

The PMO method for analysis of structural features of polycyclic aromatic hydrocarbons relevant to asphaltenes

Sócrates Acevedo, María Antonieta Ranaudo, Luis B. Gutiérrez and Gastón Escobar

Universidad Central de Venezuela, Facultad de Ciencias, Centro de Química Orgánica,
 47102 Caracas 1041 A, Venezuela
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Use of the simple perturbation molecular orbital (PMO) method allows the first-order estimation of energies of formation (E_f) of polycyclic aromatic hydrocarbons (PAH) as well as their localization (E_L) and bislocalization (E_b) energies. These calculations give theoretical support to experimental evidence in the literature which suggests that massive systems (more than six condensed aromatic rings) are not likely to be found in significant quantities in petroleum samples. From E_L and E_f it is predicted that ortho- and peri-fused systems such as pyrene are more likely than ortho-fused systems such as chrysene. The PMO method is also used for the estimation of first-order interaction energies responsible for the stabilization of free radicals. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polycyclic aromatic hydrocarbons; asphaltenes; PMO method)

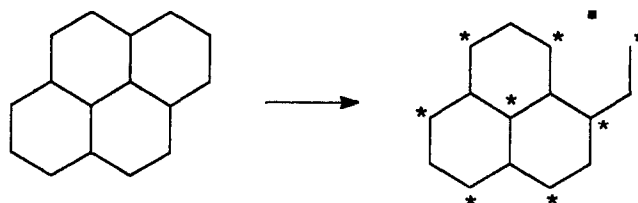
The structure of petroleum asphaltenes is a matter of considerable importance and has been the objective of many research projects^{1–12}. The formidable complexity of asphaltenes makes this a difficult if not impossible task and only so-called hypothetical structures have been reported.

Evidence from pyrolysis^{1,13}, chemical^{1,5} and physical¹ experiments suggests that large condensed polycyclic aromatic systems are absent in asphaltenes¹⁴. The purpose of the work described in this paper was to try to corroborate this theoretically using the perturbation molecular orbital (PMO) method developed by Dewar and co-workers¹⁵. This method has the advantage of being extremely simple and suited for polycyclic aromatic hydrocarbons (PAH). In spite of its simplicity, the method has been successfully applied to the prediction of chemical reactivity and equilibrium in organic chemistry¹⁵.

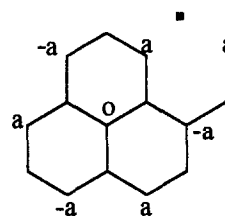
THEORY

The PMO treatment is based on the well-known Hückel treatment of π -electron systems. The advantage of the PMO method is its simplicity, which allows easy manual calculation of many important properties of PAH. The calculations require no knowledge of quantum mechanics.

The localization and bislocalization energies E_L and E_b are defined as the energies required to remove one or two carbon atoms from the aromatic system. An example of this for E_L of pyrene follows.



1. Removal of an atom from the aromatic system generates an odd hydrocarbon. Divide the atoms into two groups: starred and unstarred, beginning the starring with the atoms previously bonded to the one removed.
2. Assign a value, say a , such that the addition for starred atoms joined to a common unstarred one is zero. The result is



3. Find a using the normalization condition:

$$\sum a_i^2 = 1$$

$$a = 1/\sqrt{7}$$

4. Find the E_L value using the formula below, where a_i and

a_s are the atoms previously bonded to that removed:

$$E_L = 2\beta(a_r + a_s)$$

$$E_L/2\beta = 2/\sqrt{7}$$

Using a similar procedure the E_b values can be obtained. The details can be found in the literature¹⁵. For large

systems it is convenient to use a standard program for solving simultaneous equations.

It should be mentioned that the above calculations are first-order approximations and in general they are not appropriate for systems with heteroatoms, which are not considered here.

