A Simple Rule regarding the Chemical Reactivity of S, T Isomer Pairs of kata-annellated Benzenoid Hydrocarbons

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For S, T isomer pairs of kata-annellated benzenoid hydrocarbons the inequality $N^{S}_{min} > N^{T}_{min}$ holds, where N^{S}_{min} and N^{T}_{min} denote the lowest PMO localization energy of the S and T isomer, respectively. This empirical rule indicates that for a given S, T pair normally the S isomer will be the less reactive one.

The now well-established concept of S, T isomers [1, 2] has been widely applied to polynuclear benzenoid hydrocarbons. The relations existing between the photoelectron spectra, first ionization potentials, electron affinities, HOMO-LUMO transition energies and total π electron energies of S, T isomer pairs of polynuclear benzenoid hydrocarbons have been studied in detail [1, 2]. Characteristics directly related to chemical reactivity, however, have so far not been examined within the concept of S, T isomers.

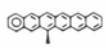
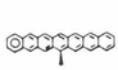
This note refers exclusively to kata-annellated benzenoid hydrocarbons. The respective lowest PMO localization energy N_{min} [3] of a given hydrocarbon is used as a measure of chemical reactivity. N_{min} values of S and T isomers are denoted by N^{S}_{min} and N^{T}_{min}, respectively.

The pairs of S, T isomers given in Table 1 stem from different topological models [1, 2] and the number of π electrons of the systems studied range from 14 to 30. N^{S}_{min} and N^{T}_{min} values are given for each pair of isomers. The circles in the hexagons denote Clar sextets [4] and the arrows on the formula mark the most reactive centres, i.e. the centres to which the N_{min} values refer.

With the exception of S, T pair 10, which has been found to exhibit "non-simple behaviour" [5], the following inequality holds

$$N^{S}_{min} > N^{T}_{min}. \quad (1)$$

Table 1. Lowest PMO localization energies (N_{min}, β units) of S, T isomer pairs of kata-annellated polycyclic aromatic hydrocarbons (arrows mark most reactive position).

	S	N^{S}_{min}	T	N^{T}_{min}
1.		1.796		1.265
2.		1.353		1.026
3.		1.668		1.353
4.		1.789		1.353
5.		1.789		1.668
6.		2.000		1.668
7.		1.093		0.800
8.		1.361		0.800
9.		1.290		1.093
10.		1.504		1.512
11.		1.504		1.290
12.		1.741		1.512
13.		1.741		1.711
14.		1.690		1.512
15.		1.711		1.690
16.		1.317		1.290
17.		1.112		0.672
18.		1.114		0.555

Although inequality 1 is an empirical observation and has not been analytically derived, the assumption seems to be justified that it is universally valid for S, T pairs of kata-annellated benzenoid hydrocarbons provided the S and T polynomials show "simple behaviour". As can be easily recognized from the examples given in Table 1, inequality 1 holds independently of the number of Clar sextets of the S and T isomers.

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