ON THE CONCEPT OF FULLY-ARENOID HYDROCARBONS*

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Abstract

The concept of fully-benzenoid hydrocarbons is reviewed and it is pointed out that the only truly fully-benzenoid hydrocarbon is benzene. A more general concept than that of fully-benzenoid hydrocarbons, that is, the concept of fully-arenoid hydrocarbons, is presented. A class of fully-arenoids, named fully-naphthalenoid hydrocarbons, is discussed and it is stated that these compounds may play an important role in the preparation of organic semi-conducting materials. Finally, the properties of fully-arenoids are summarized.

1   Introduction

The concept of fully-benzenoid hydrocarbons has been introduced by Clar and Zander[1] in 1958. Another term, all-benzenoid hydrocarbons,[2] has also been increasingly used in recent years for this class of benzenoid hydrocarbons. In our parlance benzenoid hydrocarbons are simply-connected geometrically-planar polyhex hydrocarbons which possess Kekulé structures.[3] Polyhex hydrocarbons are made up of hexagons (benzene rings) in such a way that two hexagons have exactly one common bond or are disjoint.[4]

Fully-benzenoids are defined[5] as those benzenoid hydrocarbons which can be represented by Clar's (valence structural) formulae[6] in which hexagons are either represented by isolated sextets[1,7] or are "empty", i.e., devoid conjugation. Clar and

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* Dedicated to Professor Sven J. Cyvin (Trondheim), a grandmaster of chemical combinatorics.

Zander[1] called these rings more appropriately quasi-empty rings. A rigorous characterization of fully-benzenoid hydrocarbons was recently given by Gutman and Babić.[2(f)]

The fully-benzenoid hydrocarbons represent a subclass of benzenoid hydrocarbons which show a greater benzenoid character than the related isomeric benzenoids.[8] This correlates with their pronounced chemical inertness. They are usually pale yellow, or colourless solids which are very stable and which do not decompose when exposed to air or light. They also do not dissolve in concentrated sulphuric acid and do not react with maleic anhydride.

Fully-benzenoids are rare benzenoid hydrocarbons, especially in the case of smaller benzenoids.[9] For example, in the field of 18,360 geometrically-planar simply-connected benzenoids with up to 10 hexagons, only 18 are fully-benzenoid hydrocarbons.[9(a)] An example of a fully-benzenoid is given in **Fig. 1.**
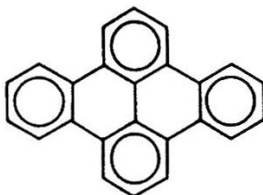

Fig. 1. Clar's formula of dibenzo[fg,op]naphthacene, an example of a fully-benzenoid hydrocarbon.

2 Problems with the concept of fully-benzenoid hydrocarbons

It has recently been pointed out[10] that the "empty" rings in fully-benzenoid hydrocarbons are not really empty at all. Quantification of the benzene character for each hexagon in the fully-benzenoid hydrocarbon by means of Clar's index (computed within the framework of the conjugated-circuit model)[11] indicated that the appreciable conjugation is present in the "empty" rings. As an example in **Fig. 2** we give Clar's indices for hexagons in dibenzo[fg,op]naphthacene.

Similarly, the ring resonance energies (REs, also computed by means of the conjugated-circuit model) in dibenzo[fg,op]naphthacene: RE(A) = 0.745 eV, RE(B) = 0.807 eV and RE(C) = 0.289 eV are also indicators that the central rings (the C-rings in

Fig. 2) are not empty and that they contribute to the RE of the molecule. The RE of the benzenoid hydrocarbon is equal to the sum of the ring REs. In the case of dibenzo[fg,op]naphthacene:

$$RE = 2[RE(A) + RE(B) + RE(C)] = 3.682 \text{ eV} \tag{1}$$

Thus, the contribution of the central rings to the RE of dibenzo[fg,op]naphthacene is 15.7%.

The above is the consequence of the fact that the benzene rings alone cannot be connected by essential single bonds to produce a fully-benzenoid hydrocarbon in which rings will be partitioned in those which contain conjugation and those which are devoid of conjugation. Essential single bonds (quasi-single bonds as Clar and Zander[1] called them or formally single bonds as Camerman and Trotter[12] called them) are bonds which are single in all Kekulé structures of the molecule.[13] Only compounds in which benzene rings are connected by essential single bonds are polyphenyls. The initial member (e.g., biphenyl) and several higher members of this class are shown in **Fig. 3**.
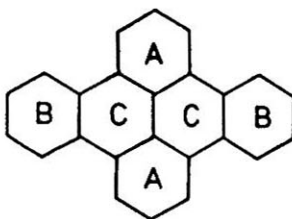
A = 0,835
B = 0,939
C = 0,204

