

Nonaromatic benzenoid hydrocarbons

Ivan Gutman

Faculty of Science, University of Kragujevac, P.O.Box 60,
YU-34000 Kragujevac, Yugoslavia

Abstract - Nonaromatic benzenoid hydrocarbons are benzenoid hydrocarbons with large number of fixed double bonds. The π -electron structure of these molecules is examined and the effects of particular rings on the total π -electron energy calculated. The main conclusion of this work is that in nonaromatic benzenoids several non-standard modes of cyclic conjugation occur, in addition to the conjugation described by Kekulé or Clar structures.

INTRODUCTION

If a certain carbon-carbon bond in a conjugated hydrocarbon is double in all its Kekulé structural formulas, then we say that it is a *fixed double bond*. Similarly a carbon-carbon bond which is single in all Kekulé structures is called a *fixed single bond*. A systematic examination of benzenoid hydrocarbons with fixed double bonds was performed by Clar and co-workers (see ref. 1 and the publications quoted therein). Clar's basic conclusion was that "fixed double bonds do not deprive polycyclic hydrocarbons of their aromatic character, provided that they have at least one Kekulé structure" (ref. 1, p. 30). Note, however, that no benzenoid hydrocarbon studied by Clar had more than four fixed double bonds.

The present paper deals with benzenoid hydrocarbons possessing large number of fixed double bonds. In spite of Clar's claim we find it reasonable to designate them as nonaromatic. Our particular concern is the π -electron conjugation in large nonaromatic benzenoid systems.

We first have to choose a suitable theoretical approach. Accurate quantum chemical calculation techniques are nowadays not applicable to large benzenoids. On the other hand, quite a few simple but efficient "topological" methods have been developed, enabling the description and the prediction of the basic physico-chemical properties of benzenoid hydrocarbons (ref. 2). We can divide these methods into four groups.

(a) Resonance theoretical approaches based on the counting of Kekulé structures (refs. 2-5; for review see ref. 6) are of no use for the present work since if only Kekulé structures are considered, then *by definition* fixed double bonds cannot participate in conjugation.

(b) Clar's aromatic sextet theory (ref. 7) and its advanced modifications (refs. 8,9) indicate the cyclic conjugation in a benzenoid molecule by drawing a circle ("aromatic sextet") in certain hexagons. A condition for locating an aromatic sextet in a hexagon H of a benzenoid system B is that the fragment B-H possesses a Kekulé structure (refs. 2,7-9). This, however, implies the existence of a Kekulé structure of B containing three double bonds in H. Then, obviously, none of the bonds of H can be fixed. As a consequence, aromatic sextets (in Clar's sense) cannot be drawn in hexagons which contain at least one fixed double or fixed single bond, i.e. within the aromatic sextet theory such hexagons are considered to be empty and to have no contribution to conjugation.

(c) The conjugated circuit model (refs. 2,10) has a similar limitation. Here only the "conjugated circuits" are assumed to have non-vanishing effects on conjugation. Since in conjugated circuits double and single bonds alternate, they cannot be fixed. In other words, fixed single and double bonds cannot belong to any conjugated circuit and thus they are irrelevant for the conjugated circuit model.

(d) Hückel molecular orbital theory is traditionally used in the topological studies of benzenoid hydrocarbons (refs. 11-14). By means of suitable graph-theoretical manipulations it is possible to express the *effect of a single cycle on the total π -electron energy* (i.e. thermodynamic stability) of a conjugated system (refs. 12,15-24). We denote this quantity by $ef(G,Z)$ where G stands for the respective molecular graph and Z for its particular cycle; $ef(G,Z)$ can be computed for any cycle of any conjugated molecule. Hence $ef(G,Z)$ does not discriminate between Kekuléan and non-Kekuléan molecules as well as between conjugated circuits and cycles containing fixed single or fixed double bonds. Among the several existing variants of this approach (refs. 12,15-24) we have chosen the one proposed by Bosanac and Gutman (ref. 15). This method enables the evaluation of the effect of the cycle Z from

the spectra of the graphs G and $G-Z$, and is therefore suitable for computer implementation. Thus in the present paper we report ef values computed by means of the formula

$$ef(G,Z) = -(2\pi) \int_0^{\infty} \log[1 + 2 \phi(G-Z, ix)/\phi(G, ix)] dx$$

where $\phi(G, x)$ and $\phi(G-Z, x)$ denote the characteristic polynomials of G and $G-Z$, respectively (refs. 15-17,21).

