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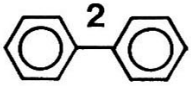

ALL-BENZENOID SYSTEMS:

TOPOLOGICAL PROPERTIES OF BENZENOID SYSTEMS. LVII

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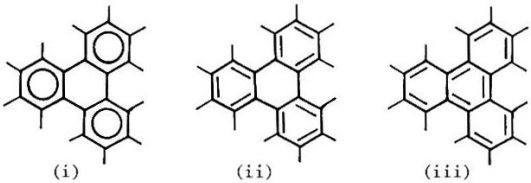
The present note is written as an appendix to the preceding article [1]. For the basic topological properties of all-benzenoid hydrocarbons references 4, 5 and 11 therein [1] may be consulted. It is also referred to the preceding article [1] for special definitions and terminology.

Here we point out a few further results on all-benzenoids. They seem to have been disregarded previously.

Proposition 1. All-benzenoid hydrocarbons are normal. In other words, every carbon-carbon bond of an all-benzenoid hydrocarbon is single in some Kekulé structures and double in some others.

Proof. Recall that a carbon-carbon bond of a conjugated molecule is said to be fixed single (resp. fixed double) if in all Kekulé structural formulas this bond is drawn as a single bond (resp. double bond). From the definition of all-benzenoid systems it is clear that the bonds forming the *F* hexagons cannot be fixed. Similarly, an all-benzenoid system cannot (by definition) possess a fixed double bond. It remains to demonstrate that the bonds belonging (exclusively) to *E* hexagons are not fixed single bonds.

In order to do this, note that every *E* hexagon in an all-benzenoid system has exactly three *F* neighbours, implying the structural detail presented on Fig. 1(i). Then, of course, there must exist Kekulé structures containing three double bonds in each of the three *F* hexagons; one such Kekulé structure is depicted in Fig. 1(ii). But then also the arrangement of the double and single bonds presented in Fig. 1(iii) is compatible with some



(i) (ii) (iii)

Fig. 1. (i) Every empty hexagon in an all-benzenoid is adjacent to three full hexagons. (ii) and (iii) Kekulé structures compatible with the Clar formula (i).

of the Kekulé structures of the molecule considered. Consequently, the carbon-carbon bonds which belong to the E hexagon are double in some of the Kekulé structures.

This proves *Proposition 1*. ■

Proposition 2. Every all-benzenoid system has at least 6 free edges.

The proof of *Proposition 2* is based on a property of benzenoid systems formulated in *Proposition 3*. Let n_2 and n_3 denote the number of vertices of degree two and three, respectively, belonging to the perimeter of the benzenoid system. Then the length of the perimeter is, of course, $p = n_2 + n_3$.

Proposition 3. For every benzenoid system, $n_2 = n_3 + 6$.

This result can immediately be proved by total induction on the number of hexagons. ■

Proof of Proposition 2. Denote the edges belonging to the perimeter by e_1, e_2, ..., e_p and the number of free edges by f. Let, by convention, the free edges be labeled as e_1, e_2, ..., e_f.

Denote by $t(e_i)$ the number of vertices of degree two, which are the endpoints of e_i. Then it is evident that

$$\sum_{i=1}^{p} t(e_i) = 2n_2.$$

On the other hand, $t(e_i) = 2$ for $i = 1, 2, \ldots, f$, and $t(e_i) \leq 1$ for $i = f+1, f+2, \ldots, p$. Consequently,

$$\sum_{i=1}^{p} t(e_i) \leq 2f + (p - f)$$

$$2n_2 \leq 2f + (p - f) = n_2 + n_3 + f$$

$$n_2 \leq n_3 + f.$$

Bearing in mind *Proposition 3*, we see that $f \geq 6$, which is just what is claimed in *Proposition 2*. ■

Note that *Proposition 2* is closely related to Theorem 3 of [2], which in [2] was stated without proof.

Proposition 4. The division of the hexagons of an all-benzenoid hydrocarbon into full (F) and empty (E) is unique.

Proof. According to *Proposition 2* an all-benzenoid system necessarily possesses free edges. Choose such a free edge and label the hexagons to which it belongs by F. Label the neighbours of this hexagon by E. Every hexagon labeled by E must have three adjacent (but mutually disjoint) hexagons labeled by F. All the neighbours of these F hexagons are to be labeled by E, etc.

We continue this labeling procedure until all hexagons are denoted by F or E. Since the number of hexagons is finite, the procedure will sooner or later reach its end. If a consistent labeling of this kind is not possible, then the hydrocarbon considered is not all-benzenoid. ■

It should be mentioned that the above proposition assumes that the benzenoid system is finite. In the case of infinite all-benzenoids, *Proposition 4* needs not necessarily hold. An example for this is provided by the graphite lattice, in which the hexagons can be divided into F and E in three distinct ways (Fig. 2).

Fig. 2. The graphite lattice considered as an all-benzenoid system. The Clar formula is not unique.

Proposition 5. (a) A catacondensed all-benzenoid hydrocarbon has $3k + 1$ hexagons, where $k \in \{0, 1, 2, \ldots.\}$. (b) The number of hexagons of a pericondensed all-benzenoid hydrocarbon may be any natural number, except 1, 2, 3, 4, 5 and 7.

Proof. Statement (a) is an immediate consequence of the fact that all catacondensed all-benzenoids can be generated from benzene (h=1) by repeated application of the one-contact addition [1].

According to *Proposition 2* every pericondensed all-benzenoid system possesses free edges. Therefore, if there exists a pericondensed all-benzenoid with h_o hexagons, then by means of repeated one-contact additions one can construct pericondensed all-benzenoids with $h_0 + 3k$ hexagons, $k \in \{1, 2, ...\}$.

There exist pericondensed all-benzenoids with h_o = 6, 8 and 9 (see Fig. 3 of [1]). Therefore, the above mentioned construction guarantees the existence of pericondensed all-benzenoids with $h = 6$ and $h \geq 8$. The nonexistence of such systems for h=7 and $h < 6$ is verified by direct checking of all the 226 possible pericondensed systems [3] with seven or less than six hexagons.

This completes the proof of *Proposition 5.* ■

Proposition 6. Denote by h_F and h_E the number of full and empty hexagons, respectively. (a) In a catacondensed all-benzenoid hydrocarbon h_F is odd, and $h_E = (h_F - 1)/2$. (b) In a pericondensed all-benzenoid hydrocarbon the ratio h_F/h_E is less than or equal to two.

Proof. One should first note that an all-benzenoid hydrocarbon has $n = 6h_F$ carbon atoms. Since in addition [4]

$$n + n_i = 4h + 2,$$

where n_i is the number of internal carbon atoms (i.e. those which do not belong to the perimeter), one immediately computes

$$h_E = (2h_F + n_i - 2)/4.$$

For catacondensed benzenoids $n_i = 0$, which immediately implies statement (a). For pericondensed molecules $n_i > 0$, and since the all-benzenoids are Kekuléan n_i must be even. This implies statement (b). ■

Examples show that the ratio h_F/h_E can be less than unity and, for sufficiently large benzenoid systems, its value can be arbitrarily close to zero.

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