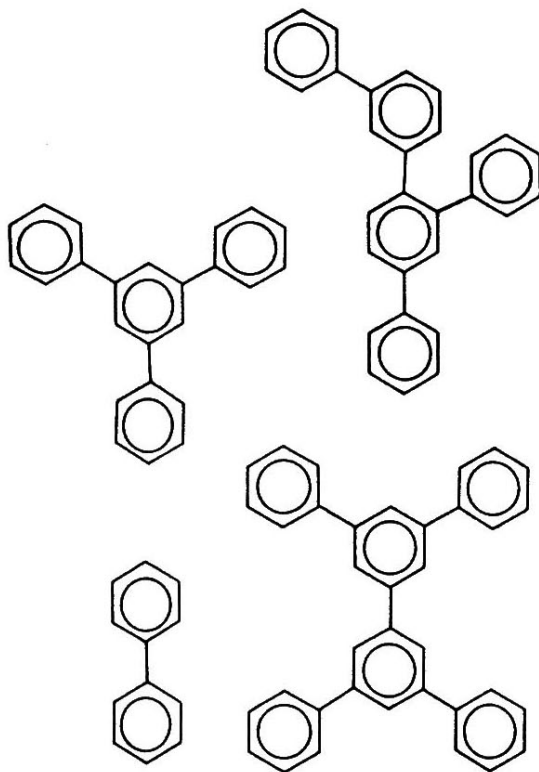**Fig. 2.** Clar's indices for hexagons in dibenzo[fg,op]naphthacene.

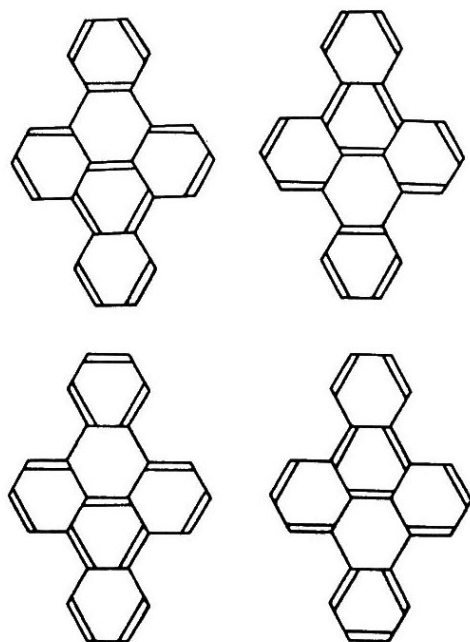**Fig. 3.** Clar's formulae of several polyphenyls.

Fig. 4. Four Kekulé structures of dibenzo[fg,op]naphthacene which contain six π-electrons in one of the central rings.

However, polyphenyls are not benzenoids according to our definition.[3] Therefore, in fully-benzenoid hydrocarbons in at least one Kekulé structure an "empty" hexagon contains six π-electrons. In the case of dibenzo[fg,op]naphthacene there are 20 Kekulé structures. Four of them indeed contain six π-electrons in the central rings. They are shown in **Fig. 4**.

The above simple analysis reveals that there are *no* truly fully-benzenoid hydrocarbons possible but benzene. This stimulated us to introduce a related concept of general validity, that is, the concept of fully-arenoid hydrocarbons. A preliminary report on this concept has already appeared elsewhere.[14(a)] The related ideas have also been discussed in several papers by Cyvin, Gutman *et al.* [14(b)-14(e)]

3   Fully-Arenoid Hydrocarbons

Fully-arenoid hydrocarbons may be defined as those benzenoid hydrocarbons which consist of smaller arenes (benzenoids of various sizes, the smallest being naphthalene) which are interlinked by essential single bonds. The term *fully-arenoid* is used to contrast the term *fully-benzenoid*. Those hexagons in fully-arenoid hydrocarbons which possess two paralled bonds (also called peri-bonds) which are essential single bonds, are now devoid of any conjugation, they are "empty" in Clar's sense. Benzenoid hydrocarbon in **Fig. 5** is an example of the fully-arenoid hydrocarbon.

In general we can schematize the fully-arenoid hydrocarbons as shown in **Fig. 6**. In other words, the fully-arenoid hydrocarbon B represents union of smaller arenes B_i:

$$B = \overset{\bullet}{\underset{i}{\cup}} B_i \qquad\qquad (2)$$

where black dot denotes the union through essential single bonds. This distinct feature (formulated as (2)) of fully-arenoid hydrocarbons is reflected in their properties (see discussion later).

3.1   Fully-Naphthalenoid Hydrocarbons

The smallest fully-arenoid hydrocarbon is perylene which has five hexagons and consists of two naphthalene units connected with peri-bonds. This benzenoid hydrocarbon is the first member of the class of fully-naphthalenoid hydrocarbons. It is depicted
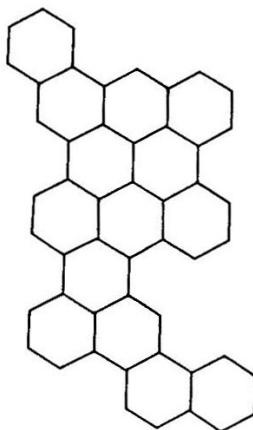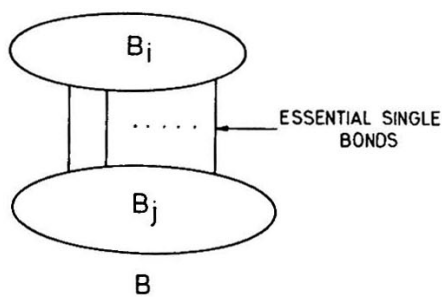
Fig. 5. Diagram of a fully-arenoid hydrocarbon.

