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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 then 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_8 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^{Σ}, 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_t:

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

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^{Σ} is formation energy without hydrogen:

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

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.

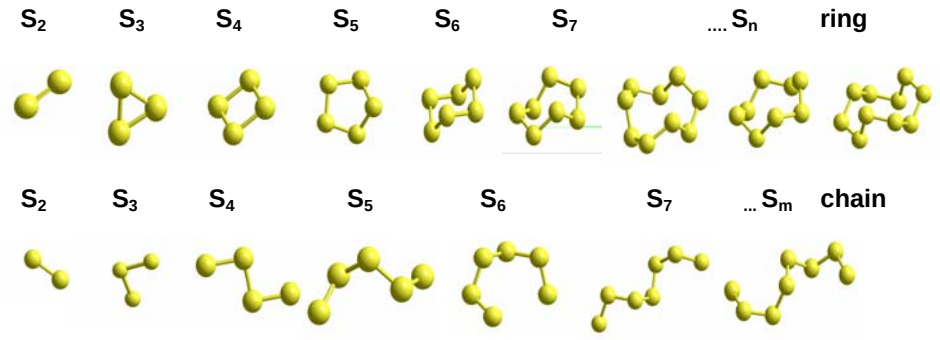

Fig. 1. Geometrically optimized ring- and chain-like sulphur clusters

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

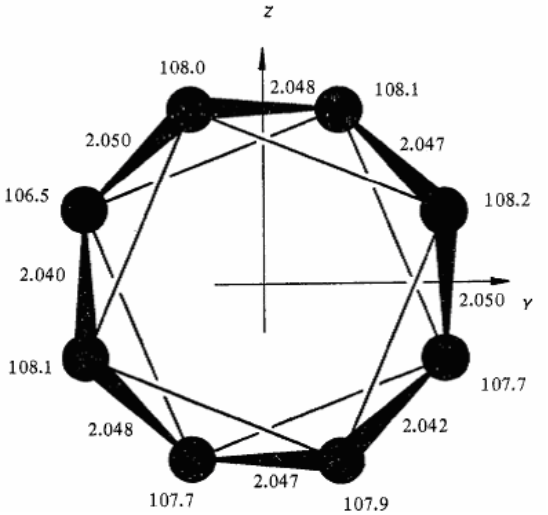

Fig. 2. Schematic image bond lengths and angles between atoms for crystalline S_8 [5, 6]

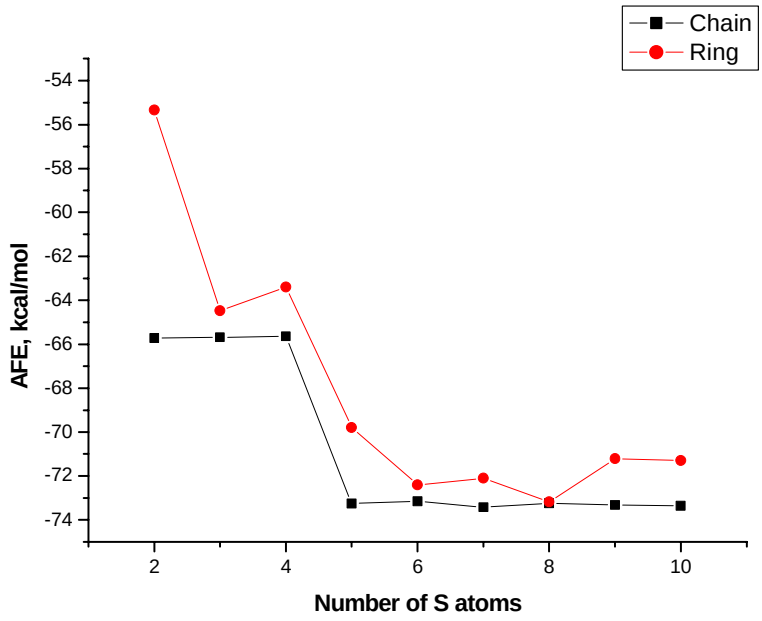

Fig. 3. Average formation energy in dependence from number of sulphur atoms

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_8- and S_6-ring are the most energy favourable for S_n-ring clusters. In case of S_m-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

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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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