Table 1 Localization (E_L) and bislocalization (E_b) energies for aromatic compounds in β units^a


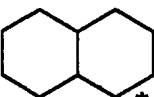
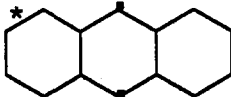
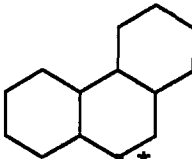
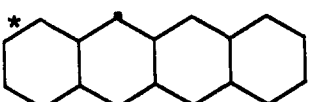
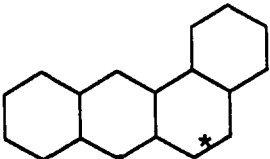
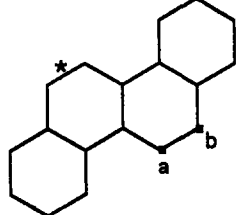
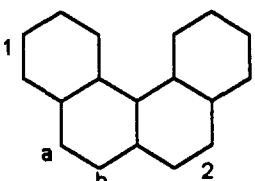
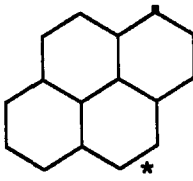
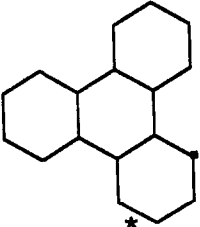
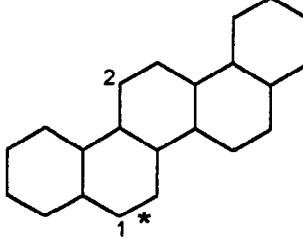
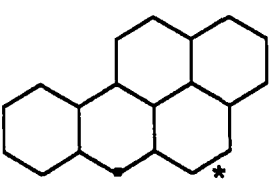
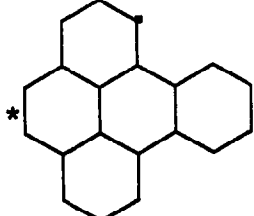
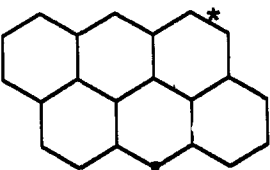
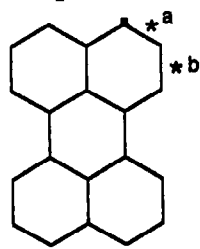
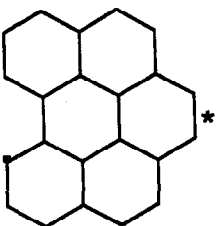
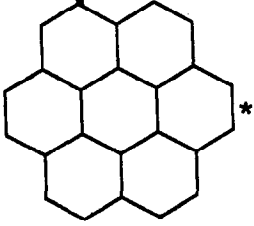
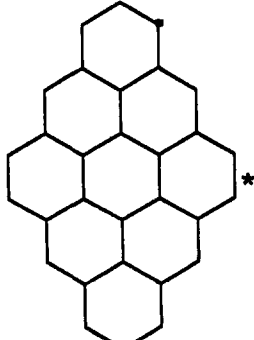
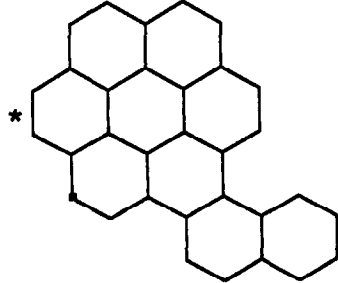
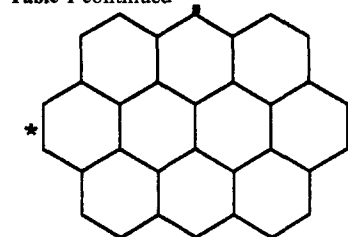
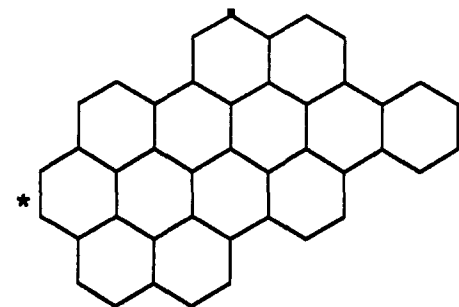
			
Benzene (1) E_L : 2.3 E_b : 3.46	Naphthalene (2) E_L E_b : 2.62 α : 1.81 β : 2.12	Anthracene (3) E_L : 1.26 E_b : 2.16	Phenanthrene (4) E_L : 1.8 E_b : 2.15
			
Naphthacene (5) E_L : 1.03 E_b : 1.86	Benz[a]anthracene (6) E_L : 1.48 E_b : 1.90	Chrysene (7) E_L : 0.95 E_L : 0.83 E_b : 2.23	
			
Benzo[a]phenanthrene (8) E_b : 1: 2.74 a: 0.89 2: 2.15 b: 0.93	Pyrene (9) E_L : 1.63 E_b : 2.04	Triphenylene (10) E_L : 2.00 E_b : 2.97	Picene (11) E_b : 2.19 E_L : 1: 0.83 E_L : 2: 0.89
			
