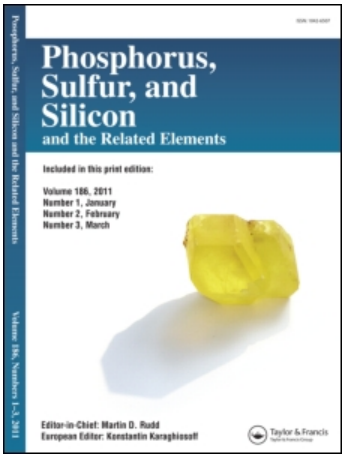

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GENERATION OF THIONITROSO COMPOUNDS FROM N,N'-THIODIAMINES. A MOLECULAR ORBITAL STUDY

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The thermal decomposition reaction of N,N'-thioamines to produce azo-derivatives and sulfur, considering thionitroso derivatives (R—N=S) as intermediates, was investigated using AM1 and Ab-Initio M.O. calculations. Thermodynamic arguments indicate an endothermic formation of the thionitroso species, but a favoured exothermic decomposition to products. Molecular and electronic structure, for the proposed intermediate four member cyclic molecule of sulfur and nitrogen ($R_2N_2S_2$), in the transformation of R—N=S to R—N=N—R and sulfur, were obtained. Estimation of kinetic parameters for the formation and decomposition of this structure, confirm the intermediate nature of it.

Key words: Sulfur-nitrogen compounds, thionitroso-derivatives, N,N'-thioanilines, MO studies, thermal decomposition.

INTRODUCTION

Previous studies, performed in our laboratory,[1a-g] have shown that the reactivity of N,N'-thiobisamines $R_2N—S—NR_2$, depends on the nature of the substituents and the degree of substitution on the amine moiety.

While the N,N'-thiobisamines are thermally stable,[2] the partially substituted analogue N,N'-thioanilines $(RNH)_2S$, decomposes on heating to produce the amine and the azobenzene[3,4] according to the following reaction:

$$\text{(I)}\ (X—C_6H_4—NH)_2S \rightarrow X—C_6H_4—NH_2 + \frac{1}{2}\,X—C_6H_4—N=N—C_6H_4—X + S$$

This decomposition reaction was postulated to occur through the intermediate thionitrosobenzene $X—C_6H_4—N=S$, according to the reaction:

$$\text{(II)}\ (X—C_6H_4—NH)_2S \rightarrow X—C_6H_4—N=S + X—C_6H_4—NH_2$$

$$\text{(III)}\ X—C_6H_4—N=S \rightarrow \frac{1}{2}\,X—C_6H_4—N=N—C_6H_4—X + S$$

The existence of the $X—C_6H_4—N=S$ molecule was demonstrated by trapping it with 2,3-dimethyl-1,3-butadiene, to produce the 1,2-thiazine derivative.

Thionitrosobenzene derivatives appear to be an elusive family of molecules that has been suggested as reactive intermediates in several organosulfur reactions.

Also, their presence as intermediates have been postulated in the reaction of benzophenone hydrazone with S_3N_3Cl,[5] and in the thermal decomposition of sulfenamides.[6] Attempts to synthesize thionitrosobenzene derivatives from the reaction of N-nitrosoamines and P_4S_{10} have failed.[7] Recently, a series of thionitrosobenzene derivatives p—X—C_6H_4—N=S have been detected by electron impact mass spectrometry of thiobisanilines (X—C_6H_4—NH)$_2$S (X=H, Br, Cl, OMe and in m-NO_2).[1g]

$$\text{(IV) } (X—C_6H_4—NH)_2S \xrightarrow{\text{E. I.}} (X—C_6H_4—NH)_2S^{\cdot +}$$

$$\text{(V) } (X—C_6H_4—NH)_2S^{\cdot +} \rightarrow X—C_6H_4—N{=}S^{\cdot +}$$

The only relatively stable compounds containing the thionitroso-group are the N—thionitrosoamines $R_2N—N{=}S$.[8,9] The existence of thionitroso structures has not been directly confirmed. Molecular orbital calculations are expected to offer valuable information concerning the thionitroso derivatives. In this work AM1[10a] and Ab—Initio M.O. calculations were carried out on the structures involved in the thermal generation of thionitroso derivatives from N,N'—thiodianilines, namely: $(RNH)_2S$ R=CH_3, C_6H_5, RN=S, R—N=N—R and RNH. Also AMl calculations of the reaction path for the formation and decomposition of the proposed four member sulfur-nitrogen ring intermediate were performed.

