
Electronic structure and reactivity of thiones and selenones

in the heteroaromatic series

V. P. Litvinov, A. A. Guliev, I. A. Dzhumaev, and I. A. Abronin

Quantum mechanical calculations were carried out for a series of thieno- and selenophenodihetero-2-thiones and selenones using the semiempirical SCF MO LCAO method and the CNDO/2 valence approximations with complete optimization of geometric parameters. The data obtained in this way was used to determine the reactivity of the compounds in processes leading to the formation of corresponding heterofulvalenes.

The synthesis of charge transfer complexes (CTC) based on tetrathiafulvalenes and tetraselenafuvalenes [1] constitutes a major achievement of the past few years in the preparation of organic substances displaying electronic conductivity similar to metals (so-called "organic metals"). Several superconductors based on these compounds are known [2-4]. Heterofulvalenes condensed with benzene or, in particular, heteroaromatic rings could also serve as prospective donor compounds in CTC. The introduction of additional heteroatoms of different natures into these systems would permit one to systematically and delicately vary the structural characteristics of the CTC, which, in turn, determine whether their phase transition properties are of the semiconductor-conductor or conductor-superconductor type.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Original article submitted March 22, 1984.
In the present paper we present the results of quantum mechanical calculations on isomeric thieno- and selenopheno-1,3-dihetero-2-thiones and selenones (I-IV).

The goal of these calculations was to determine the structural parameters of the compounds, which are missing in the literature, and also their electronic structures, which influence their reactivity to give the corresponding heterofulvalenes.

One of the principal problems in calculating the geometric parameters of compounds containing Period III and IV atoms is the choice of the basis set (sp- vs. spd-). In order to resolve this difficulty the geometric parameters of thiophene and selenophene were calculated using both of these basis sets.

The calculated C-X and C-C bond lengths and bond angles, as well as the experimental values (for thiophene and selenophene) are presented in Table 1. As seen in Table 1, the C-X bond lengths using the spd-basis set are in better agreement with the experimental values (the calculated C-C bond lengths are satisfactory using either the sp- or spd-basis sets); the bond angle calculations, however, are completely unsatisfactory using the spd-basis set. The calculated bond angles using the sp-basis set, on the other hand, differ from the experimental values by no more than 8°. For this reason, further calculations were carried out using the sp-basis set.

The calculated values for the geometric parameters of the compounds under investigation are presented in Table 2. These results indicate that all of the compounds are planar. Furthermore, these results agree with calculations for Ia and IIa using the MINDO/3 method, in which the problem of nonplanar distortion was specifically addressed [7]. According to this method, the heteroaromatic fragments retain to a large extent their individual characteristics, regardless of the nature of the heteroatom, the properties of atoms attached to it, or the method of annelation; in all cases their structural parameters are very close to those for the individual heterocycles. Replacement of a S atom with a Se atom increases the corresponding bond length with carbon by 0.25 Å, and also changes the valence angles (compare I and III, II and IV, as well as a and e, Table 2). A pronounced change in valence angles also accompanies a change in the mode of annelation — from a formal double bond with the aromatic heterocycle (I, III) to a formal single bond with the aromatic heterocycle (II, IV).

The C-X₉ bond length does not depend on the nature of the other heteroatoms in the condensed heterocycles I-IV, but is determined only by the nature of X₉ (S vs. Se). For their part the structural parameters for the condensed heterocycle fragment are also independent of the nature of X₉ (compare values for I and III or II and IV, a-h, respectively, Table 2). This leads one to propose that the structural parameters compiled in Table 2 for the cyclic fragments could be employed in calculations of the corresponding heterofulvalenes.