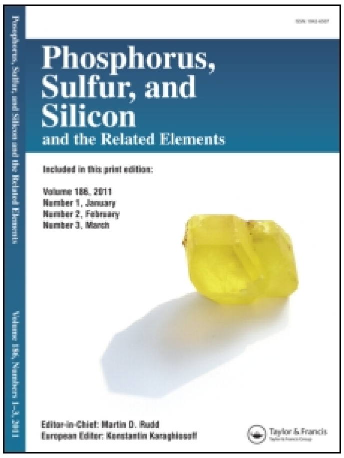

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Thionitroso Compounds: Theoretical Aspects of Structure and Reactivity

Vladimir Penkovsky[a]; Yuri Shermolovich[a]
[a] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

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THIONITROSO COMPOUNDS: THEORETICAL ASPECTS OF STRUCTURE AND REACTIVITY

VLADIMIR PENKOVSKY and YURI SHERMOLOVICH
Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Abstract The electronic structure and reactivity of thionitroso compounds is considered on the ground of MO LCAO SCF calculations.

Thionitroso compounds have been investigated least of all compounds of one-coordinated divalent sulfur in both theoretical and experimental aspect.[1] They are highly reactive which implies their rich synthetic possibilities; on the other hand, they are kinetically unstable. Hence, the application of quantum-chemical methods is desirable for studies of their structure and reactivity. Few data are available, however, in this field.[1]

We have performed wide-scale MO LCAO SCF studies of the molecular geometry, electronic structure and reactivity of thionitroso compounds using the MNDO-PM3 method. The geometry of all systems was completely optimized. The N = S bond length is almost unchanged in HNS, alkyl or polyfluoroalkyl derivatives (157-158 pm), in line with the ab initio data;[1] the bond index is nearly 2. The charge on the sulfur atom becomes positive in compounds with electron-withdrawing substituents, but is strongly negative in $(CH_3)_2NNS$ where the NS bond length increases to 164.5 pm. Hence, thionitroso compounds are polar and polarizable.

The LUMO of HNS and its derivatives are of π type, and their energies are low: from -2 to -3 eV, except that of $(CH_3)_2NNS$ (-1.0 eV). Moreover, the differences between the HOMO energy of butadiene and the LUMO energies of most thionitroso compounds vary from 6.5 to 7.7 eV, being considerably lower than that of a typical dienophile, acrylonitrile (9.32 eV), and close to that of tetracyanoethylene (6.83 eV). Thus, the known dienophilic properties of thionitroso compounds[1] are readily explained.

We also considered the site selectivity in the reactions of thionitroso compounds with isoprene. It follows from the values of the MO coefficients that the major product should be 2-R-4-methyl-3,6-dihydrothiazine. The NMR spectra of the major product indicated, however, that it was 2-t-butyl-5-methyl derivative.[2] Perhaps factors other than orbital terms play an important role in this process. One of these may be the biradicaloid nature of the transition state, due to a low singlet-triplet excitation energy of dienophiles. The stability of such biradical structures could be estimated by calculating the energies of formation of the species resulting from the attack of a free radical R^1 at either nitrogen or sulfur atom: $\Delta H_F(RNR^1S\cdot)$ and $\Delta H_F(R\dot{N}SR^1)$, respectively. The calculated $\Delta H_F(R\dot{N}SR^1)$ values are lower by 30-40 kJ/mol in case of the 2-methylallyl radical, indicating that its bonding to the sulfur atom of a thionitroso compound should be more favourable. Similar results were obtained for the bonding of the methyl radical. Consequently, the sulfur atom would be preferably attacked by a diene molecule, in line with the experimental data.

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