Details of the theory of $ef(G,Z)$ can be found elsewhere (refs. 17,19,21,22). A number of its chemical applications are reported (refs. 16,17), of which the relation with the diamagnetic susceptibility is particularly worth attention (refs. 21,27,28).

BENZENOID SYSTEMS WITH LARGE NUMBERS OF FIXED DOUBLE BONDS

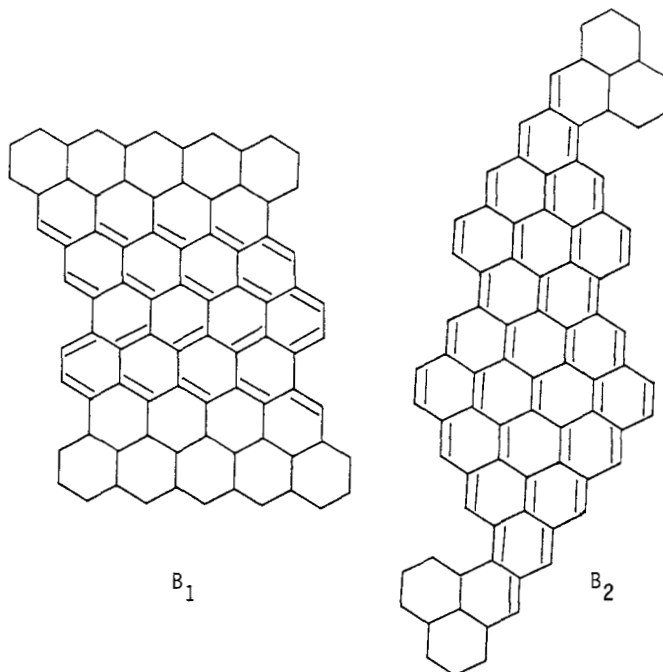
There is a plethora of ways in which benzenoid systems with large numbers of fixed double bonds can be designed. We present here two such recipes which generalize some previously published construction schemes (refs. 29,30).

1° Arrange the hexagons in m rows, $m > 2$, so that the first and the last row contain $n+1$ hexagons and the remaining rows contain n hexagons. Let for all i , $1 \leq i \leq m-1$, the first and the last hexagons of the i -th row be adjacent to the first and the last hexagons, respectively, of the $(i+1)$ -th row. Then the corresponding benzenoid hydrocarbon has $(n+2)^2$ Kekulé structures, each with $mn+m+n+3$ double bonds. Among these double bonds, $mn+m-3n-3$ are fixed.

An example is provided by B_1 for which $n = 4$, $m = 7$; only its fixed double bonds are indicated.

2° Arrange the hexagons in m rows, $m > 4$, so that the rows 1, $2m-2$ and m each contain one hexagon, the rows 2 and $m-1$ each contain two hexagons and the numbers of hexagons in the i -th and $(i+1)$ -th rows differ by at most one, $i = 1, \dots, m-1$. Let for all i , $1 \leq i \leq m-1$, except for $i = 2$ and $i = m-2$, the first and the last hexagons of the i -th row be adjacent to the first and the last hexagons, respectively, of the $(i+1)$ -th row. Then the corresponding benzenoid hydrocarbon has 9 Kekulé structures. All its double bonds except 10 are fixed.

An example is provided by B_2 for which $m = 13$; only its fixed double bonds are indicated.



