

MOLECULAR MODELING AND AGGREGATION TENDENCIES OF ASPHALTENES HEPTOL SUBFRACTIONS

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ABSTRACT

Our approach to asphaltene studies is based on a combination of molecular modeling and structural features obtained from NMR and elemental analysis data, which takes into consideration the asphaltene's propensity for aggregation [1]. Thus molecular modeling has an important role in the investigation of aggregation processes and in identification of the interactions that are involved. Our most recent work was focused on the determination of the solubility profiles of asphaltenes from Brazilian vacuum residues in mixtures of heptane and toluene, or the so-called "heptol" mixtures. The results show that asphaltenes are efficiently fractionated by heptol solutions and led to a distribution of constituents with varying degrees of aromatic content. In the present work, the formation of aggregates of these asphaltene sub-fractions A and B (Figure 1 and 2), which have similar elemental compositions, was studied by molecular modeling. Structures were generated from ¹H and ¹³C NMR, molecular weights obtained by LIAD/MS [2] and elemental analysis. Molecular modeling studies on the association of asphaltenes was used as a basis for selecting structures that would have a tendency to associate more strongly from among those that reflect the analytical data.

EXPERIMENTAL

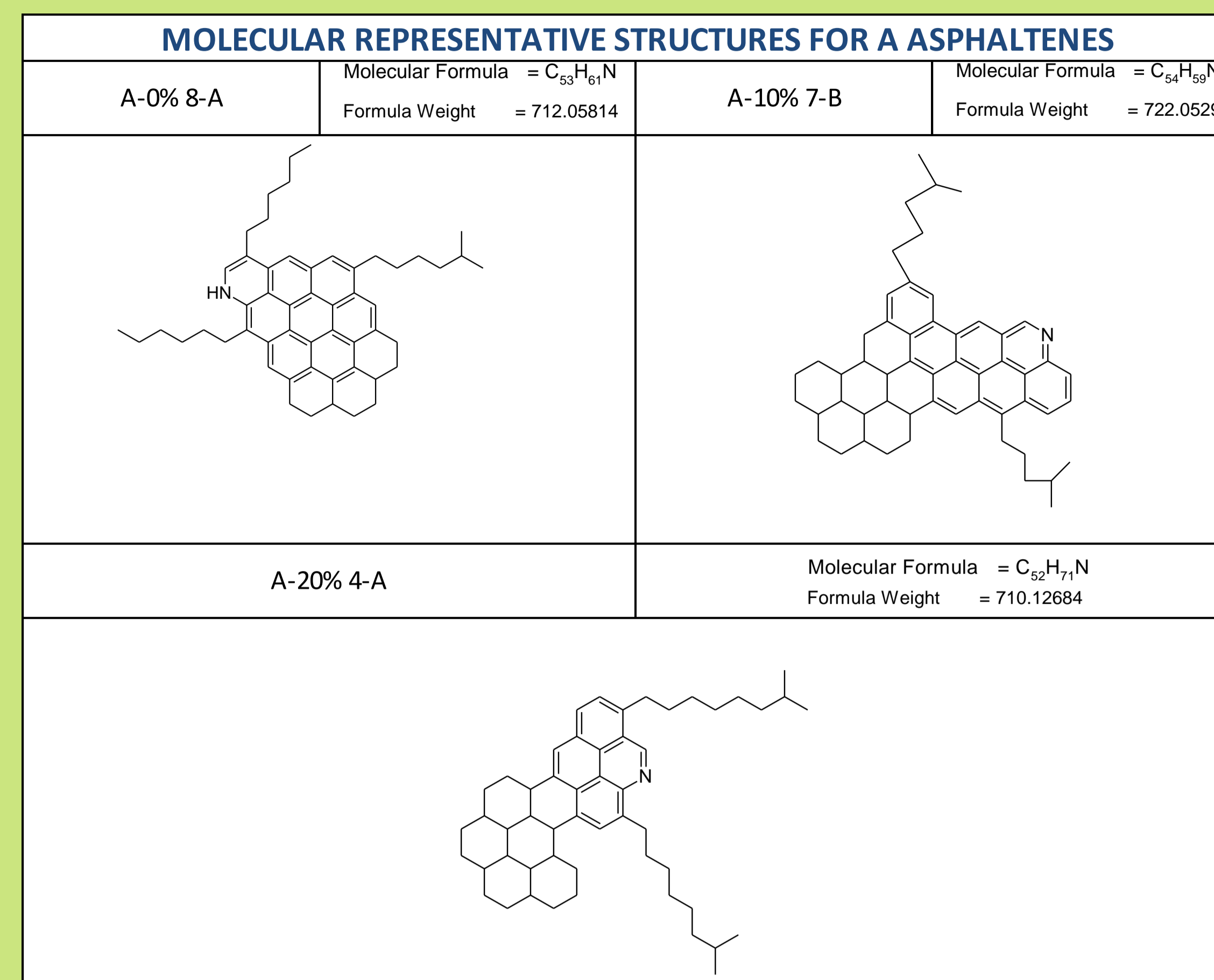
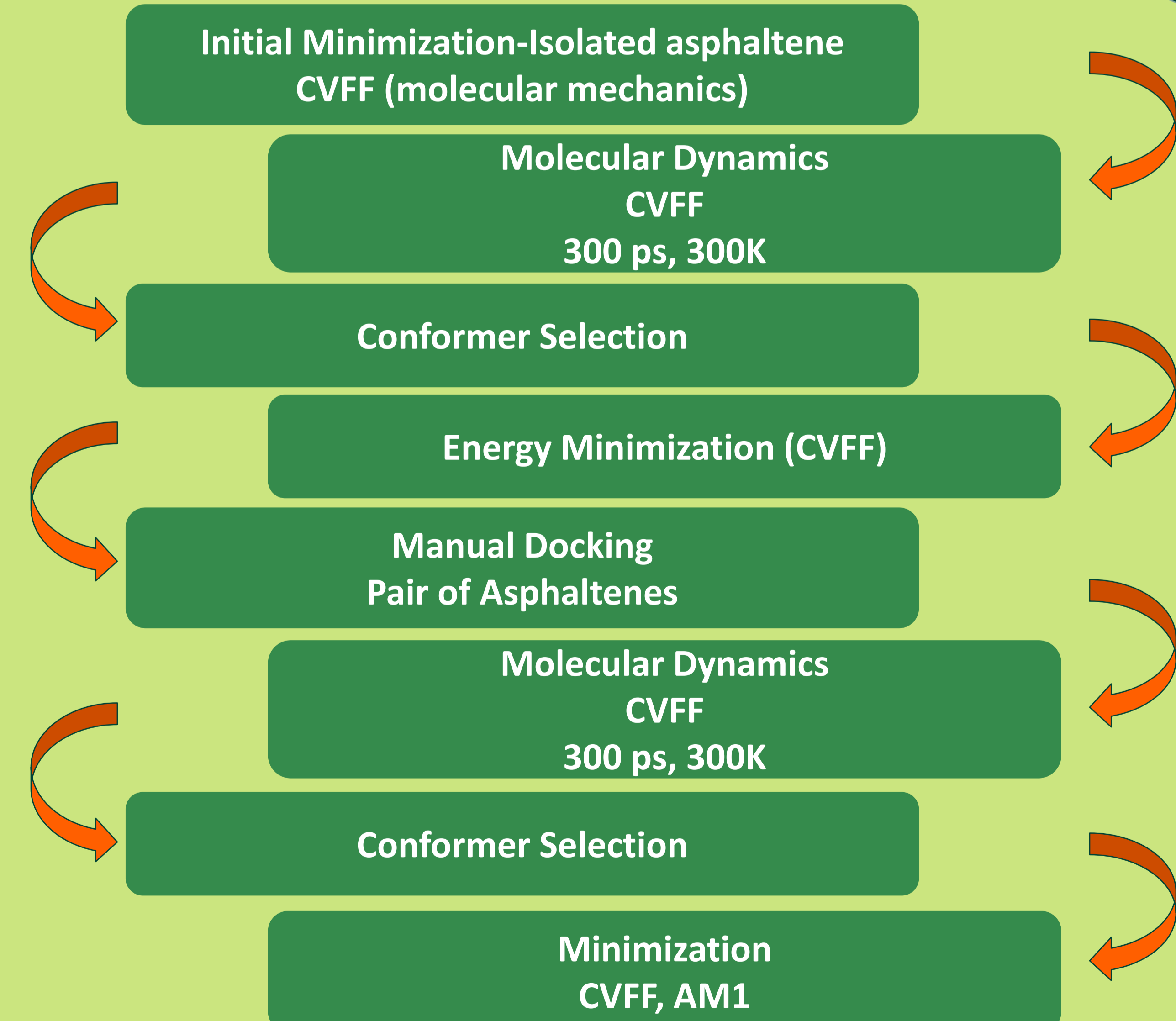


