How do the polycyclic aromatic hydrocarbons approach infinity?

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Abstract—Various topological factors governing the electronic properties of infinitely large periodic polycyclic benzenoids are analyzed graph-theoretically by drawing the density of states (DS). The existence or non-existence of NBMO's in the hypothetical cyclic dimer of the network are shown to be crucial for the profile of DS.

CATAHEXES AND PERIHEXES

Owing to the rapid progress in organic synthesis the number of experimentally accessible polycyclic aromatic hydrocarbons is ever growing (1,2). On the other hand, existence of a group of large polycyclic aromatic hydrocarbons is reported both in interstellar materials and soot (3). Existence of ball-shaped C_{60} molecule and its analogues is also reported and postulated (4,5).

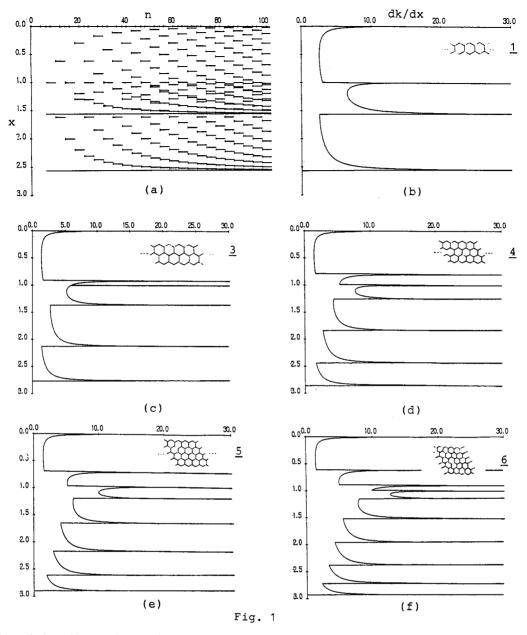
In principle, a given polycyclic aromatic compound belongs to a certain series of molecules which, at least mathematically, grow and converge to an infinitely large network with varying properties. In this talk let us confine ourselves to benzenoid hydrocarbons. Several series of those hydrocarbons are known to have interesting electronic and thermodynamic properties potentially applied to new materials, e.g., of highly conductive, semiconductive, or ferro-magnetic property. The relationship between the stability and topological structure of benzenoid hydrocarbons seems to be well analyzed by many didfferent theoretical techniques, e.g., molecular orbital (MO), valence bond (VB), resonance theory (RT), graph theory (GT), etc. (6-11). The graph-theoretical MO (GTMO) analysis has clarified the mathematical secret and thus the limitation of the so-called "Huckel's 4n+2 rule", and succeeded in extending this concept to polycyclic sysmtems (12). However, if we apply this methodology toward large 2-dimensional network converging to graphite, we shall soon be overwhelmed by the "combinatorial explosion".

Benzenoid hydrocarbons are classified into catacondensed and pericondensed ones, and may be called catahexes and perihexes, respectively (6). From GT consideration a great gap is found to exist between these two types of graphs. Although for catahexes the structure-activity relationship is satisfactorily analyzed mathematically, a large number of interesting properties are left unsolved for perihexes (13). The number of possible isomers of catahexes can be derived from the group-theoretical treatment by Polya and expressed in terms of a set of recursion formulas (14). However, for the counting of perihexes we are forced to choose computer searching (15). The useful concept of the aromatic sextet proposed by Clar needs to be modified as to propose the "super-sextet" when "fat" benzenoids are considered (16).

The purpose of the present talk is to survey the effect of the topological structure, especially the peripheral structure, of infinitely large perihexes on their π -electronic stabilities through GTMO treatment. Before going into the main theme of this talk preliminary remark should be exposed on the topological dependency of the K(G) number and stability of catahexes.