CALCULATIONS

Semi-empirical M.O. calculations were performed with the program MOPAC v. 6.0[10b] and Ab-Initio calculations were made using the program Monstergauss,[10c] both running on an Apollo DN-10000 Hewlett Packard workstation. All the calculations were performed with full geometry optimization, except the reaction path calculation, where only the reaction coordinate was not optimized. The reaction coordinate for the formation of the cyclic intermediate was chosen along the symmetric stretchings of the N—N and S—S bonds, whereas the symmetric stretching of the S—N bonds was chosen for the decomposition.

RESULTS AND DISCUSSION

N,N'-Thiodianiline (C_6H_5—NH)$_2$S

Geometry and Electronic Structure. Attempts to obtain suitable crystals of this molecule to perform X-ray diffraction studies have failed.[11] Then M.O. calculations of minimum energy structure can provide interesting geometric information about these molecules. Table I shows the AM1 optimized geometry of (C_6H_5—NH)$_2$S, and a good agreement can be observed between the calculated structure and the experimental data obtained from the related fully substituted derivatives $(R_2N)_2S$.[12a–c]

Similar to other organic and inorganic sulfur compounds, the composition of the HOMO can be mainly accounted for by the contribution of sulfur 2*p* orbit-

TABLE I

Calculated geometrical parameters for N,N-thiodianilines and experimental data for related S—N molecules

	r(S-N)[a]	∠N-S-N[b]	∠C-N-H (or C-N-C)	reference
$(C_6H_5NH)_2S$	1.61	111.34	113.6	this work(AM_1)
$(CH_3\text{-}NH)_2S$	1.61	112	114.3	this work(AM_1)
$[(CH_3)_2N]_2S$	1.688	114.5	116.5	12a (electron difraction)
$((C_6H_{11})_2N)_2S$	1.678	113.2	117.9	12b (X-ray crystallography)
$(O\bigcirc N)_2S$	1.657	110.7	112.1	12c (X-ray crystallography)

a.- bond distances in angstrons
b.- Bond angles in degrees

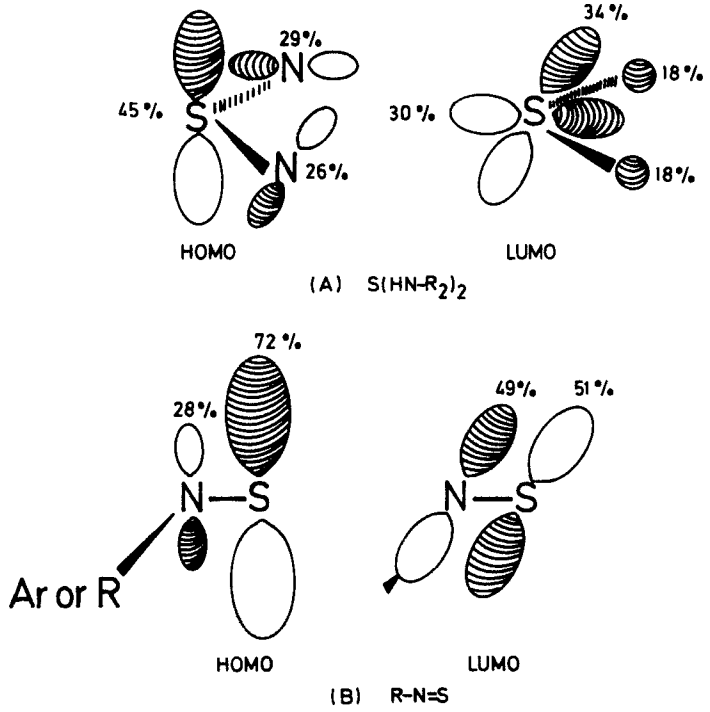

FIGURE 1 Pictorial representation of HOMO and LUMO for: (A) N,N'-thiodianilines and (B) thionitroso compounds (AM_1 level).