Benzo[a]pyrene (12) E_L : 1.15 E_b : 1.72	Benzo[a]pyrene (13) E_L : 1.63 E_b : 2.04	Anthanthrene (14) E_L : 1.03 E_b : 1.64	Perylene (15) E_L : 1.39 E_b a: 2.30 b: 2.04
			
1,12-benzoperylene (16) E_L : 1.617 E_b : 2.45	Coronene (17) E_L : 1.8 E_b : 2.33	Dibenzo[bck]coronene (18) E_L : 0.8 E_b : 1.22	Naphtho[1,2,a]coronene (19) E_L : 1.69 E_b : 1.48

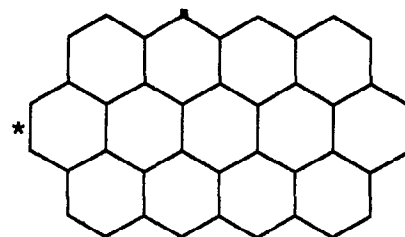
Table 1 continued



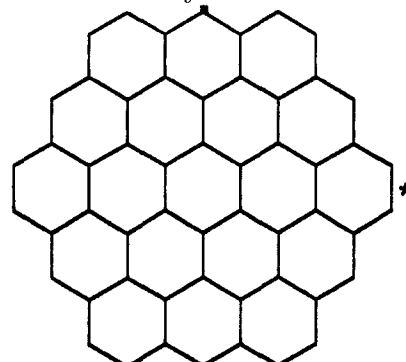
Ovalene (20)

 E_L : 1.27 E_b : 2.55

Benzo[a]phenanthro[1,2,11,12,g,f]benzo[a]coronene (22)

 E_L : 1.56 E_b : 1.91

Phenanthro[6,5,4,3,bcde]ovalene (21)

 E_L : 0.7 E_b : 2.23

Dodecabenzo[abc.....g]coronene (23)

 E_L : 1.25 E_b : 1.85

^a Dots correspond to the position where E_L is evaluated, asterisks correspond to E_b . Unless indicated, these are minimum values. The E_b values of ethylene and butadiene are 2 and 1.24 respectively.

RESULTS AND DISCUSSION

Table 1 gives the E_L and E_b values for several aromatic compounds calculated using the procedure described above¹⁵. The equivalent E_b values for ethylene and butadiene were equalized to the bonding Hückel π -energy of the respective highest occupied molecular orbital. The E_L value of ethylene, equal to 1, and its E_b value, equal to 2, can be conveniently taken as reference values for comparison purposes. As expected, pericondensation or angular placement of rings provides less reactive compounds than their 'linear' analogue¹⁶. Linear placement of rings always leads to reactive systems irrespective of the size (cf. anthracene, ovalene and compound (23), naphthacene and compound (21) etc.).

This indicates that large and small systems can have comparable reactivities. Thus, if a fossil fuel sample contains no significant quantity of large systems (say, more than six condensed rings), the reason for this is to be found elsewhere.

Mechanism for the formation of PAH

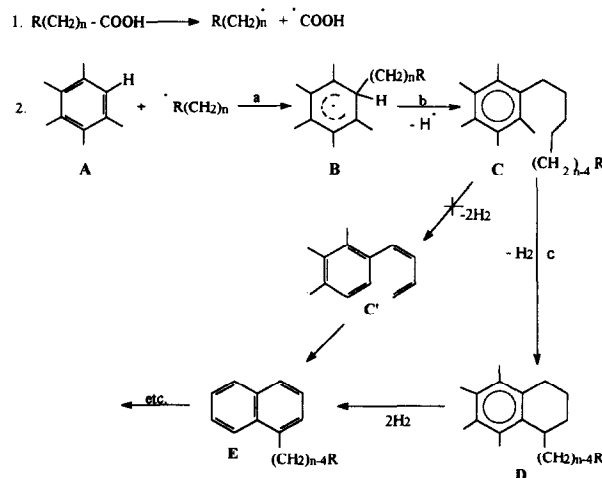
There is experimental evidence in the literature which suggests that fatty acids are important building blocks in the structure of petroleum asphaltene¹. This and other information reported for the free radical alkylation of aromatic compounds by carboxylic acids¹⁷ can be used to propose the mechanism presented in Scheme 1 for the alkylation of aromatic units in fossil fuels.

