

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

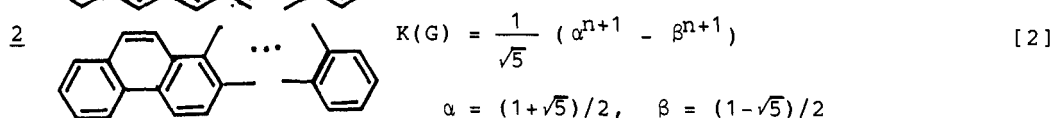
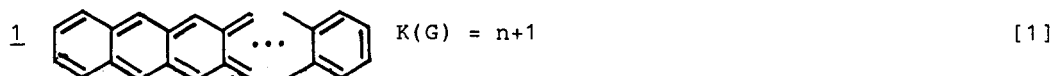
Owing to the rapid progress in organic synthesis the number of experimentally accessible polycyclic aromatic hydrocarbons is ever growing (1,2). On the other hand, existence of a group of large polycyclic aromatic hydrocarbons is reported both in interstellar materials and soot (3). Existence of ball-shaped 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, semi-conductive, or ferro-magnetic property. The relationship between the stability and topological structure of benzenoid hydrocarbons seems to be well analyzed by many different 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 "Hückel's $4n+2$ rule", and succeeded in extending this concept to polycyclic systems (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 (1) and zigzag (2) polyacenes.



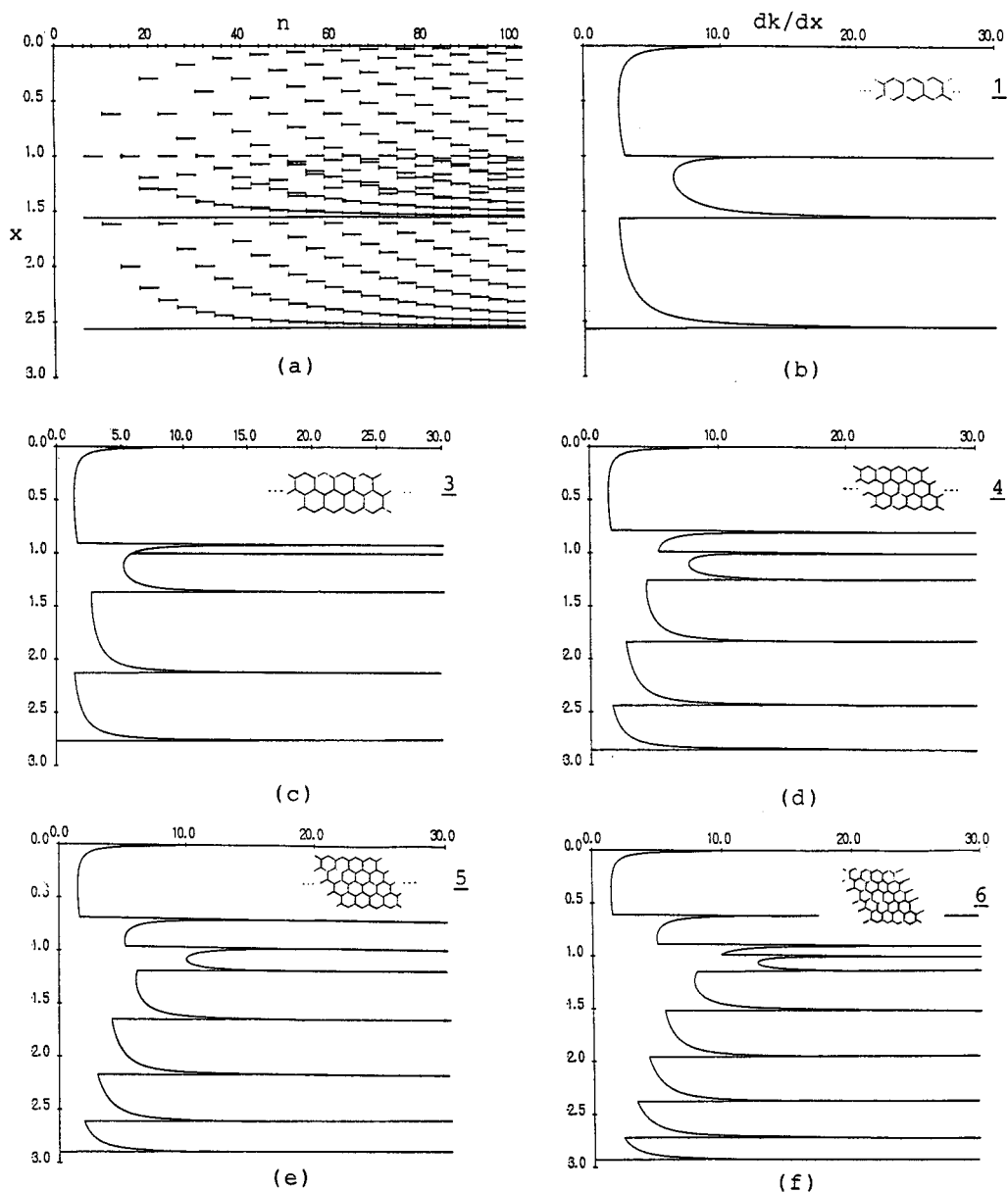
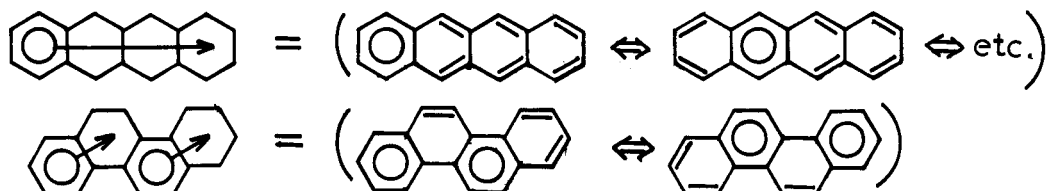


