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## CHAIN- AND RING-LIKE SULPHUR CLUSTERS: MODELING WITHIN HYPERCHEM PROGRAM

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Different types of chain- and ring-like clusters formed of 2–10 sulphur atoms were simulated using HyperChem 7.5 program. It was shown that chains consisting of 5 and more sulphur atoms as well as rings including 6 or 8 sulphur atoms are the most energetically favourable ones within covalent-bonded glassy network.

*Key words:* sulphur, ab initio calculations.

It well known, there are more than 50 sulphur modifications in dependence on preparation conditions [1, 2]. In general, we can divide these modifications into two large groups – crystalline (rhombohedral or monoclinic) and amorphous, in all these forms sulphur having tendencies to form chain or/and ring-like structural units. If sulphur atoms being interconnected between each others form so called *cis*-configurations, the ring-like molecules can be formed [2]. It takes place, in particular, provided 8 sulphur atoms are involved. Otherwise, the chain-like configurations of *trans*-interconnected sulphur atoms are formed. Chain- and ring-like structural units are kept both in crystals and in amorphous sulphur (for example, S<sub>8</sub> monoclinic modifications of sulphur [1]). In addition, all these structural units can be found in sulphur-rich chalcogenide glasses depending on their chemical composition, in particular binary As/Ge-S vitreous compounds.

In this work, the possibilities to form ring- and chain-like structural groups of sulphur are analysed using HyperChem 7.5 program. Ab initio calculations with RHF/6-311G\* basis set were used to determine the total energies of clusters in dependence on number of sulphur atoms. But, this program can calculate only molecular clusters, such as ring-like sulphur. However, the chain-like clusters are open. We should saturate bonds by hydrogen atoms having very small bond energy [3] to transform them into molecular-like form. After the procedure of geometrical optimization and single point calculations, we receive the total energy of chain-like cluster  $E^{\Sigma}$ , after that we divide energy of add hydrogen atoms  $E_H$  and energy of sulphur-hydrogen bond  $E_{S-H}$ . We got formation energy of ring-like and chain-like clusters of sulphur  $E_i$ :

$$E_t = E^\Sigma - E_H - E_{S-H} \quad (1)$$

Thus, having energy of ring-like and chain-like clusters of sulphur  $E_t$ , we divide from them energy of all sulphur atoms included in cluster  $E_{at}$ . After that we got formation energy of cluster:

$$E_f^\Sigma = E_t - E_{at} \quad (2)$$

We entered average formation energy parameter (AFE) for each our cluster, where  $N$  is the total number of atoms in cluster without hydrogen and  $E_f^\Sigma$  is formation energy without hydrogen:

$$AFE = \frac{E_f^\Sigma}{N} \quad (3)$$

Average formation energy of cluster is got by us and set to be the base criterion for determination of possibility of existence of those or other clusters.

Geometrically optimized ring- and chain-like clusters are shown on fig. 1. The bond lengths and angles between atoms are presented in table.

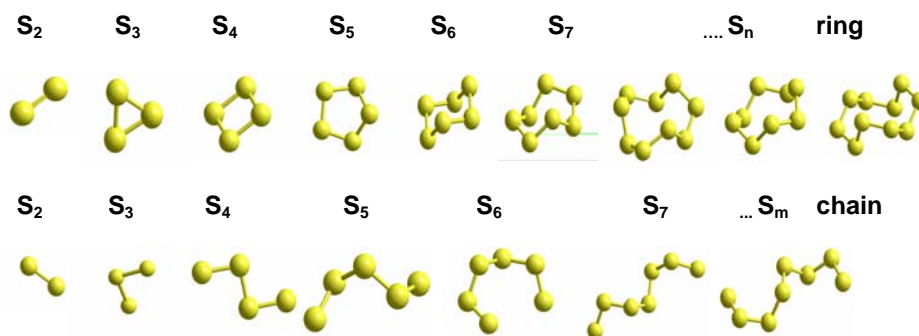


Fig. 1. Geometrically optimized ring- and chain-like sulphur clusters

The projection of experimentally determined crystallographic structure of  $S_8$  ring is shown on fig. 2 [4, 5]. Our results well correlate with proper information for crystalline analogue (the bond lengths and angles between atoms are practically equal).