In this process the steps a and c are very important in regard to the structure of the final compound. On energetic grounds, these steps are controlled by the localization energy of the carbon atoms involved.

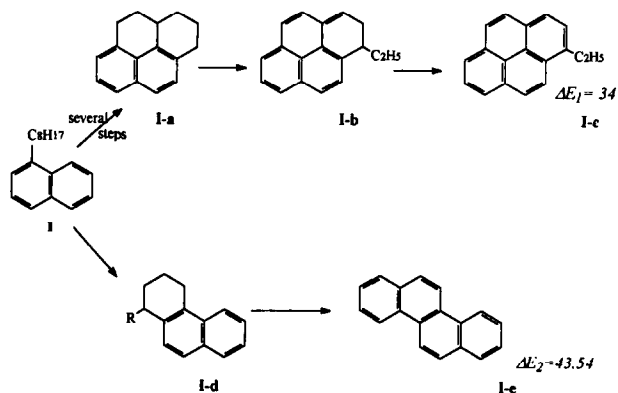
In this mechanism, it is suggested that the formation of the ring (C \rightarrow D) occurs before double-bond formation (D \rightarrow E). Inversion of this procedure leads to the butadiene derivative C'. This situation is highly unlikely

because, among other factors, the reactivity of this butadiene is very high. Using PMO, the E_L value in this case is equal to the localization energy of butadiene, namely 1.24β . Hence, this hypothetical intermediate would be hydrogenated quite easily in hydrogen exchange reaction (see below) or polymerized, avoiding the formation of E.

In Scheme 2 the formation of a pyrene derivative and chrysene starting from the α -octylnaphthalene I is considered as a particular example. The alkyl attack should occur on the α -position of naphthalene, due to its lower E_L value (see Table 1). Another attack on the adjacent α -position will lead eventually to a pyrene derivative. Using the energy values (kJ mol^{-1}) of 434.7 for the H-H bond, 397 for the C-H bond and 355.3 for the C-C bond for the σ bonds and PMO for the π changes, with a β value of 62.7 kJ mol^{-1} , the ΔE_1 and



Scheme 1 Route for the formation of PAH (see text)



Scheme 2 Routes for the formation of chrysene and 3-ethylpyrene. Energy values are in kJ mol^{-1}

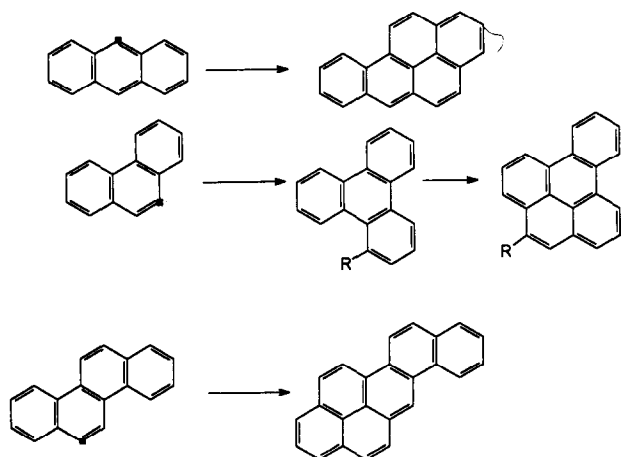
ΔE_2 could be obtained. Thus, according to this scheme, the formation of pyrene should be preferred.

In *Scheme 3* it is shown that attack on the most reactive position of anthracene, phenanthrene, chrysene or any other ortho-fused PAH will always eventually lead to a pyrene derivative.

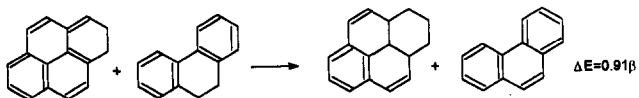
However, it should be mentioned that intermediates such as I-b (see *Scheme 2*) are highly reactive, for the same reason as given above in relation to butadiene derivatives. Thus, although the two saturated rings could be formed in a relatively easy way, their final aromatization could be hindered by hydrogen exchange.

Intramolecular and intermolecular hydrogen exchanges

The overall ΔE_1 and ΔE_2 values calculated above are highly endothermic. This is due to the large number of C-H bonds broken in this process (10 and 12 respectively). It is obvious that the formation of these hydrocarbons will be facilitated by intermolecular hydrogen exchanges. The equilibrium depicted in *Scheme 4* illustrates this point.