Fig. 6. Diagram of a generalized fully-arenoid hydrocarbon.

in **Fig. 7**. The fully-naphthalenoid hydrocarbons are also called polyrylenes,[15(a)] poly-(peri-)naphthalenes[15(b,d)] and polyperylenes.[15(c)]

Several initial members of the family of fully-naphthalenoid hydrocarbons are known. Perylene was prepared years ago,[16] whilst terrylene and quaterrylene are known since the fifties.[17] These compounds, which are shown in **Fig. 8**, have been prepared by Zinke et al.[17(a)] in 1955 and by Clar et al.[17(b)] in 1956.

Fully-naphthalenoid hydrocarbons possess unusual properties because of their particular structure: naphthalenic units connected by peri-bonds.[18] For example, Maruyama et al.[19] established that quaterrylene possesses a fairly high semi-conductivity. Hence, it appears that the fully-naphthalenoid hydrocarbons may play an important role in the preparation of organic semi-conducting materials, since HOMO-LUMO gap approaches zero for large fully-naphthalenoids $(C_{10}H_4)_x$.[20]

3.2   Properties of Fully-Arenoid Hydrocarbons

In this section we summarize a number of properties of fully-benzenoid hydrocarbons.

(1) Clar's indices for "empty" hexagons in fully-arenoid are exactly equal to zero as shown in **Fig. 9** for the case of perylene.

(2) The ring REs for "empty" hexagons in fully-arenoid hydrocarbons are also exactly equal to zero.

(3) The calculated π-electron "ring-current" intensities for A and B rings in perylene differ considerably, thus reflecting the fact that the peri-bonds do not participate in the conjugation.[21,22] The π-electron "ring-current" intensity in ring B (0.239) is 4 times smaller than in ring A (0.970).[23] The above values of "ring-currents" are expressed as multiples of the benzene ring-current. If the single-bond character of the peri-bonds is removed, for example, by blocking the peaks and valleys[24] of perylene with two benzene rings, a new benzenoid hydrocarbon is created, named peropyrene, whose diagram is given in **Fig. 10**. Two units (phenylenes) making up peropyrene are not linked by essential single bonds. Clar's indices, ring REs and "ring-current" intensities of the central ring in peropyrene are much altered in comparison with the central ring in perylene.

Clar's indices corresponding to hexagons in peropyrene are given as follows: A = 1.031, B = 1.446 and C = 1.332. Similarly, the ring REs of peropyrene are given as: RE(A) = 0.369 eV, RE(B) = 0.540 eV and RE(C) = 0.678 eV, giving for the RE of this molecule the value of 3.372 eV.

The following are the "ring-current" intensities in peropyrene:[25] A = 1.031, B = 1.446 and C = 1.332. In peropyrene the "ring-current" in ring B (the central ring) has
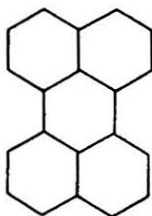
Fig. 7. Diagram of perylene, the first member of the class of fully-naphthalenoid hydrocarbons.
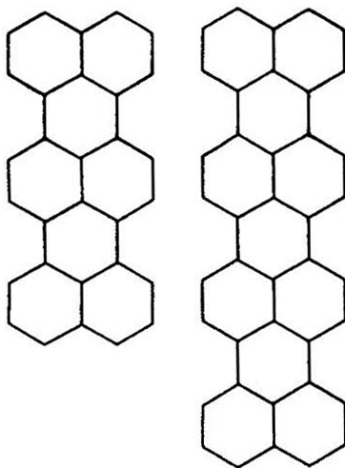

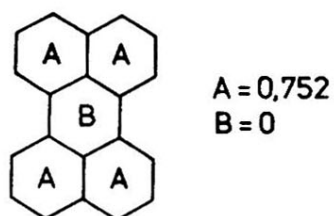**Fig. 8.** Diagrams of terrylene and quaterrylene.

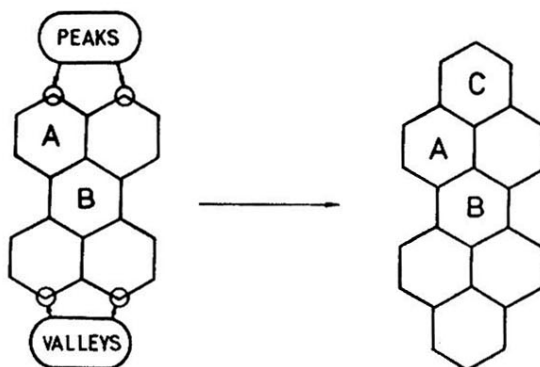**Fig. 9.** Clar's indices for hexagons in perylene.

Fig. 10. Schematic creation of peropyrene from perylene.

considerably increased and is 1.4 times bigger than in ring A. It is also 6 times bigger than the "ring-current" in the corresponding central ring B in perylene. At the first sight the B-rings in both molecules are in a similar structural environment, that is, similarly condensed with four surrounding hexagons. However, the exceptionally low-field shift (δ 9.15) of the proton closest to ring B observed in the experimental ^{1}H-NMR spectrum[22] of peropyrene, more than a whole ppm to lower field than the analogous proton in perylene,[26] is certainly consistent with the suggestion of there being a high "ring-current" intensity in ring B of peropyrene.

