SEMI-EMPIRICAL REACTIVITY STUDY ON LINEAR POLYACENES

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Linear polyacenes, although being the simplest aromatic hydrocarbons, are known up to the seventh member of the series (heptacene).[1] They are characterized by rapid increase in reactivity and decrease in stability as the chain length increases. Such an aromaticity is called by Clar[2] as acene character; it includes *meso*-rings in aromatic substituion/addition, and terminal rings in some other reactions as the most reactive sites. The following reactivity of linear polyacenes was studied in this work by semi-empirical PM3: aromatic *meso*-bromination, biochemical and artificial *ortho*-oxidation, total hydrogenation, *meso*-additions (hydrogenation, photochemical oxidation, addition of bromine and maleic acid anhydride) and *meso*-oxidation to quinones. The geometries of reactants and products were optimized, and heats of reactions calculated from heats of formation and total energies of the molecules. Molecular descriptors as graph-theoretical and PM3 resonance energy, hardness and Dewar's localization, para- and ortholocalization numbers were calculated. The heats of the reaction were analyzed as a function of chain length, and the reactions with similar energy profile were studied by Principal Component (PCA) and Hierachical Cluster Analysis (HCA). Partial Least Squares Regression (PLS) related heats of reaction to the molecular descriptors and the chain length. Energy profiles for *meso*-ring reactions have the same shape. They are described well in PCA by one Principal Component (over 99% of original information). Both PCA and HCA show that acene character begins with anthracene, with high similarity between molecules having the same number of different reactive sites. Both analyses distinguish *anti-* from *syn-* and in-plane oriented reactions. PLS models ($Q>0.96$, $R>0.98$) are superior to linear regression models ($R>0.75$).

1 W. J. Bailey, C.-W. Liao, J. Amer. Chem. Soc. **77** (1955) 992-994.

2 E. Clar: The Aromatic Sextet, Wiley&Sons, New York, 1972.