EFFECT OF 6-MEMBERED CYCLES ON THE STABILITY OF AROMATIC BENZENOID HYDROCARBONS

In this and the subsequent section we give $ef(G, Z)$ values for six-membered rings of benzenoid hydrocarbons. The numerical results are expressed in units of $10^{-4} \beta$, where β is the resonance integral in standard Hückel molecular orbital theory. In Fig. 1 are collected some typical results for benzenoid hydrocarbons without fixed double or single bonds; these are generally considered as prototypes of aromatic molecules. The aim of Fig. 1 is to document that for these compounds the conclusions based on $ef(G, Z)$ are precisely the same as the conclusions obtained from resonance/aromatic-sextet/conjugated-circuit theory.

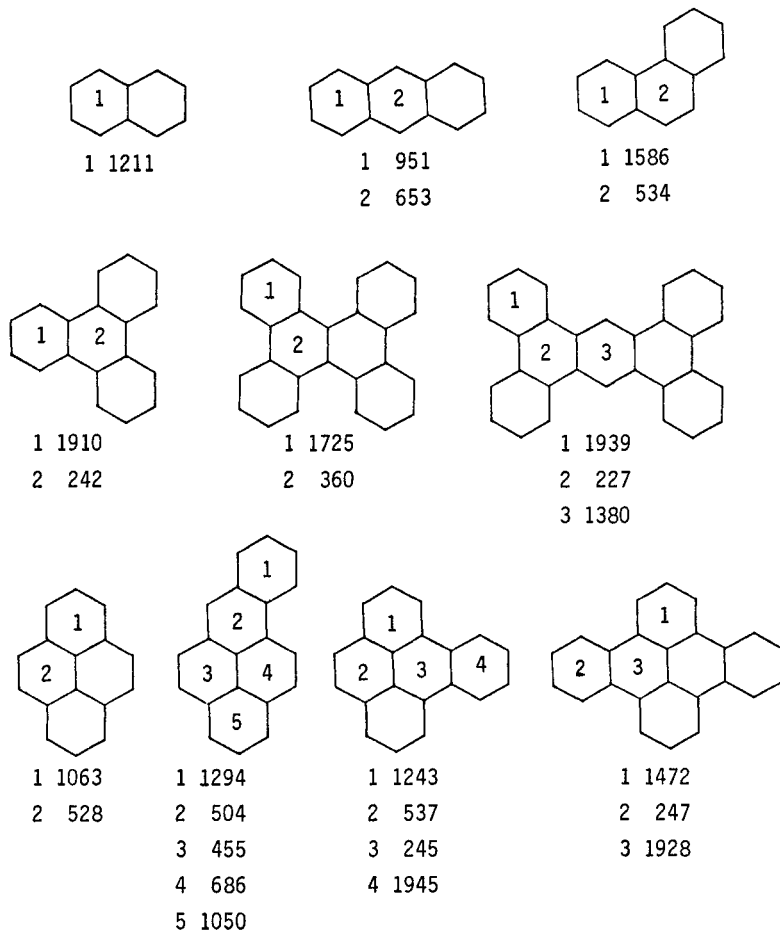
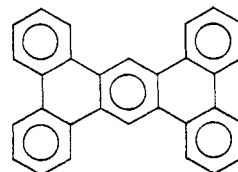


Fig. 1. ef values of the six-membered cycles of some benzenoid hydrocarbons without fixed single or double bonds.