Fig. 1

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 physico-chemical 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 1 can be explained by the weak aromatic sextet character diluted all over the component hexagons in a row, whereas in 2 so many aromatic sextets as half the number of the component hexagons can be resonant with each other (17).



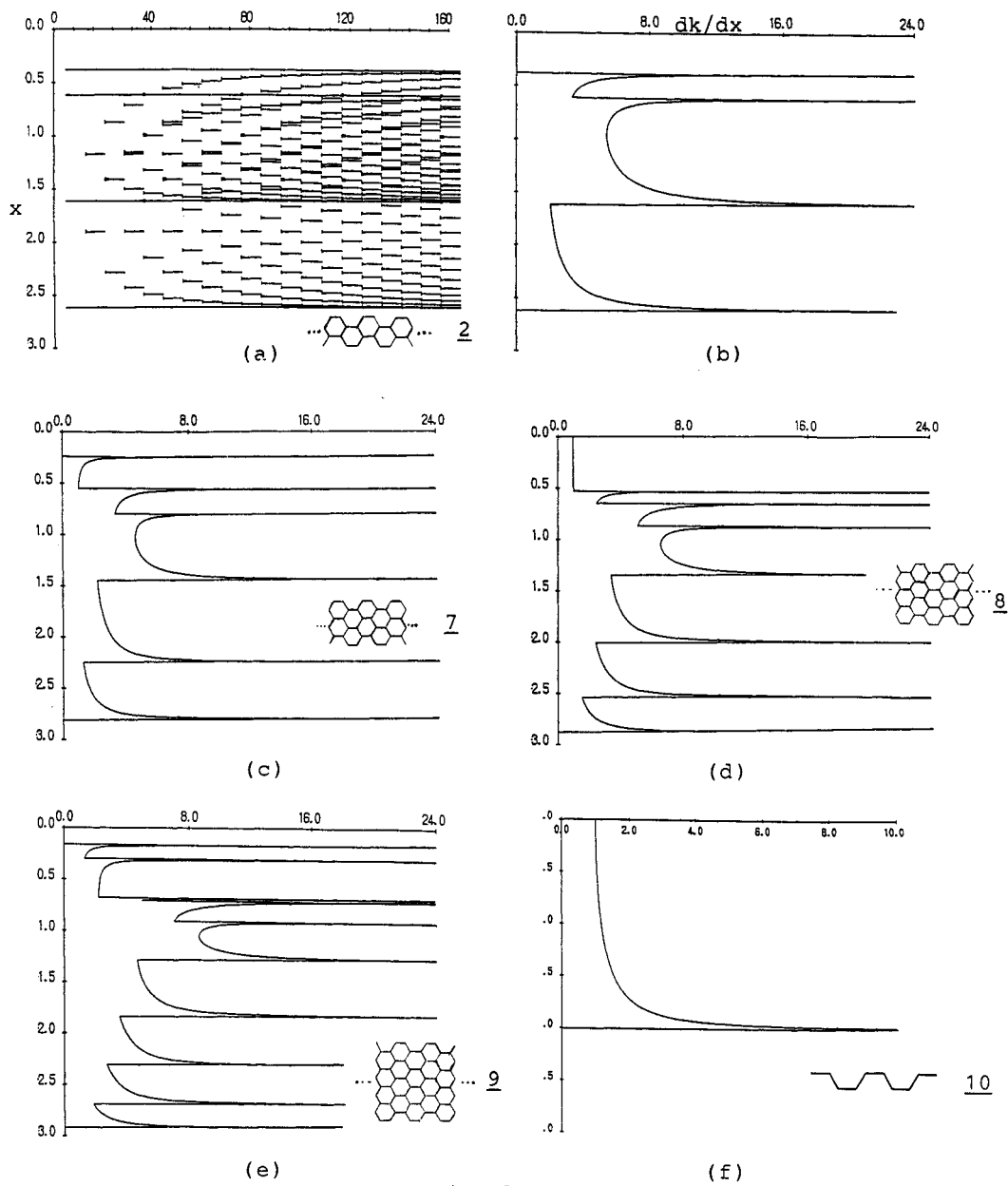


Fig. 2