Scheme 3 Formation of pyrene derivatives starting from anthracene, phenanthrene and chrysene. The most reactive positions are indicated by dots



Scheme 4 Formation of phenanthrene by intermolecular hydrogen exchange

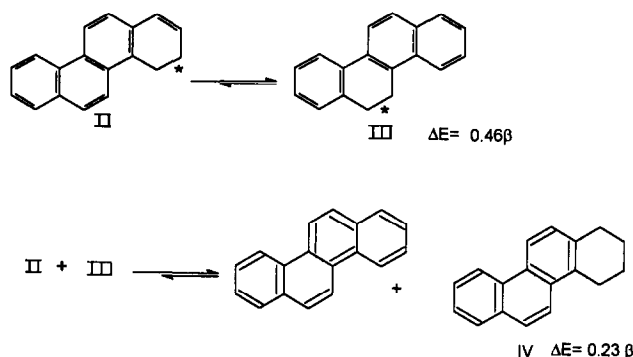
In this exothermic process, the energy difference is merely the difference between the bislocalization energies of butadiene and phenanthrene (see *Table 1*). The aromatization energy of 9,10-dihydrophenanthrene amounts to about $+221.5 \text{ kJ mol}^{-1}$ without hydrogen exchange. Thus, although this type of scheme would allow the aromatization of phenanthrene or any other compound, it will hinder the formation of pyrene. It should be mentioned that pyrene and its benzoderivatives (see *Table 1*) are themselves very reactive, having E_L values close to that for ethylene. Therefore, after they are formed, hydrogen exchange reactions could restore them to their hydrogenated precursors.

By similar arguments, intramolecular hydrogen exchange should also be an important consideration in the formation of PAH. For instance, equilibrium such as that shown in *Scheme 5* will lead to the formation of chrysene after the conversion of II to the tetrahydro-derivative IV.

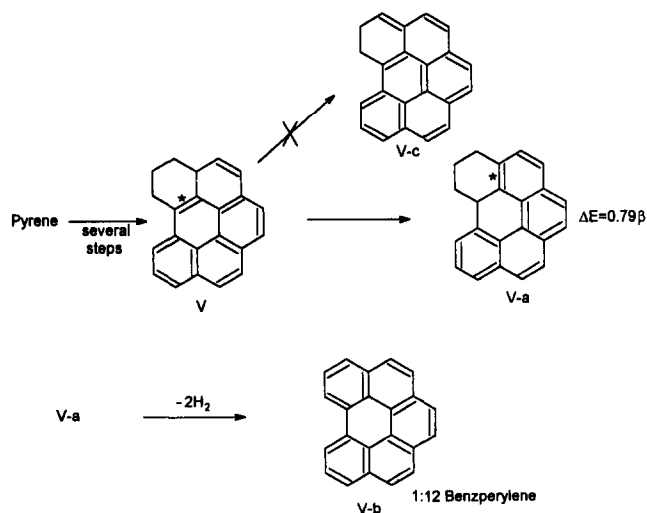
Another interesting scheme is that shown in *Scheme 6* for the formation of 1:12 benzperylene (V-b) starting from pyrene

In this case the intramolecular hydrogen exchange avoids the reactive intermediate V-c, allowing the eventual formation of V-b. It is possible that the most difficult path in the formation of V-b and other ortho- and peri-fused compounds such as coronene is the formation of pyrene (see above).

It can be concluded that the expected concentration of



Scheme 5 Formation of chrysene by hydrogen exchange



Scheme 6 Formation of 1:2-benzperylene from pyrene. ΔE is the difference between the E_b values of the indicated bond (see *Table 1*)

large systems with six or more condensed rings in petroleum and other relatively young sediments should be very low. Both hydrogen exchange and reactive intermediates are important barriers in their formation. This is in agreement with the experiment evidence quoted above.

According to the previous finding, it is suggested that the ortho-and-peri-fused compounds such as pyrene, benzopyrene and coronene found in fossil fuels are formed through a mechanism such as that depicted in *Scheme 1*. Ortho-fused PAH such as phenanthrene, chrysene and picene have their main source in natural products such as those derived from steroids. It is recognized that hopanes, cholestanes and other steranes are found in crude oils and other fossil sediments¹⁸.