(4) The number of Kekulé structures K(B) of a fully-arenoid hydrocarbon B is simply equal to the product of the numbers of Kekulé structures $K(B_i)$ of constituting arenes B_i:

$$K(B) = \prod_i K(B_i) \tag{3}$$

For example, this formula reduces for fully-naphthalenoid hydrocarbons to:

$$K(B) = 3^{NU} \tag{4}$$

where NU is the number of the naphthalene units in the molecule. The above formula must have been known to Shrivastava and Speakman[27] already in 1960, although they did not put it down on the paper. Formula (4) was also known to Yen[28(a)] and discussed by Cyvin and Gutman.[28(b)]

Formula (4) can be generalized for fully-arenoid hydrocarbons which contain always the same arene B_i as a repeating constituting unit:

$$K(B) = \prod_i [K(B_i)]^{NA} \tag{5}$$

where NA is the number of repeating B_i's in B. This formula was also known to Yen[28(a)] and Cyvin and Gutman.[28(b)]

(5) The resonance energy RE(B) of a fully-arenoid hydrocarbon B is clearly equal to the sum of the resonance energies $RE(B_i)$ corresponding to constituting arenes B_i:

$$RE(B) = \sum_i RE(B_i) \tag{6}$$

(6) The fully-arenoid hydrocarbons can possess only composite 2-factors. A 2-factor of a benzenoid B is a spanning subgraph of B with all vertices of valency 2.[9(a)]

Examples of 2-factorable fully-arenoid hydrocarbons are already given in **Fig. 5,** **Fig. 7** and **Fig. 8**. Each of these fully-arenoids possesses a single composite 2-factor. A composite 2-factor corresponding to arene in **Fig. 5** is depicted in **Fig. 11**.

All fully-arenoids do not possess 2-factor. The necessary and sufficient conditions for a fully-arenoid hydrocarbon B to be 2-factorable are that its constituents are 2-factorable. The necessary and sufficient conditions for a benzenoid to be 2-factorable are discussed in detail elsewhere.[9(a),29] An example of a non-2-factorable fully-arenoid hydrocarbon is given in **Fig. 12**.

(7) We have assumed that the HMO spectra (or their parts) of the constituting arenes will be contained in the HMO spectrum of a fully-arenoid hydrocarbon. However, this was only partly so. For example, the HMO spectra of naphthalene and perylene share only two eigenvalues, that are ± 1.0000. Therefore, they exhibit a weak subspectrality.[30] It is also observed in the case of fully-naphthalenoids that the eight elements (all equal to ± 1.0000) of the perylene HMO spectrum are contained in the HMO spectra of higher poly-naphthalenes, but in the case of terrylene. In this case perylene and terrylene share six of these elements. The multiplicity of eigenvalue 1 in the spectra of poly-naphthalenes with n naphthalene units is given by $n + n \bmod 3 - (n \bmod 3) \bmod 2$. The multiplicity of eigenvalue "+1" vs. n is depicted in **Fig. 13**. In **Table 1** are given positive elements of the HMO spectra for naphthalene, perylene and higher members of the fully-naphthalenoids with up to 18 naphthalenic units. In these spectra it is also seen how the HOMO-LUMO gap decreases rapidly with increasing molecular size.

(8) The HMO bond orders for the essential single bonds are expected to be the smallest in comparison with bond orders corresponding to other bonds in the fully-arenoid hydrocarbon. This is the case. For example, the bond orders for two bonds connecting two naphthalene units in perylene are 0.4137. All other bond orders in perylene have much higher values.[31] The above value of the bond order gives by means of Coulson-Golebiewski's bond order-bond length relationship[32] for the length of the peri-bonds in perylene 1.44 A. The bond lengths in perylene have been predicted by Pauncz and Wilheim[33] in 1957. The experimental values for the lengths of peri-bonds in perylene are somewhat larger (av.: 1.471 ± 0.005 A)[34] than predicted. The prediction could be improved if the bond order-bond length relationship is modified.[15(b)]

In the case of quaterrylene the peri-bonds were first found to be rather large (av.: 1.527 ± 0.005 A), but a more recent raport gave the average value of 1.465 ± 0.005 A,[35] a result which is much more in a line with the corresponding values for perylene.

(9) As we already mentioned, the fully-arenoid hydrocarbons start with perylene and then their numbers rapidly increase. In **Fig. 14, Fig. 15** and **Fig. 16** we give diagrams of all nonisomorphic fully-arenoid hydrocarbons with up to 6, 7 and 8 hexagons, respectively.
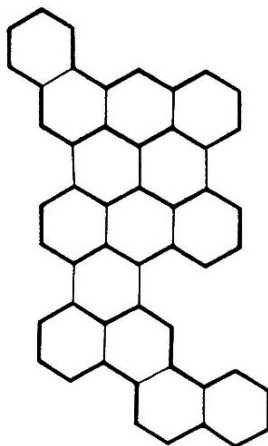
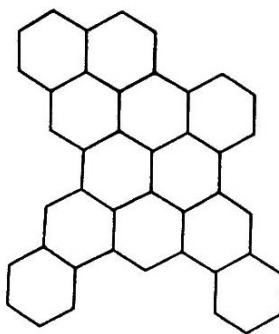**Fig. 11.** Composite 2-factor belonging to arene diagrammed in **Fig. 5.**

Fig. 12. Diagram of a non-2-factorable fully-arenoid hydrocarbon.