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 series of 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 π -electronic network of 1 one can obtain by using the periodic boundary condition the following result:

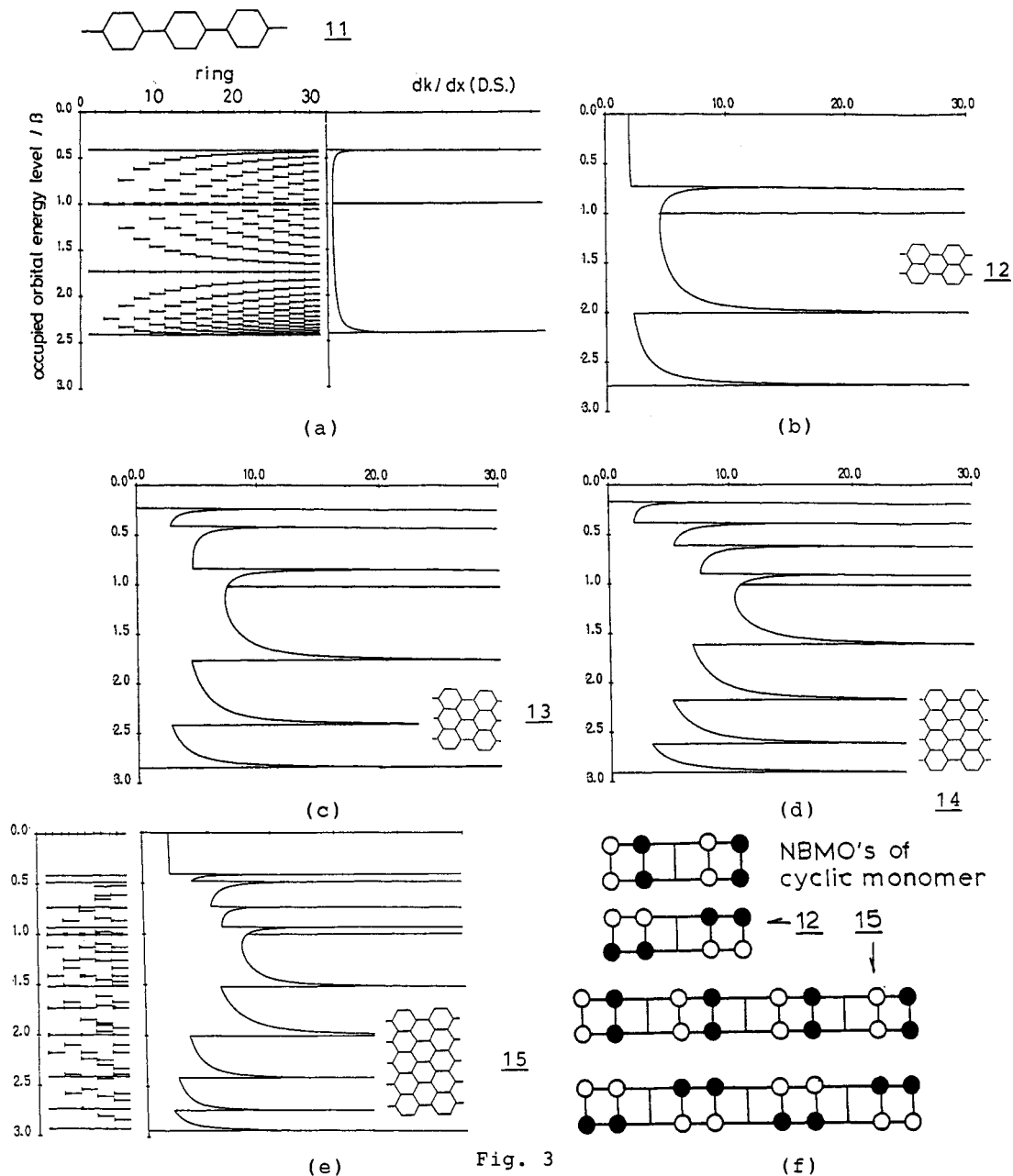
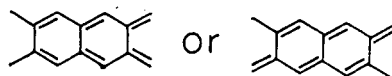


Fig. 3

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

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



kagome graphs. By doing extensive calculations of variable-, version 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.