It is believed that the use of PMO in general and the above results in particular could give important clues in the structural investigation of petroleum asphaltenes and other fossil samples. A review of the literature shows that many of the aromatic structures proposed for petroleum asphaltenes are based on massive fused PAH^{4,9,10}. As shown above, their presence in crude oils in any significant amount is very unlikely. A structure built from smaller aromatic units (no more than four or five rings) joined by aliphatic chains is a better proposition, in the present state of knowledge.

Free radicals

The presence of free radicals in carbon compounds has been reported several times in the literature^{8,9}. These species are very reactive and in general it is expected that they can exist only as intermediates for short periods of time. According to simple molecular orbital theories, the

bonding energy of the 'odd electron' is zero. Thus it is anticipated that when they form, a recombination reaction leading to stable compounds should follow immediately.

Systems with the structural feature of perinaphthyl (see *Scheme 7*) with an odd number of aromatic carbons should have a longer life than their even-number analogues, owing to their inability to aromatize. In any case, to remain in the medium, these free radicals must be stabilized by an electron transfer mechanism. The PMO theory could be used to justify the origin of such stabilization in the manner illustrated in *Scheme 7*. The corresponding change in π energy is equal to that for the conversion of an even to an odd hydrocarbon, namely $2\beta(1 - a_0)$ ¹⁵. This is illustrated in part (c) of *Scheme 7*.

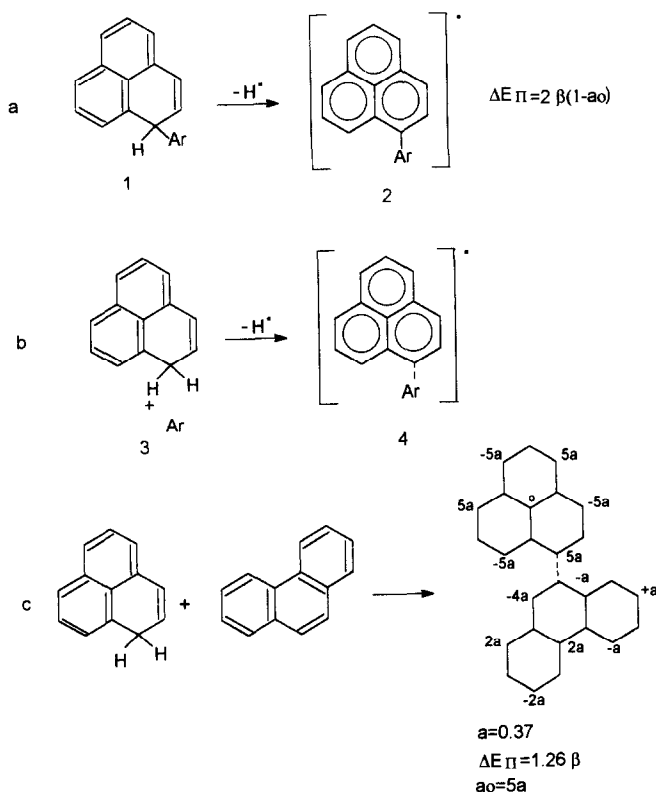
It is expected that in this case the value of β would be lower than that for a 'normal' double bond (about 62.7 kJ mol^{-1}). In any case, this study suggests that stabilization by electron transfer complexes could be very important in favourable cases where the two aromatic units could approach each other to bond distances.

By an extension of the arguments above, another even hydrocarbon could be attached to any other starred carbon of the radical 4 and provide an even larger reduction in energy. For instance, attaching another phenanthrene unit will lead to a ΔE_π value of 1.31β . Hence, it could be concluded that the free radicals present in petroleum samples could be stabilized by the formation of electron transfer aggregates. The corresponding first-order stabilization energies could be found quite easily using the PMO method.

Recent experiments have shown that after the extraction of Cerro Negro asphaltenes with acetone-THF mixtures, a fraction amounting to $\sim 12 \text{ wt}\%$ of the total asphaltenes was isolated. This material was insoluble in all solvents that dissolve asphaltenes (toluene, THF, pyridine, benzene etc.), suggesting the presence of very strong intermolecular associations. It is believed that this insoluble material is composed of molecular aggregates which, at least in part, are due to the presence of stabilized free radicals. The expected strong interactions described above are consistent with this solubility behaviour.

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Scheme 7 (a) The conversion of an even hydrocarbon (1) into an odd one (2), is equivalent to (b) the formation of the corresponding electron transfer complex (4). (c) calculation of the first-order change in the π energy (ΔE_π) for the perinaphthene and phenanthrene

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