			2.329	1.951	1.954	1.840	1.708	1.562	1.474	1.361	1.258
			2.474	2.035	1.946	1.803	1.738	1.601	1.470	1.287	1.308
			2.512	2.138	1.931	1.748	1.769	1.636	1.550	1.402	1.378
			2.6156	2.279	1.9036	1.9128	1.8067	1.6676	1.5682	1.624	1.383
			2.663	2.340	1.9959	1.9311	1.8366	1.7406	1.6180	1.534	1.433
			2.7027	2.4403	2.0063	1.9440	1.8530	1.7518	1.6729	1.5514	1.462
			2.7247	2.5162	2.1410	1.9565	1.8916	1.7880	1.6758	1.6074	1.4882
				2.5613	2.2298	1.9960	1.9245	1.8326	1.7229	1.6674	1.543
				2.6531	2.3290	1.9985	1.9360	1.8445	1.7676	1.6658	1.549
				2.6773	2.4112	2.0136	1.9516	1.8714	1.7709	1.6653	1.576
				2.7077	2.4847	2.1399	1.9777	1.9053	1.8137	1.7708	1.638
				2.7259	2.5483	2.2222	1.9879	1.9341	1.8523	1.7744	1.678
					2.605	2.2972	1.9970	1.9402	1.8571	1.7815	1.651
					2.601	2.3364	2.0013	1.9577	1.8866	1.7963	1.726
					2.6658	2.4364	2.1221	1.9762	1.9165	1.8344	1.732
					2.7115	2.5138	2.2078	1.9994	1.9419	1.8656	1.780
					2.7269	2.5574	2.2381	1.9973	1.9439	1.8698	1.738
						2.628	2.3626	2.0233	1.9627	1.8993	1.816
						2.6619	2.4109	2.0337	1.9790	1.9258	1.810
						2.6925	2.4628	2.1351	1.9907	1.9471	1.871
						2.744	2.5480	2.2712	1.9977	1.9844	1.826
						2.7776	2.5562	2.2422	2.0075	1.9669	1.909
							2.6674	2.4079	2.1076	1.9814	1.937
							2.6713	2.4660	2.1839	1.9117	1.901
							2.6978	2.5224	2.2261	1.9973	1.539
							2.7166	2.5709	2.3229	1.9975	1.704
							2.7282	2.6132	2.3370	2.1016	1.934
								2.6493	2.454	2.2179	1.926
								2.6709	2.4638	2.2425	1.991
								2.7021	2.5469	2.3374	2.045
								2.7187	2.5698	2.3361	2.052
								2.7287	2.6672	2.4247	2.169
									2.6651	2.4768	2.204
									2.6652	2.5245	2.324
									2.7057	2.5674	2.309
									2.703	2.6056	2.456
									2.729	2.6389	2.455
										2.6772	2.504
										2.6905	2.562
										2.7086	2.547
										2.7216	2.619
										2.7294	2.687
											2.740
											2.698
											2.711
											2.727
											2.737
2.6961											
2.7720											

Table 1

The positive parts of the HMO spectra of naphthalene, perylene, terrylene, quaterrylene and higher members of the fully-naphthalenoid family with up to 18 naphthalenic units. Digits on the top of each column denote the number of the naphthalenic units in a poly-naphthalene.
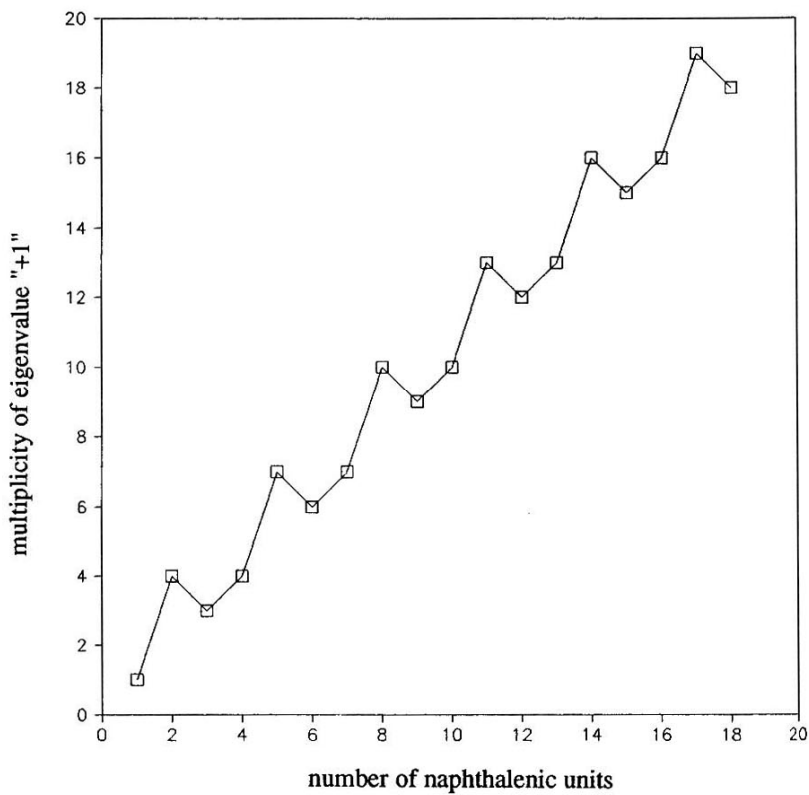
Fig. 13. The multiplicity of eigenvalue "+1" vs. the number of naphthalenic units in the spectra of poly-naphthalenes.
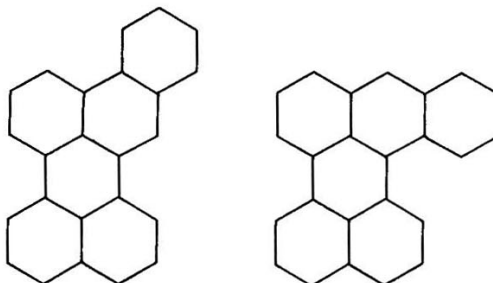
Fig. 14. Diagrams of all nonisomorphic fully-arenoid hydrocarbons with 6 hexagons.