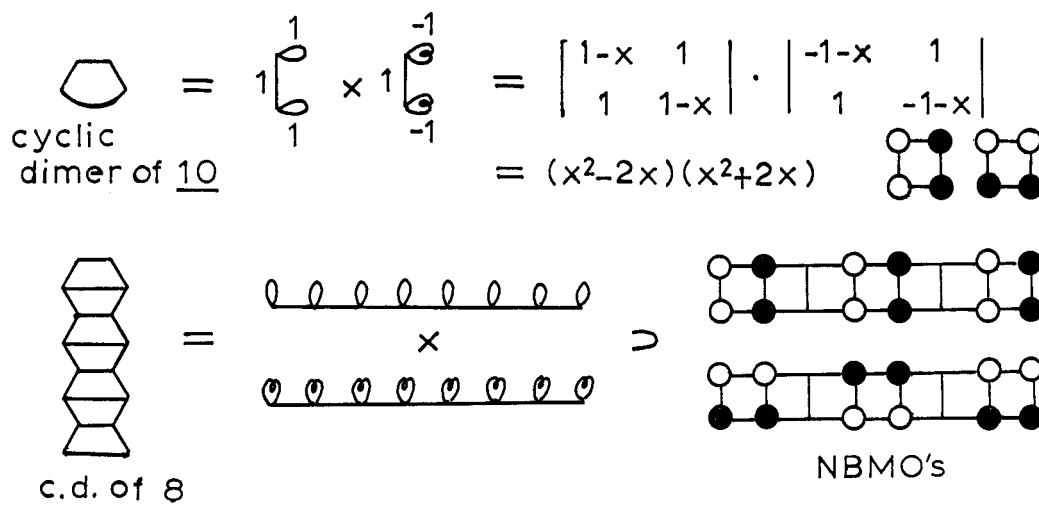


Fig. 5

REFERENCES

1. E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London (1964).
2. J. R. Dias, *Handbook of Polycyclic Hydrocarbons*, Elsevier, Amsterdam (1987).
3. A. Leger, L. d'Hendecourt, and N. Boccara eds., *Polycyclic Aromatic Hydrocarbons and Astrophysics*, Reidel, Dordrecht (1986).
4. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162-163 (1985).
5. D. J. Klein, T. G. Schmalz, G. E. Hite, and W. A. Seitz, *J. Am. Chem. Soc.*, **108**, 1301-1302 (1986).
6. M. Aida and H. Hosoya, *Tetrahedron*, **36**, 1317-1326 (1980).
7. N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, Florida (1983).
8. I. Gutman and O. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin (1986).
9. T. Au-Chin, K. Yuan-Sun, Y. Guo-Sen, and T. Shu-San, *Graph Theoretical Molecular Orbitals*, Science Press, Beijing, 1986.
10. M. Randić, *Chem. Phys. Lett.*, **38**, 68-70 (1976).
11. W. C. Herndon, *J. Am. Chem. Soc.*, **95**, 2404-2406 (1973).
12. H. Hosoya, K. Hosoi, and I. Gutman, *Theor. Chim. Acta*, **38**, 37-47 (1975).
13. S. E. Stein and R. L. Brown, *J. Am. Chem. Soc.*, **109**, 3721-3729 (1987).
14. R. C. Read, in *Chemical Applications of Graph Theory*, A. T. Balaban (ed.), Academic Press, London (1976), pp. 25-61.
15. J. V. Knop, W. R. Müller, K. Szymanski, and N. Trinajstić, *Computer Generation of Certain Classes of Molecules*, SKTH/Kemija u industriji, Zagreb (1985).
16. N. Ohkami, A. Motoyama, T. Yamaguchi, H. Hosoya, and I. Gutman, *Tetrahedron*, **37**, 1113-1122 (1981).
17. E. Clar, *The Aromatic Sextets*, John Wiley, London (1972).
18. H. Hosoya, *Comp. & Maths. with Appls.*, **12B**, 271-290 (1986).
19. S. J. Cyvin and I. Gutman, *Lecture Notes in Chemistry*, **46**, Springer, Berlin (1988).
20. S. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil Soc.*, **36**, 193-200 (1940).
21. H. Hosoya, M. Aida, R. Kumagai, and K. Watanabe, *J. Comput. Chem.*, **8**, 358-366 (1987).
22. W. Ledermann, *Proc. Roy. Soc.*, **A182**, 362-378 (1944).
23. H. Kumazaki, Master Thesis, Ochanomizu Uni., 1989.
24. U. Norinder and O. Wennerstrom, *Tetrahedron, Lett.*, **25**, 1397-1940 (1984).