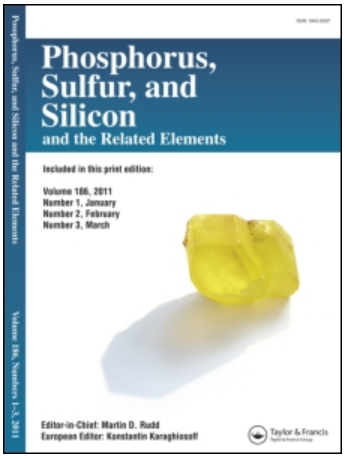

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ELECTRONIC STRUCTURE OF *N*-THIONITROSOAMINES AND PHOTOELECTRONIC SPECTRUM OF *N*-THIONITROSODIMETHYLAMINE

V. V. Penkovsky[a]; Yu G. Shermolovitch[a]; A. V. Solovyov[a]; V. I. Vovna[b]; A. V. Borisenko[b]
[a] Institute of Organic Chemistry, Academy of Sciences of the Ukraine, Kiev, Ukraine [b] Research Physico-Technical Institute at Far East University, Vladivostok, Russian Federation

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ELECTRONIC STRUCTURE OF *N*-THIONITROSOAMINES AND PHOTOELECTRONIC SPECTRUM OF *N*-THIONITROSODIMETHYLAMINE

V. V. PENKOVSKY†, Yu G. SHERMOLOVITCH and A. V. SOLOVYOV
Institute of Organic Chemistry, Academy of Sciences of the Ukraine
Murmanskaya 5, Kiev 253094, Ukraine

and

V. I. VOVNA and A. V. BORISENKO
Research Physico-Technical Institute at Far East University, Uborevitcha 25, Vladivostok 690600, Russian Federation

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Quantum-chemical calculations of molecular geometry, energies and structure of MO and electron density distribution in *N*-thionitrosoamines were carried out. The photoelectronic spectral data for *N*-thionitrosodimethylamine obtained correlated satisfactory with calculated eigenvalues of occupied MOs. Results of the investigation explain the stability of aliphatic *N*-thionitrosoamines.

Key words: *N*-thionitrosoamines; electronic structure; MO calculations; PES data.

Thionitroso compounds R—N=S are successfully used in organic synthesis due to their high reactivity but are mostly unstable.[1] One of few exceptions is thionitrosodimethylamine S=N—N$(CH_3)_2$ (**1**).[2] Absence of steric hindrance in **1** implies that its relative stability is due to its special electronic structure. However, no experimental data about the electronic structure of *N*-thionitrosoamines are available, and few quantum-chemical studies in this field are known[3–5]; in particular, the electronic structure of **1** has been studied so far only using the INDO and CNDO/S methods.[3]

We have performed quantum-chemical MNDO and *ab initio* calculations on the electronic structure of **1** and the model compounds

S=N—$NHCH_3$ (**2**), S=N—NHC_2H_5 (**3**), S=N—NH_2 (**4**) and S=NH (**5**)

Their molecular geometries have been completely optimized. Influence of the amino group causes a considerable elongation of the S=N bond relative to **5** and an increase of the SNX valence bond angle up to 120° (Table I). The N—N bond being considerably shorter than that of hydrazine (144.9 pm[6]). The S=N bond index in **1–4** is lower than that for the "purely double" S=N bond in **5**, and the N—N bond index is considerably higher than unity. The electron density is delo-

†Author to whom correspondence should be addresses.

TABLE I

Theoretical bond lengths and valance bond angles of thionitroso compounds

Compound	Distance N=S, pm		Distance N-N, pm		Valence angle XNS, °	
	ab initio[a]	MNDO	*ab initio*[a]	MNDO	*ab initio*[a]	MNDO
1		152.7		129.6		121.9
2		152.9		129.1		119.4
3		153.0		129.0		119.4
4	168.5	152.9[b]	126.7	128.7	120.5	119.6
5	160.4	149.1[b]	101.1	101.3	114.6	113.6

[a] 4-31G basis set

[b] Ref.5

calized onto the S—N—N unit and for its central nitrogen atom a small charge results (Table II). This picture is almost independent on the number and length of alkyl groups at the amino nitrogen. Results of our calculations indicate that the dipolar structure $\dot{N}{=}N{-}\bar{S}$ must contribute considerably to the overall electronic structure of **1–4**. One may note that contributions of dipolar structures should be much lower with OH or SH substituents.[5]