Figure 1. Molecular Representative Structures for A Asphaltenes

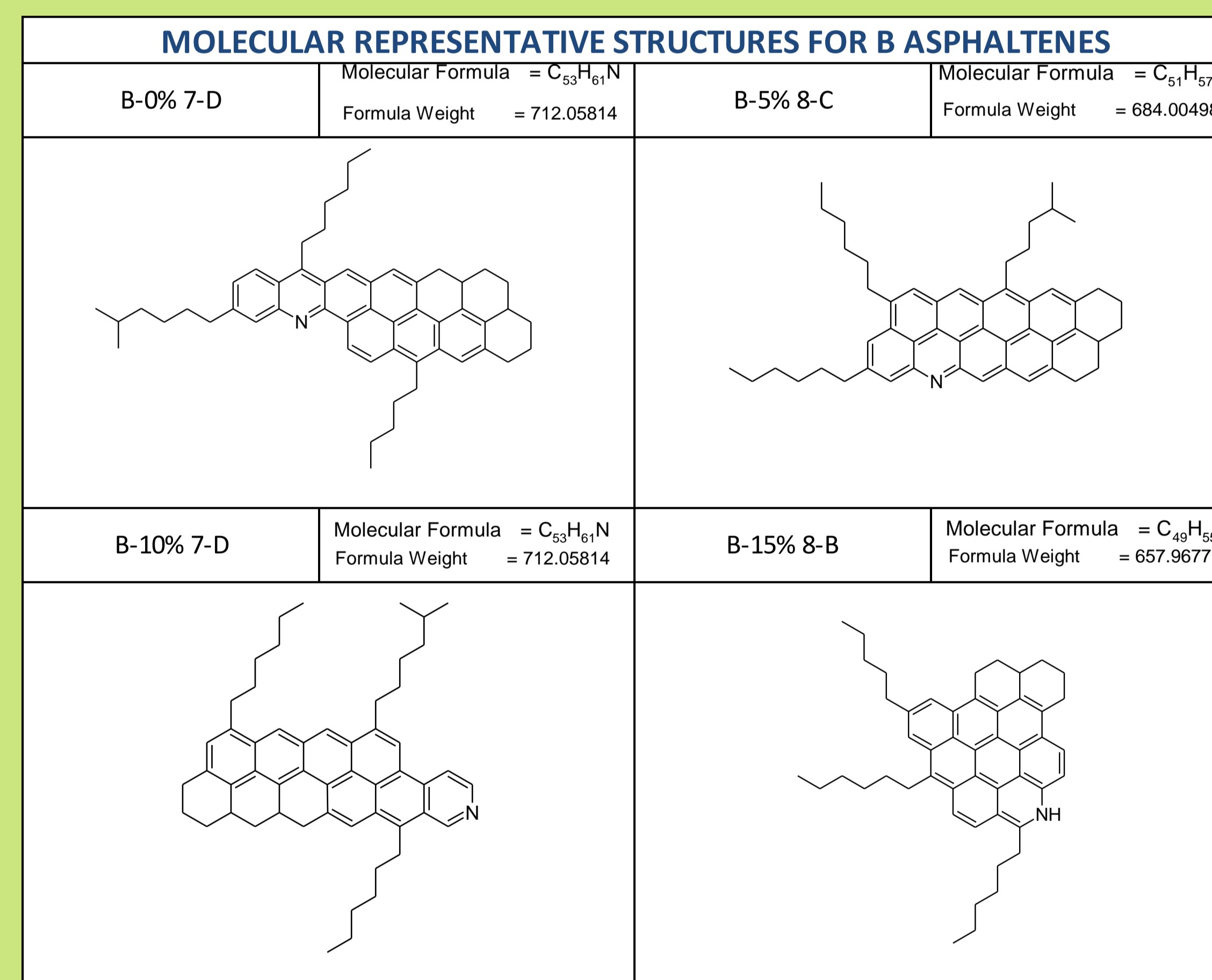


Figure 2. Molecular Representative Structures for B Asphaltenes

VR-A Dimers	Distance (Å)	VR-B Dimers	Distance (Å)
A-0%	3,50	B-0%	3,70
A-10%	3,67	B-5%	3,72
A-20%	3,97	B-10%	3,75
		B-15%	3,71

Table 1. Variation of the distance between aromatic ring systems for asphaltene heptol subfractions.

For all the models, the calculated energies are very consistent, mainly for pairs of asphaltenes for which aggregation is most favoured. Table 1 illustrates the variation in the distance between the two monomers of the aggregate during the simulation time.

Distances between aromatic rings for the more stable dimers in VR-B asphaltenes remained at a value around 3.7 Å. However it was observed that for the VR-A asphaltene sub-fractions, this distance undergoes a tenuous change. The shortest distance was found for the dimer formed by monomers A-10%.

CONCLUSIONS

Modifications on separation techniques may be important to identify different features in the compounds that are present in asphaltenes. According to RMN analytical data, A-10% sub-fraction, was the one with a higher aromatic content and the largest number of aromatics rings. Possibly this fraction has a higher tendency towards aggregation, and may have a lower degree of steric interference. This is a very interesting result, because it reflects the relationship between molecular modeling and structural properties related to aggregation processes.

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