als.[13a-c] Some contribution from the nitrogen 2*p* orbitals is also observed. The LUMO is mainly the contribution of sulfur 2*p* orbitals, orthogonal to that in the HOMO, and a minor contribution from nitrogen 2*s* orbitals. A pictorial representation of these orbitals is shown in Figure 1A. AM1 net atomic charges are +0.48 on the sulfur and −0.48 on the nitrogen, as expected for these systems.[1c,14a,b]

Thionitroso Derivatives R—N=S

Geometry and Electronic Structure. To test the validity of the AM1 geometrical and electronic results in these sulfur atom containing systems, we have also performed Ab-Initio full geometry optimization calculations at 3-21G* level, to include *d* orbitals from the sulfur explicitly. This calculation was performed in the simplest model to study, the methyl derivative CH_3—N=S. These geometrical results are shown in Figure 2A.

The differences between the AM1 and the Ab-Initio calculated geometries are rather small (less than 3% in the bond angles and less than 6% in the bond lengths), which support the use of the AM1 method. Figure 2A shows that the nitrogen has an sp^2 hybridization, in agreement with the structure found in the related com-

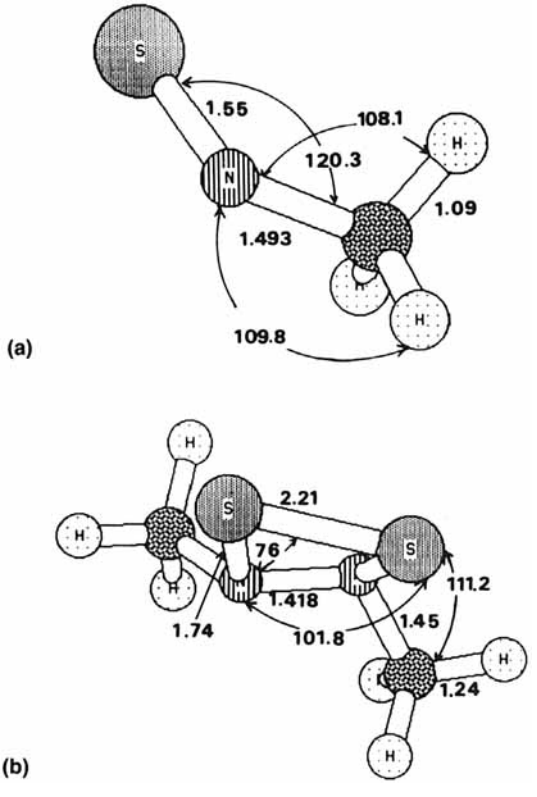

FIGURE 2 Optimized geometries for the sulfur-nitrogen intermediates: (A) CH_3—N=S (Ab-Initio,3-21 G* level) (B) $(CH_3)_2N_2S_2$ (AM_1 level) (bond distances in angstroms and angles in degrees.

pounds R—N=SXn and X—N=SXnOm.[15a-e] The N=S bond distance is around 1.5 Å, close to expected for a sulfur nitrogen double bond 1.56 Å.[16]

The HOMO of these structures is mainly composed of a π sulfur-nitrogen bond, with a major contribution from the sulfur p orbital. The LUMO is also a π sulfur nitrogen orbital, but with antibonding character. These results are in agreement with previously reported data obtained for other sulfur nitrogen compounds.[1c,14a,b] A pictorial representation of the frontier orbitals is shown in Figure 1B. The nature of the AM1 frontier orbitals is the same as the ab-initio 3-21G* orbitals. This result suggests that the contribution of sulfur *d* orbitals to the chemistry of these molecules is not important. For thionitrosomethane, the 3-21G* net atomic charges are +0.6 on the sulfur and −0.6 on the nitrogen, whereas AM1 atomic charges are +0.13 on the sulfur and −0.25 on the nitrogen atom. These values are in qualitative agreement with those calculated in similar S—N compounds.[1c,14a,b]