In more detail the LUMO of the compounds **1–4** expectedly is the antibonding three-centered π-MO with dominating contribution from the central nitrogen (see Figure 1); its energy increases from **1** to **5** by *ca.* 1 eV. Similar results were obtained in *ab initio* calculations of **4** and **5**. In contrast, the HOMO of **1–5** is non-bonding and largely localized at the sulfur center and therefore virtually identical to a sulfur lone-pair orbital (n_S). For moledules **1–4**, the three-centered π MO is calculated

TABLE II

Net atomic charges and bond indices of thionitroso compounds from MNDO calculations

Compound	Net atomic charge			Bond index	
	S	N1	N2[a]	N=S	N-N
1	-0.210	+0.031	-0.290	1.617	1.278
2	-0.216	+0.044	-0.266	1.618	1.296
3	-0.222	+0.045	-0.258	1.618	1.303
4	-0.215[b]	+0.047[b]	-0.237	1.616[b]	1.316
5	+0.031[b]	-0.110[b]		2.004[b]	

[a] Atom N of the amino group

[b] Ref.5

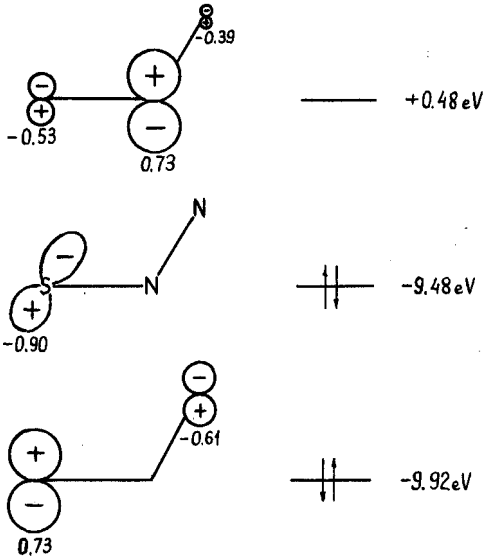

FIGURE 1 MNDO eigenvalues of the inner molecular orbitals of compound **1** including the AO coefficients.

to be below and with dominant contributions from the sulfur and amine nitrogen centers. The next two MOs of σ and π type are localized at the S=N group.

To confirm our assignment of occupied MOs of I, the unknown photoelectron spectrum (PES) of the title compound **1** was recorded.

A comparison of the calculated eigenvalues of **1** and **4** suggests that introducing two methyl groups should increase the energies of the HOMO and the next π-MO by 0.3–0.4 eV (see Table III). With the results of *ab initio* calculations for **4** and applying the Roopmans theorem, we may assume the n_S and the next π-ionization energies should amount to 8–9 eV. In this region the PES of I exhibits two bands. The first one (with a threshold at 7.7 eV and a maximum at 8.0 eV) may be

TABLE III

Calculated energies of occupied molecular orbitals for compounds **1** and **4** and the photoionization energies of **1**

Compound	Method	Energy, eV			
		n_S	π	σ	π
1	MNDO	-9.48	-9.92	-12.63	-13.58
	PES	8.0	8.9	11.2	11.8
4	MNDO	-9.71	-10.27	-12.97	-15.29
	Ab initio 4-31G	-8.93	-9.39	-13.23	-16.33

evidently associated with the n_S MO; its broad contour indicates a simultaneous vibronic excitation at the ionization. The second band therefore is assigned to the π-ionization. Two next bands are also assigned based on our calculations: they should arise from the ejection of an electron into radical cation states represented by the lower π MO and the σ MO.

Thus, both the quantum-chemical calculations for the molecules **1–4** and the PES investigation of the compound **1** leads to a conclusion that the HOMO of these compounds is essentially localized on the negatively charged sulfur atom; these too are the main factors for the reactivity of **1**. On the other hand, **1** should be a less effective electron acceptor and dienophile than **4** or other thionitroso compounds,[5] due to the higher energy of the LUMO and the lower sulfur contribution to it. Reactivity of **1** towards electrophiles should be also low, as expected from the small charge on the central nitrogen and thus enhance the relative stability of **1**. Differences in the electronic structure of compounds **1–3** are negligible and therefore, any aliphatic N-thionitrosoamine should be more stable than other thionitroso compounds. This conclusion may promote further attempts for synthesis and isolation of new compounds belonging to this class.

EXPERIMENTAL

Compound **1** was prepared according to Reference 2. The PE spectra were recorded using a He(I) lamp ($\eta\nu$ = 21.22 eV) and calibrated with the Rr lines (14.00 and 14.67 eV). For the measurement a spectrometer ES-3201-DVK3-SM4 was used containing an inlet system for low-volatile compounds; the accuracy of measurements was $\pm$0.1 eV.

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