4   Concluding Remarks

The concept of fully-arenoid hydrocarbons is discussed. It is pointed out that this concept is more general than the concept of fully-benzenoid hydrocarbons. A simplest class of fully-arenoids is the class of fully-naphthalenoid hydrocarbons. This class of fully-arenoids has properties, such as the diminishing HOMO-LUMO gap with the size, which may be essential for the preparation of organic semi-conductors.

Most of the properties of fully-arenoid hydrocarbons are either additive (eg., the resonance energies) or multiplicative (e.g., the Kekulé numbers). If fully-arenoids are 2-factorable, then they generate only composite 2-factors. Fully-arenoid hydrocarbons are much more numerous than the fully-benzenoids.

The concept of fully-arenoid hydrocarbons can be straightforwardly extended to polycyclic heterosystems which are then named fully-arenoid heterosystems.[14(a)] Most of the properties listed for fully-arenoid hydrocarbons are also exhibited in a modified form by fully-arenoid heterosystems. Work on the fully-arenoid heterosystems is in progress.
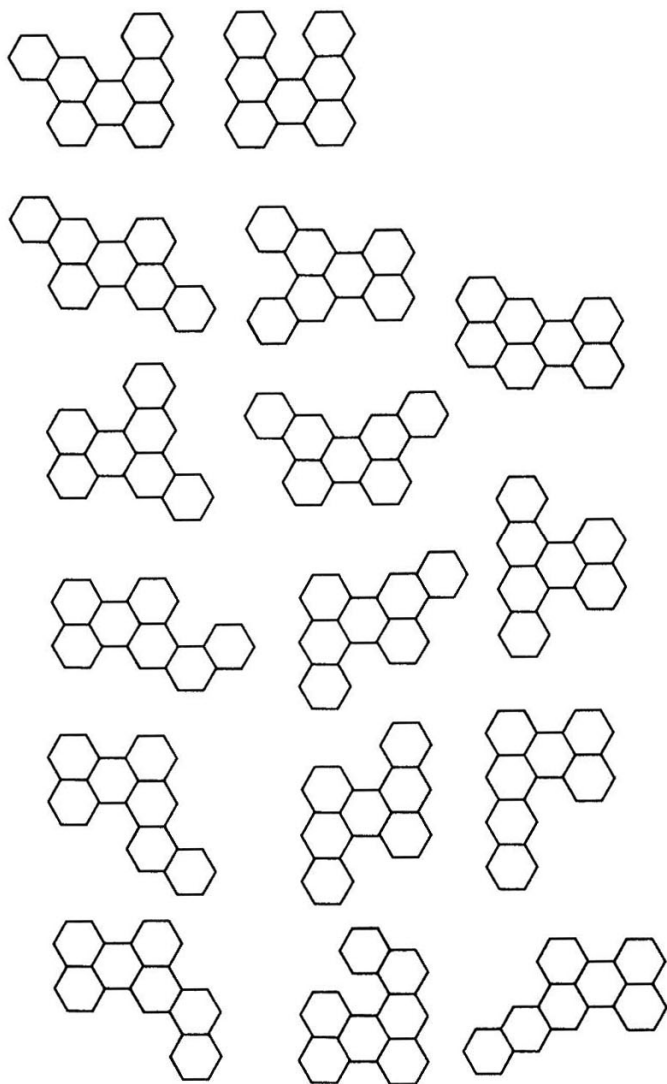
Acknowledgements