For instance, the ef values of tetrabenzanthracene are in full harmony with the Clar-formula representation of this molecule, viz.:

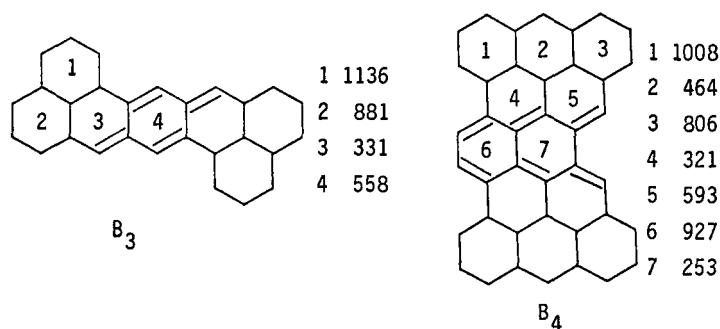
The circuits drawn in this formula stand for the most important conjugated circuits. Note that the above depicted Clar formula represents 32 out of a total of 40 Kekulé structures of tetrabenzanthracene. In complete agreement with this, the rings 1 and 3 have substantially higher energy effects than the rings 2.



EFFECT OF 6-MEMBERED CYCLES ON THE STABILITY OF NONAROMATIC BENZENOID HYDROCARBONS

In the case of benzenoid hydrocarbons with fixed double and single bonds the results of the $ef(G, Z)$ -considerations are often in variance with the conjugation anticipated by resonance/aromatic-sextet/conjugated circuit theory. Let us start with two examples, B_3 and B_4 .

According to the traditional view B_3 and B_4 are composed of two delocalized naphthalene and anthracene units, respectively, joined together by a few localized single and double bonds. The ef values of B_3 are essentially in agreement with the Kekulé/Clar picture. It must be observed, however, that the "empty" rings 3 and 4 have fairly different energy effects. One may also ask why the ring 1 has a pronouncedly larger effect than the ring 2.



Resonance/aromatic-sextet/conjugated-circuit theory predicts that the rings 4,5,6 and 7 of B_4 have no (or, in the best case, very small) contribution to overall conjugation. On the other hand, significant contributions are expected from the rings 1 and 3 and, to a smaller extent, from the rings 2. The remarkable finding is that the rings 5 and especially the ring 6 have unusually large ef values. The energy effect of the ring 6 is comparable to that of the rings 1 and 3. Thus the ef values imply that the degree of conjugation in the rings 1, 3 and 6 is large and roughly equal whereas the rings 2, 4 and 5 have comparable but much smaller importance in the overall conjugation.

A systematic examination of this and many other observed anomalies revealed that in nonaromatic benzenoid systems one encounters a new pattern of cyclic conjugation.

Some insight into this phenomenon is gained by comparing the ef values of the central ("empty") rings of isomeric tetrabenzoperylene, Fig. 2. An inspection of the data given in Fig. 2 clearly shows that the rings having an angular position to the "empty" ring increase its extent of cyclic conjugation. Thus we see that *in addition to* the traditional conjugation modes one has to take into consideration also the cyclic conjugation represented by means of non-standard aromatic-sextet formulas of the above type.

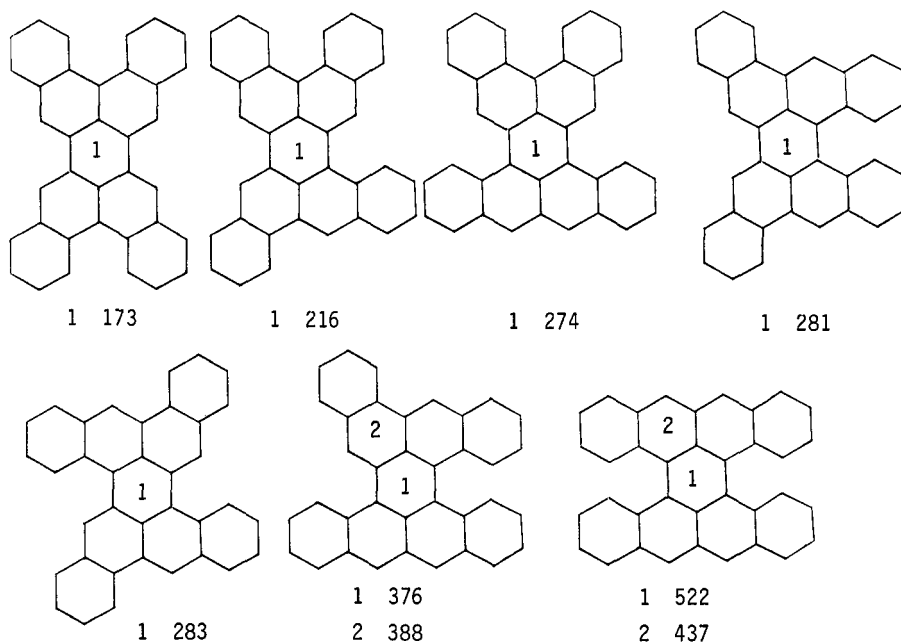
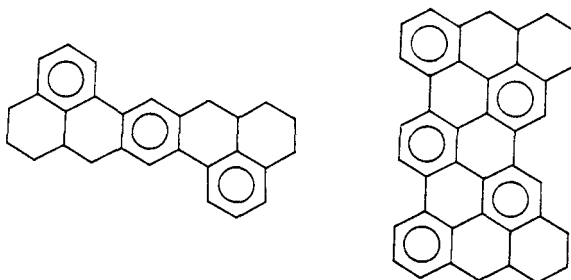


