient observed by Petersen *et al.*[9,10] According to the quantum chemical results the intense band at 493 nm in the flash spectrum cannot be due to a $\pi\pi^*$ transition of the aromatic chromophoric system. For **4** and **4a** the intense long-wavelengths $\pi\pi^*$ transition should rather occur between 350 and 370 nm. The CNDO/S calculations predict only a weak $n\pi^*$ transition in the region of 500 nm where the flash-spectrum of the transient shows a strong absorption. Moreover, any weak transition in the infrared region of **4** which could support the presence of the thionitroso group has not been found so far.

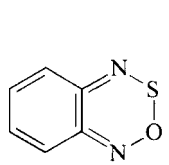
TABLE III

CNDO/S calculated $n\pi^*$ transition energies and absorption maxima of the weak $n\pi^*$ band

Compound	Transition energies		Absorption maxima		Ref.
	$\Delta E[\mu m^{-1}]$	λ[nm]	$\Delta E[\mu m^{-1}]$	λ[nm]	
1	0.780	1282	—	—	
	2.346	426	—	—	
1a	1.439	695	1.29	775	32
	6.644	151	—	—	
1b	1.922	520	1.71	585	33
1c	3.554	281	3.39	295	34
2	0.810	1234	—	—	
	2.037	491	—	—	
2a	1.361	735	1.33	750	35
	4.935	203	—	—[a]	
2b	1.708	585	1.75	573[b]	35
2c	3.197	313	3.06	327	35
3	1.523	657	1.706	586[c]	8
	2.452	408			
3a	2.153	464	2.67	374	37
	5.531	181	—	—	
3b	2.799	357	2.740	365[d]	38
3c	3.968	252	5.03	199	39
4	0.727	1375	—	—	
	1.272	787	—	—	
	1.999	500	—	—	
4a	0.748	1336	—	—	
	0.783	1277	—	—	
	2.355	424	—	—	
	2.573	389	—	—	
4b	2.844	352	2.86	350	40
	3.155	317			

[a] Probably hidden under $\pi\pi^*$ bands.
[b] Taken from thioacetophenon.
[c] The extremely weak absorption at 705 nm found in Ref. 8 might be assigned to an *S-T*-transition.
[d] Taken from NN-dimethyl-acetamide.

The theoretical results suggest that the transient resulting from the photolysis of benzo[c]-1,2,5-thiadiazole-2-oxid does not contain the thionitroso group. Indeed, some alternative structures of primary reaction products, among them the valence isomers **5** and **6** can be formulated as well.



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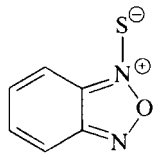

6

In order to solve this problem further experimental and theoretical investigations are necessary.

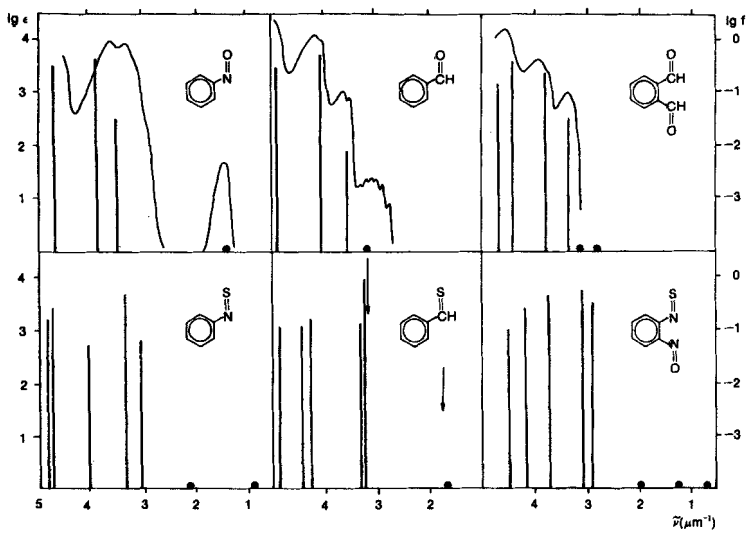

FIGURE 3 Transition energies and spectral curves, as far as available, for the benzenoid carbonyl, thiocarbonyl, nitroso and thionitroso compounds. The $n\pi^*$ transition energies were obtained by CNDO/S, $\pi\pi^*$ transition energies by PPP calculations. The arrows indicate the absorption maxima taken from Ref. 36.

Singlet-Triplet-Splitting

Due to the small energy gap between the lowest singlet state S_0 and the first excited $n\pi^*$ singlet state S_1 an extremely small splitting between the states S_0 and T_1 should be expected for thionitroso compounds. This necessitates some considerations about the multiplicity of the ground state, especially for small thionitroso compounds, such as **1**. In Table IV the ab initio total energies of the equilibrium geometries for **1** and **1a** are collected. It can be seen that, in the framework of the 3-21G basis, the T_1-state of **1** is of 80 kJ mol^{-1} lower in energy than the singlet ground state. However, a similar result has been found for **1a**. For the latter molecule more sophisticated calculations have revealed, however, that both extension of the basis set and inclusion of some electron correlation inverses the order of states.[20,41] For **1** calculations of this computational level have not been done so far.

In any case, the S_0-T_1 gap for simple thionitroso compounds should be extremely small and comparable with those for oxygen, carbene, nitrene *et al.*

TABLE IV

Total energies of the compounds HNX in the S_0 and T_1 states obtained by ab initio calculations using a STO-3-21G basis set

Compound	State	Total energy a.u.	Ref.
HNS	S_0	−450.189108	this work
HNS	T_1	−450.219692	this work
HNO	S_0	−129.03829	12
HNO	T_1	−129.056361	this work

4 CONCLUSIONS

According to quantum chemical calculations simple thionitroso compounds such as **1** and **2** are planar, polar, easily polarizable and colored substances. They should be highly instable due to their large electron affinity, to their low-energy $n\pi^*$ excited states (a weak $n\pi^*$-transition should occur in the infrared region) and to a small energy gap between their lowest-energy singlet and triplet states. Simple thionitroso compounds might equilibrate with or even exist in the triplet state.

Introduction of electron donors directly bonded at the N=S group increases the singlet-singlet $n\pi^*$-transition energy and decreases the electron affinity compared with those of the parent thionitroso compounds **1** and **2**. This is connected with a stabilizing effect of the N=S functional which becomes evident by the successful preparation of thionitrosoamines and complexes with N=S groups in the ligand sphere.

Thionitroso compounds show a similar close relationship to nitroso compounds as the thiocarbonyl show to the carbonyl systems.

Further efforts to obtain thionitroso compounds should be attempted at low reaction temperatures, in absence of reducing agents and under conditions allowing the observation of short-living transients.

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