Energy Analysis

Calculated total energies and heats of formation of products and reactants for the thermal decomposition of N,N'-thiodianilines (see reaction I) are shown in Table II. These results show that the overall reaction should be endothermic (ΔH = 64 KJ/mol), consistent with the thermal induced nature of the decomposition. However, this calculated value can not be compared with experimental data, due to the lack of heat of formation for most of the species in the reaction. Although, an estimation of the reaction energy can be made using data for bond energies[17a-c] and the heat of formation of aniline (ΔH = 87 KJ/mol), considering that the C_6H_5NH— fragment remains unaltered during the reaction. The reaction enthalpy obtained in this way is 75 KJ/mol, which is in reasonable agreement with the calculated value (64 KJ/mol).

TABLE II

Total energies and heats formation calculated by the AM1 method for the *thermal decomposition reaction of N,N'-thiodianilines*

Molecule	E(KJ/mol)	ΔH_f(KJ/mol)
$(CH_3\text{-}NH)_2S$	-94098	-17.76
$(C_6H_5\text{-}NH)_2S$	222772	230.53
$CH_3\text{-}N{=}S$	54897	190.78
$C_6H_5\text{-}N{=}S$	119249	313.8
$C_6H_5NH_2$	103330	85.76
$CH_3N{=}NCH_3$	72456	149.97
$C_6H_5N{=}NC_6H_5$	198555	418.38
$(CH_3)_2N_2S_2$	109794	369.99

Assuming the thionitrosobenzene molecule to be an intermediate, the overall decomposition reaction can be divided in equations (II) and (III). Reaction (II), leading to the intermediate $C_6H_5N{=}S$, should be endothermic (ΔH = 169 KJ/mol), while the decomposition of the thionitroso derivative, to give α, α'-azobisbenzene and sulfur, should be exothermic (ΔH = −105 KJ/mol). Therefore, the intermediate nature of the species $C_6H_5N{=}S$ can arise from two facts: i) The low equilibrium concentration of $C_6H_5N{=}S$, due to its high energy content; and, ii) The thermodynamic favored decomposition of $C_6H_5N{=}S$ to give $C_6H_5N{=}NC_6H_5$ and sulfur.

Neglecting entropic contributions, an approximate equilibrium constant for the processes just mentioned, can be calculated†:

$$\text{(VI)}\ (C_6H_5NH)_2S \xrightarrow{K = 10^{-30}} C_6H_5N{=}S + C_6H_5NH_2$$

$$\text{(VII)}\ 2C_6H_5N{=}S \xrightarrow{K = 10^{18}} C_6H_5N{=}NC_6H_5 + 2S$$

The most likely mechanism for reaction (VII) has been proposed by Davis,[3] and involves the dimerization of two thionitroso molecules to give a tetranuclear cyclic species:

$$\text{(VIII)}\ 2C_6H_5N{=}S \rightarrow \begin{array}{l} C_6H_5{-}N{-}S \\ \quad\quad\ |\ \ | \\ C_6H_5{-}N{-}S \end{array}$$

A cyclic intermediate similar to this has been suggested to be involved in reactions of thiocarbonyl compounds.[18a-c] To obtain more information about the nature of this S—N cyclic intermediate, we have calculated the AM1 energy and reaction profile for the transformation:

$$\text{(IX)}\ 2CH_3N{=}S \rightarrow [(CH_3)_2N_2S_2] \rightarrow CH_3NNCH_3 + 2S$$

The chosen reaction coordinates corresponds to the symmetric S—S and N—N stretchings for the formation of the ring, and the S—N symmetric stretching for the decomposition of the ring. This is probably the most likely mechanism for this reaction, however we can not exclude other possibilities. All the other coordinates, except the reaction coordinate, were optimized along the reaction path calculation.

