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RESEARCH NOTE:

CHARACTERISTIC GRAPHS AND BENZOID CHARACTER ORDERS OF ALTERNANT POLYCYCLIC AROMATIC HYDROCARBONS

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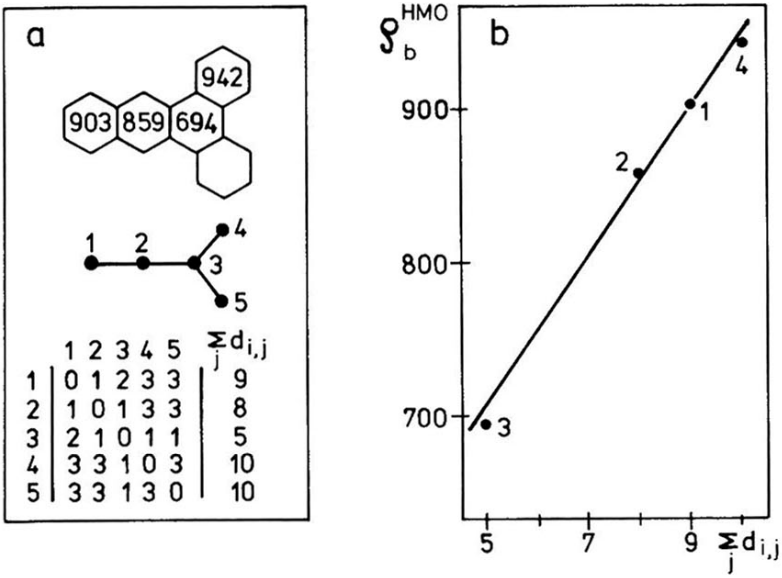
The pars-orbital approach introduced by Polansky and Derflinger [1] consists in formally dividing a conjugated molecule into partial structures L and defining a "character order" ρ whose value measures the analogy of the π-electron system of L against that of a reference compound. The ρ values (obtained in HMO approximation) have been shown to correlate well with both experimental data [2] and theoretical parameters [3]. This Note refers to the "benzoid character orders" ρ_b of the six-membered rings of alternant polycyclic aromatic hydrocarbons (a-PAH) [1].

The six-membered rings of a-PAH are reduced in their "characteristic graphs" (CG) [4] to vertices. Therefore simple relationships were expected to exist between the ρ_b^{HMO} values and invariants of the CG's. To follow a fairly rough concept, the ρ_b^{HMO} value of a given benzoid partial structure $L_{b(i)}$ should be the lower the higher is the "interaction" with the remaining L_b's of the entire molecule. Furthermore, this interaction is expected to increase with (i) the total number of L_b's, i.e. the total number of π-electrons in the entire system, (ii) the number of L_b's to which $L_{b(i)}$ is directly linked, and (iii) the number of linear annellations in which $L_{b(i)}$ participates (see also [1]). All these topological features can be deduced from the CG's.

To quantify these topological features use is made of the distance matrix of the CG's [5]. Fig. 1 shows by way of example the structural formula, the CG, and the distance matrix of the CG of dibenzo[a,c]anthracene. The numbers in the hexagons are the respective ρ_b^{HMO} values [6]. To account for the lower interaction that results from angular annellation compared to linear annellation of benzene rings, the normally applied (uniform) metric ($d(i,i)=0; d(i,j)=1$ for P_1 [7]) was modified with respect to one particular circumstance: If a path consists of 2 edges and these form a 120° angle in the CG, then $d(i,j) = 3$ is used, i.e. in those cases $d(i,j) = 1.5$ for P_1. Although the numerical value (1.5) is rather arbitrary, it is nevertheless reasonable in a qualitative sense and, furthermore, the application of the irregularily edge-weighted CG's improves correlations of numbers derived from the matrices with the ρ_b^{HMO} values. It was expected that the sum $\sum_j d_{i,j}$ of the distance matrix elements in each row (see Fig. 1a) corresponds with the strength of interaction of the respective benzene unit with the remaining benzene units of the entire system in such a manner that $\sum_j d_{i,j}$ increases with decreasing interaction. In Figure 1b the $\sum_j d_{i,j}$ derived for dibenzo[a,c]anthracene are plotted against the corresponding ρ_b^{HMO} values. A further example taken from the series of peri-condensed a-PAH (benzo[b]perylene) is given in Figure 2a and b.



	1	2	3	4	5	$\sum_j d_{i,j}$
1	0	1	2	3	3	9
2	1	0	1	3	3	8
3	2	1	0	1	1	5
4	3	3	1	0	3	10
5	3	3	1	3	0	10

Fig.1: a) Dibenzo[a,c] anthracene - Formula, benzoid character orders, characteristic graph, and its distance matrix

b) Plot of ρ_b^{HMO} against the sum $\sum_j d_{i,j}$ of the elements in each row of the distance matrix. (The numbers denote the respective benzene unit).

Since the discrimination power of the $\sum_j d_{i,j}$ is not very high, strong correlations with the ρ_b^{HMO} cannot be expected. On the other hand, the existence of uniform linear correlations between $\sum_j d_{i,j}$ and the corresponding ρ_b^{HMO} values for kata-annellated systems of different topology but with the same number of π-electrons corroborate the underlying ideas:

(I) kata-annellated a-PAH with 18 carbon centers:

$$\rho_b^{HMO} = 51.56 \sum_j d_{i,j} + 576.41 \qquad (1)$$

(Benz [a] anthracene, chrysene, triphenylene; 8 rings with different ρ_b^{HMO} values [8])

standard deviation s = 13.38

correlation coefficient r = 0.987 [9]

no outliers.

