On Topology-Property Relations of Polycyclic Aromatic Hydrocarbons

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The hydrogen-depleted graphs of polycyclic aromatic hydrocarbons contain two types of vertices (with regard to their degree) and correspondingly three types of edges. The respective sums of these edges reflect the molecular topology of the hydrocarbons and were used for constructing a new topological index for kata-annellated aromatic hydrocarbons that correlates well with their topological resonance energies per electron. Dependent on the degrees of their first neighbours, the vertices of degree 2 of polycyclic hydrocarbons can be distinguished as to high, medium and low chemical reactivity of the corresponding carbon atoms, in agreement with the results from MO theory and experiments.

The electronic and other types of molecular properties of polycyclic aromatic hydrocarbons (PAH) depend strongly on the molecular topology of the systems [1]. The topology of PAH can be conveniently formulated in mathematical terms by means of so-called "topological indices" [2]. If such indices fulfill certain presuppositions [3] they correlate well with theoretically derived and experimental data and thus enable the chemist to obtain information relevant for his practical work, e.g. information on stability, reactivity etc. of as yet unknown hydrocarbons. In this note a new topological approach to *kata-annellated* PAH is presented.

The hydrogen-depleted graphs ("Hückel graphs" [4]) of PAH contain two types of vertices, i.e. vertices of degree 2 and 3 (denoted here by $v_{(2)}$ and $v_{(3)}$). Accordingly they contain three types of edges: $e(v_{(2)}, v_{(2)})$, $e(v_{(2)}, v_{(3)})$ and $e(v_{(3)}, v_{(3)})$ [5]. The corresponding sums of these edges

$$\sum_n e(v_{(2)}, v_{(2)}) \equiv E_{2,2},$$

$$\sum_n e(v_{(2)}, v_{(3)}) \equiv E_{2,3},$$

$$\sum_n e(v_{(3)}, v_{(3)}) \equiv E_{3,3}$$

reflect the topology of the individual PAH. By way of example, with increasing "branching" [6, 7] (e.g. tetracene, triphenylene) $E_{2,3}$ decreases while $E_{2,2}$ and $E_{3,3}$ increases. The ratio $E_{2,3}/E_{3,3}$ proves to be particularly suitable for designing new topological indices.

For the purpose of correlation analyses "topological resonance energies per electron" (TREPE) [8] were used because TREPE depend strongly on the topology of PAH and, furthermore, are linearly connected with other important (theoretical and experimental) parameters, e.g. first ionisation potentials of PAH [9]. For *isomeric* kata-annellated PAH linear correlations were found to exist between TREPE and the ratio $E_{2,3}/E_{3,3}$:

$$\text{TREPE}\,(\beta) = A_1 \left(\frac{E_{2,3}}{E_{3,3}}\right) + A_0 \,. \qquad (1)$$

C-numbers (C), A_0 and A_1 values, sample sizes (n) and correlation coefficients (r) are given in Table 1.

Although the ratio $E_{2,3}/E_{3,3}$ is not solely a function of branching but reflects to some extent also the size (number of carbon atoms) of the systems, an additional term is necessary to cope with PAH of different size in a single regression equation. The sum E_{tot} of all edges present in the graphs was taken as a measure for size, and multiple regression analysis did yield

$$\text{TREPE}\,(\beta) = -\,0.00379 \left(\frac{E_{2,3}}{E_{3,3}} + 0.05\,E_{\text{tot}}\right) + 0.04878. \qquad (2)$$

The correlation coefficient is 0.971 for a sample size $n = 34$. The sample included systems with 14, 18, 22, 26 and 30 carbon atoms (i.e. PAH with 3 to 7 rings) and did not include linear annellated PAH (acenes: anthracene, tetracene etc.).