The cyclic intermediate is a non planar molecule, with tetrahedral sulfurs and pyramidal nitrogens, as shown in Figure 2B. The long bond distances in the ring (S—S 2.21 Å and S—N 1.74 Å) allow the non-planarity of this structure. These bond lengths are greater than those found in other four and five membered S—N rings.[19a-e] The planar species also converges during the calculation, but it is 54 KJ/mol more energetic, and probably corresponds to the transition state of the ring inversion process of the minimum energy structure.

The HOMO of this cyclic molecule is mainly π^* (S—S) in character, similar to that found for the dialkyldisulfides,[20a,b] which evidences the high degree of formation of the S—S bond. There is also a minor contribution from π^* (N—N),

†Using the equation $\Delta G = -RT \ln K$, T = 300 K.

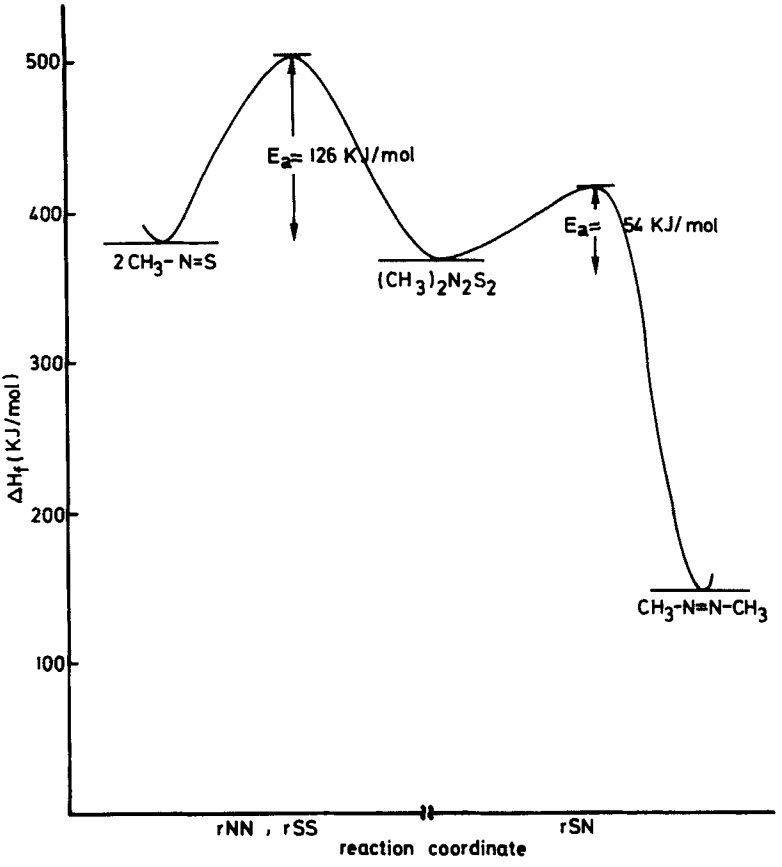

FIGURE 3 Schematic energy profiles for the thermal decomposition of CH_3—N=S to CH_3—N=N—CH_3 and sulfur. Energies obtained from AM_1 calculations.

favouring the formation of the N—N bond. A small contribution from σ^* (S—N) is also observed, suggesting a certain degree breaking of the S—N bonds.

Figure 3 shows the calculated energy profile of the calculated reaction coordinate for the formation and decomposition of the cyclic intermediate. The high energy content of the species involved makes it difficult to isolate them and corroborate the mechanism proposed experimentally by Davis.[3]

Finally, from this work we have provided some interesting geometrical and electronic features of unstable structures, containing sulfur and nitrogen. We have also found theoretical evidence about the existence of a four membered intermediate ring, and explored the energy surface along one of the most probable reaction coordinates for the formation and decomposition of it.

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