PHOSPHORUS, SULFUR, AND SILICON
https://doi.org/10.1080/10426507.2018.1490282

Synthesis, Characterization and Theoretical Study of the Chemical Reactivity of New Cyclic Sulfamides Linked to Tetrathiafulvalene

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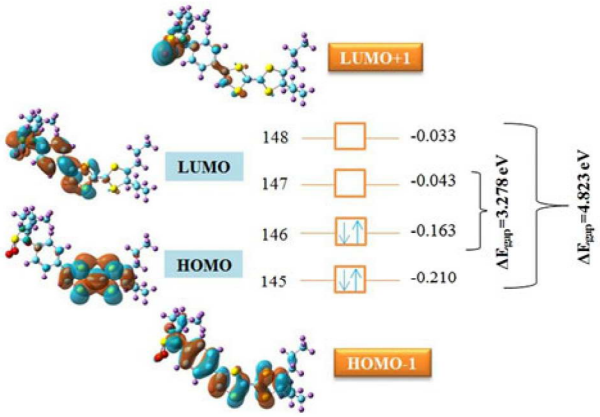
ABSTRACT

The synthesis of the title compounds has been carried out by condensation via a Wittig-type reaction of a pyridinium hexafluorophosphate with a phosphonate ester to give the desired (4-nitrophenyl)tetrathiafulvalene the nitro group of which was reduced to an amino group. Reaction of the amine with chlorosulfonyl isocyanate and subsequently with *tert*-butyl alcohol gave the corresponding open-chain sulfamide. Cyclization under basic conditions and de-protection led to 2-[4-(4′,5′-dipropyltetrathiafulvalen-4-yl)]phenyl-1,2,6-thiadiazinane 1,1-dioxide. Finally, *N*-alkylated and *N*-acylated cyclic sulfamides linked to tetrathiafulvalene were obtained. Their electron donor ability was measured by cyclic voltammetry. A detailed DFT study based on B3LYP/6–31G (d,p) of electronic properties is also presented. The calculated molecular electrostatic potential shows that, the negative charge covers the nitro and sulfamide function, while positive charge is located at the hydrogen atoms of the amine and sulfamide rings. The calculated HOMO and LUMO energy reveals that charge transfer occurs within the molecule. The chemical reactivity parameters reveal that tetrathiafulvalene 1 is highly reactive, which facilitates the desired formation of the cyclic sulfamide. The first hyperpolarizability β_{tot} shows that compounds 1 and 5 are good candidates as a NLO material.

ARTICLE HISTORY
Received 2 April 2018
Accepted 13 June 2018

KEYWORDS
Cyclic sulfamide; tetrathiafulvalene; density functional theory; computational chemistry

GRAPHICAL ABSTRACT



Introduction

Sulfur and nitrogen containing heterocyclic compounds are key building blocks used to develop compounds of biological or medicinal interest. Heterocyclic compounds also have a practical use as components in dyes, antioxidants, copolymers, bases, and ligands. They are not only used as drugs but also in the field of electronics and superconductors.[1] Tetrathiafulvalenes belong to the most representative examples. Due to their unique π-donor properties, tetrathiafulvalene (TTF) and its derivatives represent the basis of the large majority of organic metals and superconductors known so far.[2] One of the trends in TFF research has been and still is the incorporation of various spacer groups into the central double bond as a means to achieve better overlap between the molecules in the solid state, as well as lowering the electron-electron repulsion in the molecule.[3,4] Initially, they were extensively studied in the context of organic electronics due to their ability to form conductive, semi-conductive, and superconductive solid-state phases.[2]

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