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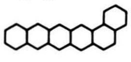
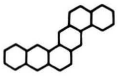
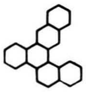
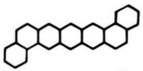
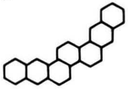
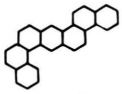
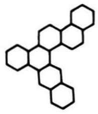
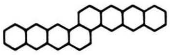
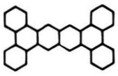
Table 1. Parameters related to (1).

C	A_0 ($\times 10^2$)	A_1 ($\times 10^2$)	n	r
18	4.436	− 0.365	4	0.986
22	4.288	− 0.341	9	0.977
26	4.265	− 0.377	10	0.980
30	4.349	− 0.437	10	0.980

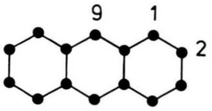
Table 2. Topological resonance energies per electron (β units).

PAH	TREPE (Eq. 2)	TREPE (Ref. [8])
	0.0384	0.0378
	0.0315	0.0308
	0.0343	0.0349
	0.0379	0.0374
	0.0325	0.0325
	0.0344	0.0341
	0.0359	0.0361
	0.0371	0.0374
	0.0309	0.0303
	0.0363	0.0382

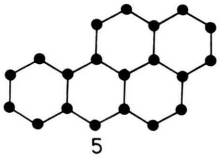
To test further the quality of the relationship, TREPE were calculated according to (2) for 10 randomly chosen kata-annellated PAH that were not contained in the original sample and compared with analytically derived TREPE [8] (Table 2). The deviation between approximate and exact TREPE values is in the range from 0 to 5% and the averaged deviation amounts to 1.6%. Thus the proposed new topological index

$$V = \frac{E_{2,3}}{E_{3,3}} + 0.05\,E_{\mathrm{tot}} \qquad (3)$$

seems to work quite satisfactorily. The design of related topological indices applicable to both kata-annellated and peri-condensed PAH should be possible.



I



II

Another feature of this topological approach related to chemical reactivity shall be mentioned briefly. The hydrogen-depleted graphs of PAH contain three types of vertices of degree 2 (i.e. positions that can react in substitution reactions), viz. $v_{(2)}$ adjacent to 2 vertices $v_{(2)}$ (e.g. the **2**-position in anthracene (**I**)), v_2 adjacent to 1 vertex $v_{(2)}$ and to another vertex $v_{(3)}$ (e.g. the **1**-position in **I**) and $v_{(2)}$ adjacent to 2 vertices $v_{(3)}$ (e.g. the **9**-position in **I**). Generally the reactivity of PAH increases in this order, as the comparison with reactivity indices derived from MO theory [10] and experimental data shows. Even in highly unsymmetrical PAH with many different reactive positions the most reactive position can in many cases thus be clearly identified by inspection of the graphs. By way of example, the hydrogen-depleted graph of benzo[a]pyrene (**II**) contains only 1 vertex $v_{(2)}$ adjacent to 2 vertices $v_{(3)}$, and it is well established that this 5-position (see formula **II**) is the most reactive one.

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[2] see: A. T. Balaban, in: Steric Fit in Quantitative Structure-Activity Relations (A. T. Balaban, A. Chiriac, I. Motoc, and Z. Simon), p. 22, Lecture Notes in Chemistry, No. 15, Springer-Verlag, Berlin-Heidelberg-New York 1980; D. H. Rouvray, in: Chemical Applications of Topology and Graph Theory (R. B. King, ed.), p. 159, Elsevier, Amsterdam 1983.
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[5] For an introduction to graph theory see: F. Harary, Graphentheorie, R. Oldenbourg-Verlag, München 1974.
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[7] M. Zander, Naturwiss. **69,** 436 (1982).
[8] I. Gutman, Coll. Sci. Papers, Faculty of Science, Kragujevac, Yugoslavia **3,** 43 (1982) (this paper contains a full list of references on the concept and applications of TREPE).
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[10] see: A. Streitwieser, Molecular Orbital Theory for Organic Chemists, p. 328, John Wiley & Sons, Inc., New York 1961.