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DFT study of the self-aggregation of asphaltene model compounds

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Abstract: Asphaltenes are compounds found in the heavier fractions of the oil as a supramolecular aggregates [1]. The chemical complexity of these fractions of oil creates difficulties for their understanding and the prediction of their behavior. However, many authors have performed studies related to their chemical structure and properties, proposing molecules as asphaltene models, mainly based on data obtained by nuclear magnetic resonance (NMR), elemental analysis and molecular weight [2]. Asphaltenes can cause serious problems in oil exploration, triggered mainly to their deposition that is due to the level of molecular aggregation. The problems caused by the deposition of asphaltenes are present from the exploration to the refining of the petroleum. Thus, it is extremely important to know the mechanisms of aggregation of asphaltenes.

In this work, we performed a theoretical study of the homodimerization and self-aggregation of asphaltene model compounds A and B (Figure 1). These model compounds contain fused aromatic rings and heterocyclic fragments representative of asphaltenes tethered with butyl linkers to represent archipelago asphaltenes [3]. The ability of the DFT functional ωB97X-D and 6-31+G (d, p) basis set to predict the optimized geometry and the thermochemistry of aggregation was evaluated [4,5].

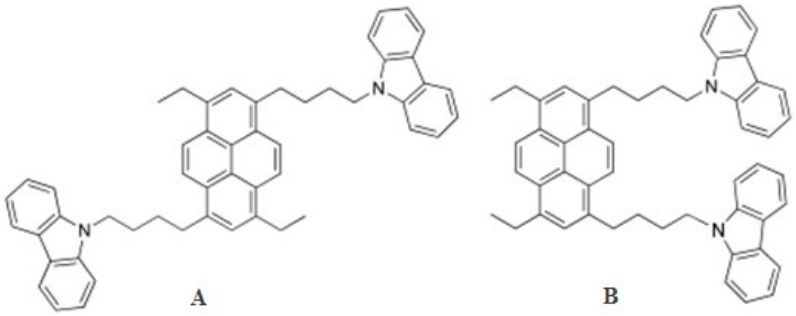

Figure 1. Chemical structures of the asphaltene model compounds A and B**.**

Through the optimized structures A and B, two self-aggregation arrangements, called "Hamburger" and "Self-aggregation" were proposed (Figure 2). The aggregation free energies, given relative to the free energy of the optimized asphaltene structure without self-aggregation (open structure), are listed in Table 1.

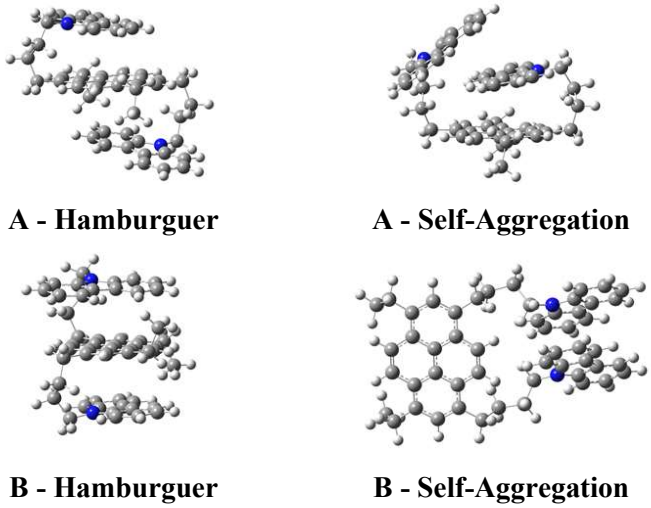

Figure 2. Self-aggregation structures of the asphaltene model compounds (A and B).

Table 1. Values of the free energy difference of the asphaltenes structures.

Model Compound	Hamburguer	Self-aggregation
A	-9.83	-8.54
B	-16.15	-13.86

Therefore, as observed for both cases, the proposed structure of self-aggregation "hamburger" has substantially lower free energy and would be the most probable conformation of these asphaltene model compounds.

Keywords: asphaltenes, aggregation, DFT, free energy.
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