Table

The bond lengths and angles between atoms for modelling  $S_8$  cluster

Bond lengths, $10^{-4}$ nm	2068,7	2069,0	2068,7	2067,9	2068,8	2069,1	2068,6	2068,1
Angles between atoms, grad.	107,50	107,49	107,53	107,51	107,49	107,47	107,53	107,50

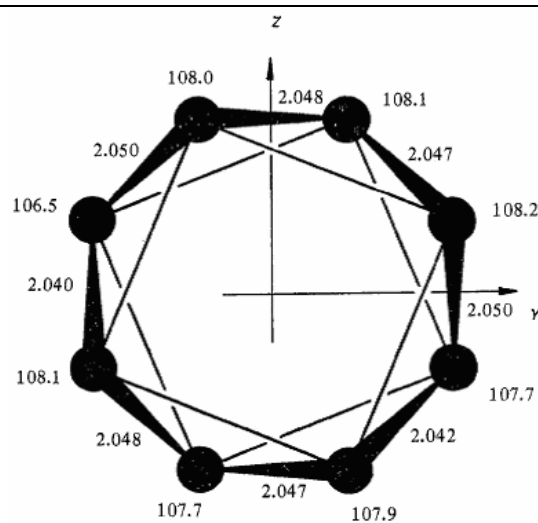


Fig. 2. Schematic image bond lengths and angles between atoms for crystalline S<sub>8</sub> [5, 6]

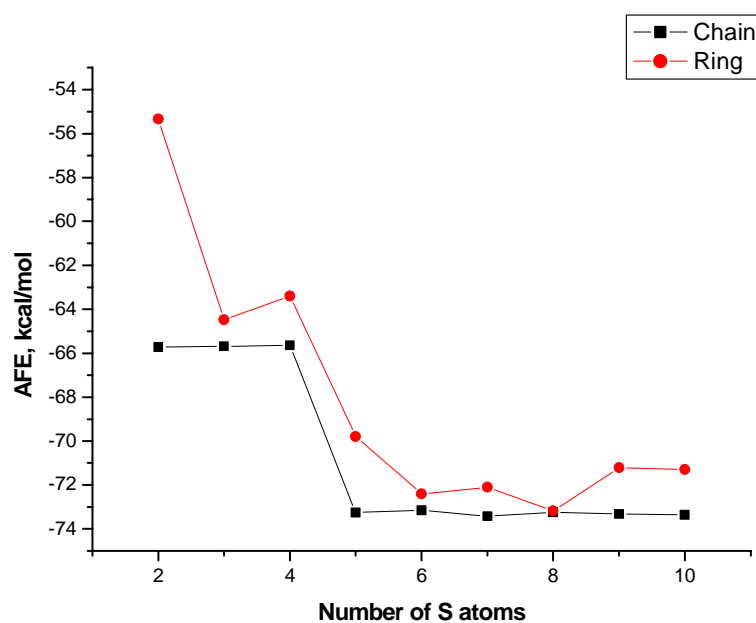


Fig. 3. Average formation energy in dependence from number of sulphur atoms

The AFE in dependence on number of sulphur atoms for ring- and chain-like clusters is shown on fig. 3. The performed calculations showed that S<sub>8</sub>- and S<sub>6</sub>-ring are the most energy favourable for S<sub>n</sub>-ring clusters. In case of S<sub>m</sub>-chain-like clusters, this

situation is apparently different. The chains involving 5 or more sulphur atoms have the minimal AFE.

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#### ЛАНЦЮГОВО- ТА КІЛЬЦЕПОДІБНІ СІРКОВІ КЛАСТЕРИ: МОДЕЛЮВАННЯ ЗА ДОПОМОГОЮ ПРОГРАМИ HYPERCHEM

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За допомогою програми HyperChem 7.5 проведено квантово-хімічні числення ефективності утворення ланцюгових та кільцеподібних кластерів сірки, що містять 2–10 атомів. Показано, що енергетично вигідними є ланцюги сірки, що мають 5 і більше атомів, а також кільця з 6 та 8 атомів сірки.

*Ключові слова:* сірка, ab initio обрахунки.

**ЦЕПЕ- И КОЛЬЦЕОБРАЗНЫЕ СЕРНЫЕ КЛАСТЕРЫ:  
МОДЕЛИРОВАНИЕ С ПОМОЩЬЮ ПРОГРАММЫ HYPERCHEM****В. Бойко<sup>1,2</sup>, М. Хиля<sup>3</sup>, О. Шпотюк<sup>1</sup>**

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С помощью программы HyperChem 7.5 проведены квантово-химические расчеты эффективности образования цепеобразных и кольцеобразных кластеров серы, которые содержат 2–10 атомов. Показано, что энергетически выгодными являются цепи серы, которые имеют 5 и больше атомов, а также кольца с 6 и 8 атомов серы.

Ключевые слова: сера, ab initio расчет.

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