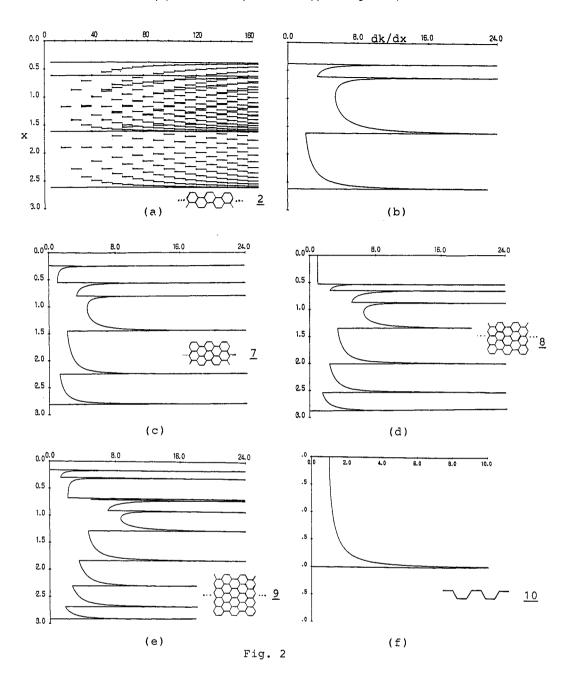
It is well known that K(G) of a benzenoid hydrocarbon increases with the number of kinks and branches. This feature is dramatically shown by quite the different mathematical expressions for the K(G) number of the linear $(\underline{1})$ and zigzag (2) polyacenes.

1
$$K(G) = n+1$$
 [1]
2 $K(G) = \frac{1}{\sqrt{5}} (\alpha^{n+1} - \beta^{n+1})$ [2]
 $\alpha = (1+\sqrt{5})/2, \quad \beta = (1-\sqrt{5})/2$



The K(G) values of Eq. [1] increases only linearly with n, while that of Eq. [2] exponentially explodes. There have been known a number of physicochemical properties, such as, spectroscopic, photoconductive, thermodynamic, and chemically reactive properties, which reflect the difference in this simple mathematical index.

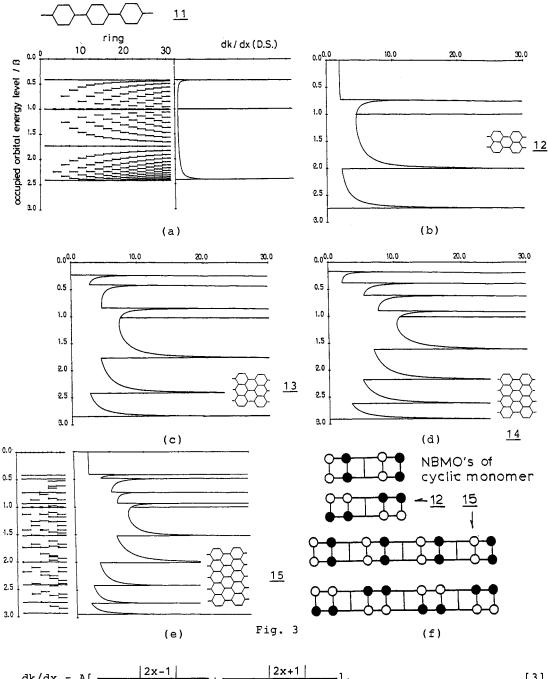
According to Clar the instability of $\underline{1}$ can be explained by the weak aromatic sextet character diluted all over the component hexagons in a row, whereas in $\underline{2}$ so many aromatic sextets as half the number of the component hexagons can be resonant with each other (17).



A number of interesting mathematical properties of K(G) and aromatic sextet for various series of benzenoid hydrocarbons are exposed and discussed (16-19). If we extend the GTMO method this discussion can be further deepened.

DENSITY OF STATES

Another theoretical quantity that well represents the electronic state of a large conjugated network is the density of states, dk/dx. In Fig. 1a the HMO energy levels of the occupied π orbitals of the sereis of $\underline{1}$ are plotted against the number, n, of the composed hexagons. The vacant orbitals are omitted from the figures, since they are just the mirror image of the occupied orbitals as guaranteed by the pairing theorem (20). With the increase of n the the number, dk, of the energy levels per given energy range, dx, increases but converges to a certain band profile as Fig. 1b, i.e., the density of states, dk/dx. Actually for the infinitely large $\pi\text{-electronic}$ network of $\underline{1}$ one can obtain by using the periodic boundary condition the following result:



$$dk/dx = A\left[\frac{|2x-1|}{\sqrt{-(x^2-x)(x^2-x-4)}} + \frac{|2x+1|}{\sqrt{-(x^2+x)(x^2+x-4)}}\right],$$
 [3]

which is derived from the equation governing the orbital energies of the network (21). Since Ledermann already proved that the profile of the dk/dx curve is independent of the boundary condition, all our calculations were performed for the infinitely large cyclic polymers (22). The merit of the HMO treatment is that for a fairly large number of cases one can derive analytical expressions of dk/dx. Although the rigorous expressions for the several members of multi-layered polyacenes, 3-6, and multi-layered zigzag polyacenes, 7-9, were not obtained, we can draw quite accurately their dk/dx curves as in Figs. 1c-f and 2c-e (23).