Fig. 2. ef values of the central ring in tetrabenzoperylene; cyclic conjugation in the "empty" ring (1) may exceed the cyclic conjugation in a "non-empty" ring (2).

The situation is somewhat more perplexed in the homologous series presented in Fig. 3. In line with the previous examples one may be inclined to propose the following aromatic-sextet representations:

These, however, are incorrect since they disagree with the calculated ef values.

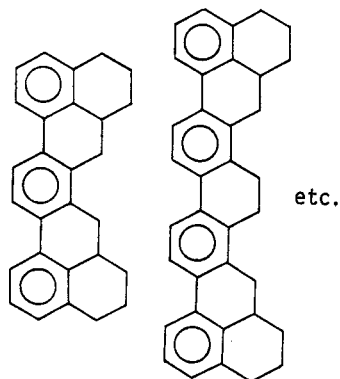
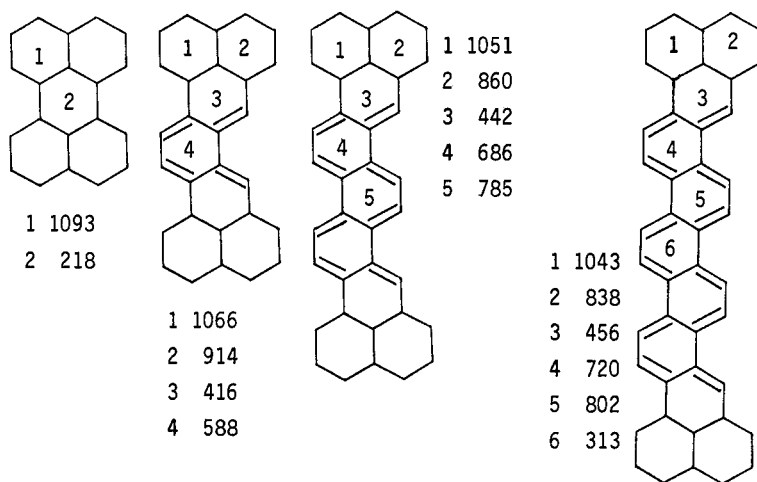


Fig. 3. ef values of the six-membered cycles of some benzenoid hydrocarbons with fixed single and double bonds.



CONCLUSIONS

We gave evidence that two kinds of conjugation effects are to be distinguished in benzenoid hydrocarbons: the *standard conjugation* modes described by means of Kekulé or Clar structures and the conjugation which we will denote as *non-standard*. Because of the limited space available we could show only a few representative examples, supporting the conclusion that the non-standard conjugation not only exists, but sometimes plays a quite significant role in benzenoid hydrocarbons. In aromatic benzenoid molecules the standard conjugation is dominant and it usually screens the effects of non-standard modes. This explains why the non-standard conjugation seems to be long time overlooked by the majority of the researchers in this field.