(II) kata-annellated a-PAH with 22 carbon centers:

$$\rho_b^{HMO} = 34.32 \sum_j d_{i,j} + 570.84 \qquad (2)$$

(6 systems; 23 rings with different ρ_b^{HMO} values [8])

s = 23.69, r = 0.938, no outliers.

(III) kata-annellated a-PAH with 26 carbon centers:

$$\rho_b^{HMO} = 23.94 \sum_j d_{i,j} + 565.08 \qquad (3)$$

(Hexacene, dibenzo [p,g] chrysene, benzo [c] picene; 8 rings with different ρ_b^{HMO} values [8])

s = 39.46, r = 0.848, no outliers.

The slopes V of the 3 straight lines correlate with the number n of π-electrons according to:

$$V = -3.46\, n + 112.8 \qquad (r = 0.989) \qquad (4)$$

Statistical tests show that it is allowed to form a mean value from the intercepts of the 3 straight lines. Consequently a uniform correlation is obtained for the 12 systems (39 rings with different ρ_b^{HMO} values):

$$\rho_b^{HMO} = (-3.46\, n + 112.8) \sum_j d_{i,j} + 570 \qquad (5)$$

The correlation coefficient of the function $\rho_b^{HMO} = \rho_b$(calculated according to eq.5) amounts to 0.907.

Analogous relationships exist for peri-condensed a-PAH:

(IV) peri-condensed a-PAH with 20 carbon centers:

$$\rho_b^{HMO} = 39.15 \sum_j d_{i,j} + 582.24 \qquad (6)$$

(Perylene, benzo [e] pyrene, benzo [a] pyrene; 11 rings with different ρ_b^{HMO} values [8])

s = 27.09, r = 0.943, no outliers.

(V) peri-condensed a-PAH with 24 carbon centers:

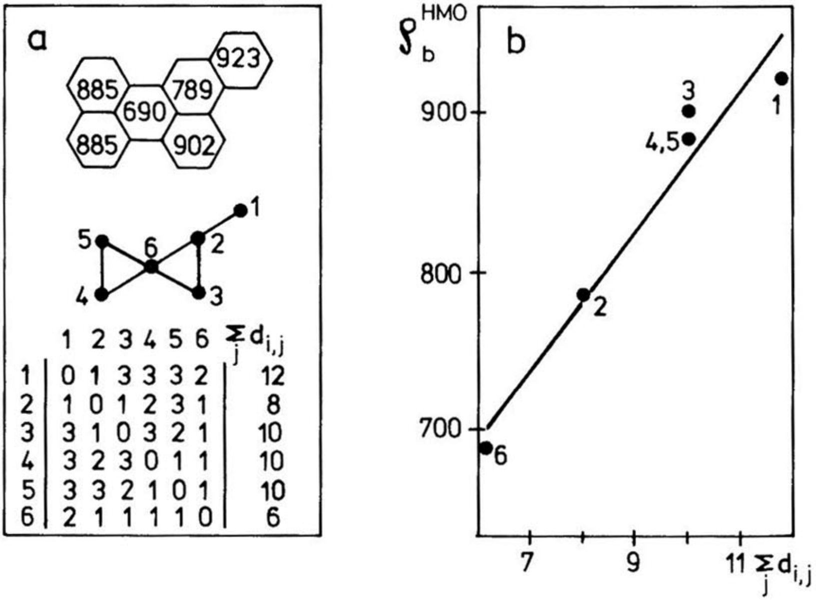
$$\rho_b^{HMO} = 37.82 \sum_j d_{i,j} + 484.40 \qquad (7)$$

(Dibenzo [a,e] pyrene, benzo [b] perylene, zethrene; 16 rings with different ρ_b^{HMO} values [8])

s = 25.11, r = 0.952, no outliers.

A uniform relationship between $\sum_j d_{i,j}$ and ρ_b^{HMO} might also exist for peri-condensed systems with different C numbers, but this has not been studied.

Although the regression analyses presented above support our view of the relation between characteristic graphs and benzoid character orders of alternant polycyclic aromatic hydrocarbons, they cannot, for fundamental reasons, prove our deliberations. In a future publication we shall analyze certain "building principles" (topologies) of alternant polycyclics using the approach presented in this Note with the aim of achieving a deeper understanding of the relationships between topology and the "benzoid pattern" of the compounds.



	1	2	3	4	5	6	$\sum_j d_{i,j}$
1	0	1	3	3	3	2	12
2	1	0	1	2	3	1	8
3	3	1	0	3	2	1	10
4	3	2	3	0	1	1	10
5	3	3	2	1	0	1	10
6	2	1	1	1	1	0	6

Fig.2: a) Benzo [b] perylene - Formula, benzoid character orders, characteristic graph, and its distance matrix

b) Plot of ρ_b^{HMO} against the sum $\sum_j d_{i,j}$ of the elements in each row of the distance matrix.

(The numbers denote the respective benzene unit).

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[5] K.-D.Gundermann, C.Lohberger and M.Zander, Z.Naturforsch., 36a, 1217 (1981).

[6] The original figures are multiplied by a factor of 1000.

[7] Notation according to F.Harary "Graphentheorie", R.Oldenburg Verlag, München-Wien 1974.

[8] Benzoid character orders are taken from: l.c. [1]; H.Sofer, O.E.Polansky and G.Derflinger, Mh.Chem., 99, 1879 (1968); private communication from Professor O.E.Polansky.

[9] The r's of the fits 1-7 cannot be directly compared because the number of points in them are different.