It is to be noted that for all the members of the former series, i.e., the homologues of the linear polyacene, no HOMO-LUMO band gaps are observed. Of course, if bond alternation, such as

is taken into consideration, we can observe a small HOMO-LUMO gap but not yet compatible with the large gap for the zigzag polyacene networks. A large number of the variable- β , γ version of PPP-type claculations for the same series of hydrocarbons reveals that the HOMO-LUMO gaps obtained from the HMO and PPP methods are almost linearly correlated with each other giving a good support for our HMO calculation (23).

Contrary to the case of the homologues of $\underline{1}$, the homologues of $\underline{2}$ show an interesting feature in dk/dx. Namely, while the singly ($\underline{2}$), doubly ($\underline{7}$), and quadruply ($\underline{9}$) zigzag polyacenes have a relatively large HOMO-LUMO gap, the triply zigzag polyacene ($\underline{8}$) has no gap as seen in Fig. 2d. It is to be noted that the polyacetylene network without bond-alternation ($\underline{10}$) can be deemed as the zero-th member of the "n-ply" zigzag polyacene and has no HOMO-LUMO gap (See Fig. 2f). Quite similarly the homologous series of the poly-phenylene ($\underline{11}$), polynaphthalene ($\underline{12}$), polyanthracene ($\underline{13}$), etc. were found to have some periodicity in the zero HOMO-LUMO gap. The results are shown in Fig. 3a-e, where the members of n=2 ($\underline{12}$) and 5 ($\underline{15}$) have zero HOMO-LUMO gap contrary to the other members of relatively stable π -electronic networks.

CYCLIC DIMER

Although it is evident in the routine derivation of the density of states of periodic networks the importance of the hypothetical cyclic dimer (monomer in some cases) has not been recognized until quite recently (21,23,24). Namely, almost all the singular points of the dk/dx curve are nothing else but the energy levels of the cyclic dimer. For example, the secular determinant of the cyclic dimer $\underline{16}$ of $\underline{1}$ can be factored out to be the product of cyclic Huckel monomer $\underline{17}$ and cyclic Mobius monomer $\underline{18}$ as shown in Fig. 4 (21,24),

where the symbols \bigcirc and \bigcirc respectively mean the additive contributions of β and $-\beta$ to the corresponding bond.

Fig. 4

Note that this determinant has the same form as the denominator of Eq. [3]. Thus in this case all the orbital energies of the cyclic dimer of $\underline{1}$ coincide with the singular points of its density of states. Further, note that the dk/dx curve of $\underline{1}$ has no HOMO-LUMO gap comes from the fact that the cyclic dimer $\underline{16}$ of the "kagome" graph has the following NBMO's.



Similarly, all the cyclic dimer graphs for the networks in Fig. 1b-f are shown to be kagome graphs and have a pair of NBMO's as



Further, it is straightforward that among all the networks in Figs. 1-3 only the cyclic dimer of such networks that hve no HOMO-LUMO gap has NBMO's, and vice versa. Namely, in Fig. 3f are given the NBMO's of the cyclic monomers of $\underline{12}$ and $\underline{15}$ indicative of no HOMO-LUMO gap in the density of states of their polymer networks. Figure 5 demonstrates the NBMO's of the cyclic dimers of $\underline{10}$ and $\underline{8}$ indicative of no HOMO-LUMO gap.

Thus the secret of the infinitely large perihex netowrks are shown to be hidden in the hypothetical cyclic dimer graphs, which are either polyomino or

kagome graphs. By doing extensive calculations of variableversion of PPP MO for the hypothetical cyclic dimers we could reconfirm these findings. The interesting GT judgement for zero HOMO-LUMO gap by searching the NBMO's in a given polyomino or kagome graph was also shown to be essentially valid by the PPP calculations (23). Works are being in progress.

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