In nonaromatic benzenoid molecules the non-standard conjugation has a much greater (relative) importance. By using suitably chosen theoretical methods it can be made easily recognizable. In the study of the π -electron properties of nonaromatic benzenoid hydrocarbons it is not legitimate to neglect the non-standard conjugation modes. In some cases (which are perhaps extremes) the non-standard conjugation modes may even be more important than the standard modes.

Anyway, the π -electron structure of nonaromatic benzenoid hydrocarbons seems to be much less simple than could be inferred from the Kekulé/Clar picture.

Acknowledgement

The financial support of the Royal Norwegian Council for Scientific and Industrial Research (1988) and the Fulbright Program (1989) is gratefully acknowledged.

REFERENCES

1. E. Clar, Polycyclic Hydrocarbons, chapter 5, Academic Press, London (1964).
2. I. Gutman and S.J. Cyvin, Introduction to the Theory of Benzenoid Hydrocarbons, Springer-Verlag, Berlin (1989).
3. W.C. Herndon, J.Am.Chem.Soc. 95, 2404-2406 (1973).
4. W.C. Herndon and M.L. Ellzey, J.Am.Chem.Soc. 96, 6631-6642 (1974).
5. W.C. Herndon, J.Am.Chem.Soc. 96, 7605-7614 (1974).
6. W.C. Herndon, Israel J.Chem. 20, 270-275 (1980).
7. E. Clar, The Aromatic Sextet, Wiley, London (1972).
8. H. Hosoya and T. Yamaguchi, Tetrahedron Lett. 4659-4662 (1975).
9. W.C. Herndon and H. Hosoya, Tetrahedron 40, 3987-3995 (1984).
10. M. Randić, J.Am.Chem.Soc. 99, 444-450 (1977).
11. B.A. Hess and L.J. Schaad, J.Am.Chem.Soc. 93, 2413-2416 (1971).
12. J. Aihara, J.Am.Chem.Soc. 99, 2048-2053 (1977).
13. S.E. Stein and R. Brown, J.Am.Chem.Soc. 109, 3721-3729 (1987).
14. H. Hosoya, M. Aida, R. Kumagai and K. Watanabe, J.Comput.Chem. 8, 358-366 (1987).
15. S. Bosanac and I. Gutman, Z.Naturforsch. 32a, 10-12 (1977).
16. I. Gutman and S. Bosanac, Tetrahedron 33, 1809-1812 (1977).
17. I. Gutman, J.Chem.Soc.Faraday II 75, 799-805 (1979).
18. I. Gutman, Croat.Chem.Acta 53, 581-586 (1980).
19. I. Gutman and O.E. Polansky, Theor.Chim.Acta 60, 203-226 (1981).
20. I. Gutman, Theor.Chim.Acta 66, 43-49 (1984).
21. N. Mizoguchi, Chem.Phys.Lett. 106, 451-454 (1984).
22. I. Gutman, Chem.Phys.Lett. 117, 614-616 (1985).
23. N. Mizoguchi, J.Phys.Chem. 92, 2754-2756 (1988).
24. N. Mizoguchi, Chem.Phys.Lett. 158, 383-388 (1989).
25. I. Gutman and S. Bosanac, Bull.Soc.Chim.Beograd 42, 499-502 (1977).
26. I. Gutman, Croat.Chem.Acta 58, 359-369 (1985).
27. J. Aihara, J.Am.Chem.Soc. 103, 5704-5706 (1981).
28. N. Mizoguchi, Bull.Chem.Soc.Japan 60, 2005-2010 (1987).
29. S.J. Cyvin and I. Gutman, J.Serb.Chem.Soc. 50, 443-450 (1985).
30. J. Brunvoll, B.N. Cyvin, S.J. Cyvin and I. Gutman, Match 23, 209-227 (1988).