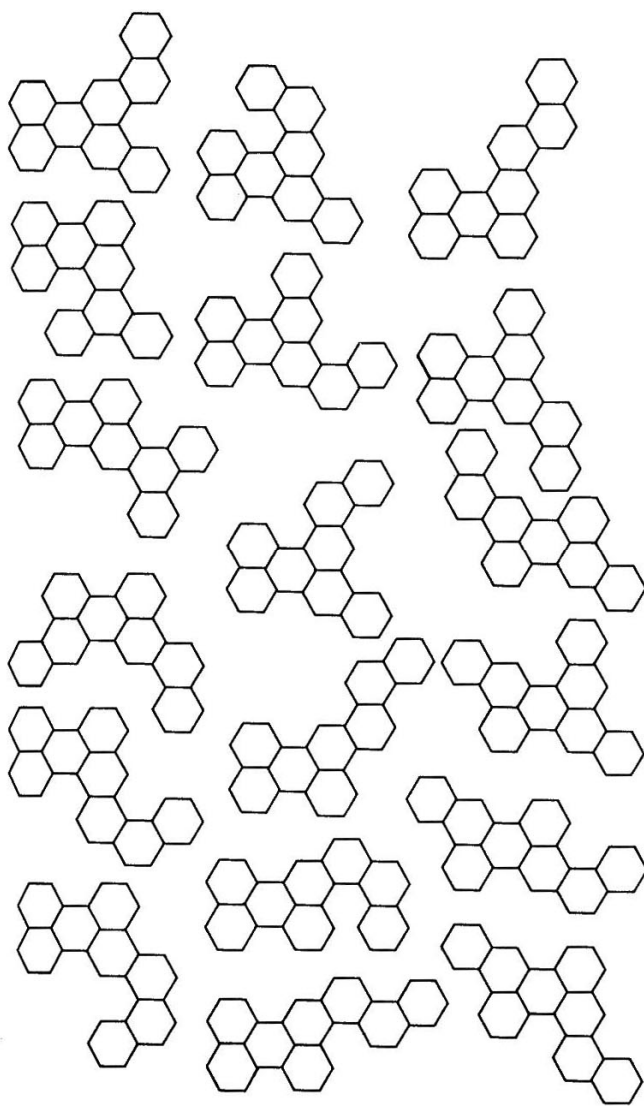**Fig. 15.** Diagrams of all nonisomorphic fully-arenoid hydrocarbons with 7 hexagons.

