

STABILITY OF SILICON DOPED C₆₀ DIMERS*Pedro A. Marcos¹, María J. López² and Julio A. Alonso²**¹Dpto. de Física, Universidad de Burgos, EPS, C/ Villadiego, s/n, 09001 Burgos, Spain**²Dpto. de Física Teórica, Universidad de Valladolid, 47011 Valladolid, Spain**pamarcos@ubu.es*

Since the discovery of fullerenes in 1985 [1], many researchers have focus their interest on the possibilities which these molecules offers from their chemistry point of view. In principle it was assumed that these molecules were electronically neutral, however it is well known their capacity to react with different elements due to their electrophile character. For this reason, many new materials of relevant technological interest have been synthesized, based on doping carbon structures using atoms of different species. One of the natural candidates used for doping is silicon, essentially due to its similar valence electronic structure with carbon.

On the one hand, it is well known the extensive production of silicon doped fullerenes in a experimentally way [2,3], and also, from a theoretical point of view, it has been demonstrated that silicon could be used, either to replace carbon atoms at the fullerene, or for covering the surface of this molecule, without destabilizing its cage structure [4-6].

On the other hand, polymerized structures using fullerenes such as C₆₀ are known to be stable. This kind of compounds are proposed to be good candidates for substituting diamond as the hardest material. However, the interaction process between the individual molecules is not totally clear [7]. In this sense we suggest the use of silicon doped fullerenes for designing new types of polymerized chains. The crucial aspect arises form the preference of silicon for a *sp*³ hybridization, which provides a favorable layout for connecting fullerenes due to the three dimensional framework which the bonds offer.

We present a theoretical study of the stability of different dimeric configurations consisting on two molecules having C₆₀-like geometry, bridged through covalent bonds provided by silicon atoms. Silicon atoms could act in a substitutional or exohedral arrangement, so that we have performed a systematic for generating the configurations as a function of the number of silicon atoms and their relative positions at the dimer. Understanding the mechanisms which take part into the bridging of two molecules could give a reasonable insight about the formation of larger chains, and extensively, about other kind of packing.

In this work, firstly we study geometries containing a number which ranges form 1 to 4 silicon atoms only in substitutional arrangement. The dimers suggested are: C₅₉Si-C₅₉, C₅₉Si-C₆₀, C₅₉Si-C₅₉Si, C₅₈Si₂-C₅₉Si, and C₅₈Si₂-C₅₈Si₂. For every dimer of those proposed here, we have checked a high number of possible configurations, characterized by the relative orientation of the atoms during bridging process. The argument to define the stability of those configurations lies on the energetic contribution of bonds involved in the connection of the individual molecules. Comparing the results obtained, we choose those having higher values of this bonding energy. Method employed for relaxation of geometries is the Conjugate Gradients (CG) technique, using Density Functional Tight Binding model (DFTB) due to Porezag and coworkers [8], for describing interactions between atoms. This model has been extensively used for the simulation of condensed matter systems, as well as for clusters and nanostructures.

Obtained results have shown that stability increases as the number of silicon atoms grows. The only exception occurs for the C₅₉Si-C₅₉ dimer, where bonding energy is the highest one.

Bonding involving four silicon atoms by means of two Si–Si bonds, noticeable improves our results achieved for pure C₆₀–C₆₀ dimer.

In order to complete the study of the stability, secondly we investigate the evolution of these systems as a function of temperature, to detect their possible applicability for designing larger polymer chains and their potential use in electronics. Starting from configurations at 0 K, we rise progressively the temperature of the system increasing the kinetic energy of the atoms. The method implemented for calculating thermodynamic averages is constant energy Molecular Dynamics (MD). The length of trajectories varies between 25 and 50 ps, using a time step of 0.5 ps for integrating the equations of motion.

What we obtain is that dimers connected by more than one covalent bond manifest good thermal stability since the structure remains intact for upper values than room temperature. In contrast, couples of molecules bridged only by one Si–C or Si–Si bond, break into two fragments at very low temperatures. Some structures perform structural changes before fragmentation occurs, giving rise to isomers which are more stable than those used as starting point for heating.

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