Fig. 16. Diagrams of all nonisomorphic fully-arenoid hydrocarbons with 8 hexagons.
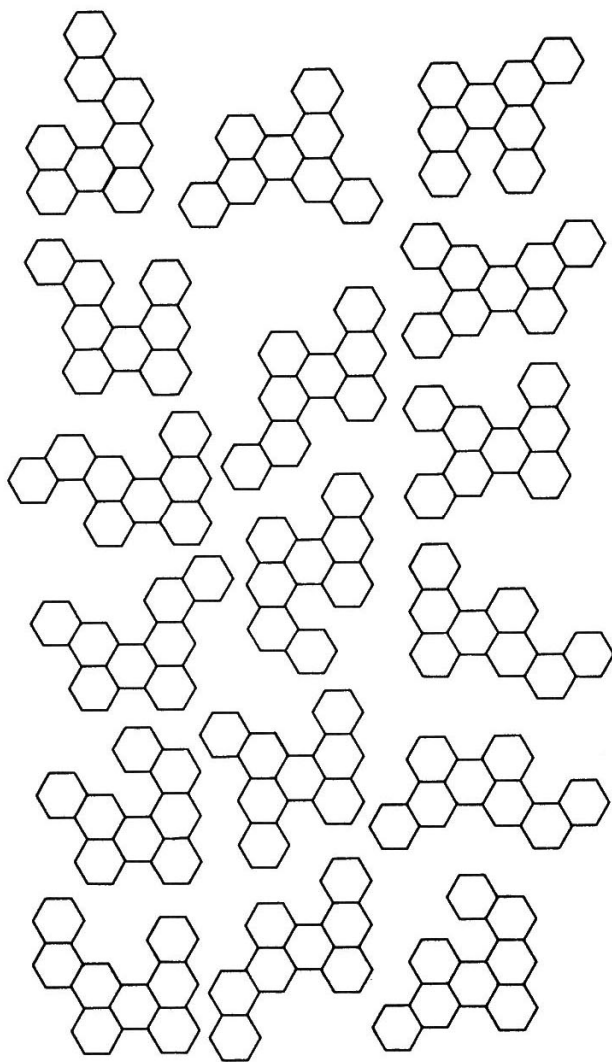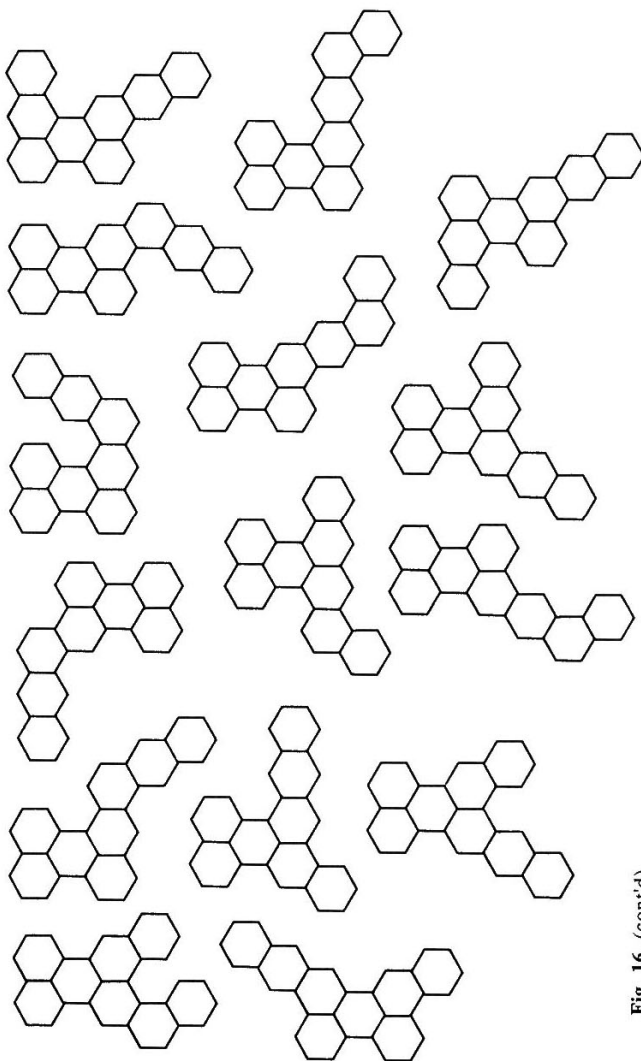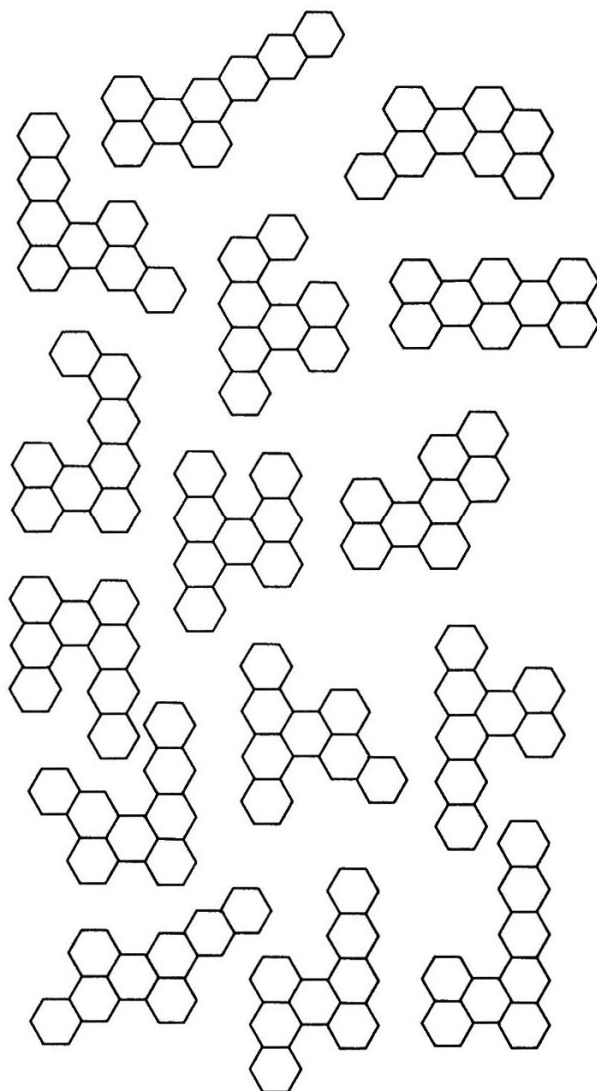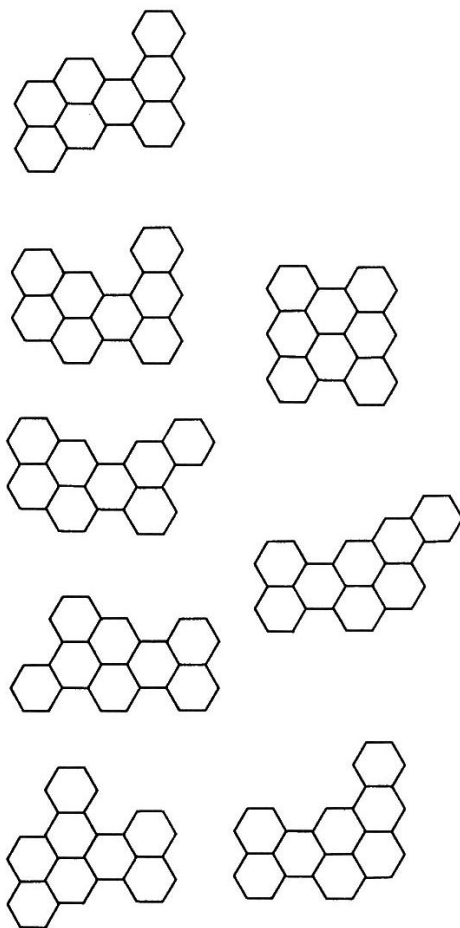
Fig. 16. (cont'd)

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