FULLY–ARENOID HYDROCARBONS

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Abstract

Knop et al. defined recently [Math. Chem. **29**, 81 (1993)] the class of so–called fully–arenoid hydrocarbons. Their definition, however, is not a generalization of the concept of fully–benzenoid hydrocarbons, introduced 35 years ago by Clar and Zander. Namely, according to Knop et al. there are no truly fully–benzenoid systems other than benzene. In this paper we point out another definition of fully–arenoid systems, that is of the Clar–Zander type, that is a proper generalization of the concept of fully–benzenoids, and that embraces as special cases the fully–arenoids of Knop et al. The new concept enables a better understanding of the conjugation modes in benzenoid molecules. A few examples, justifying its introduction and demonstrating its chemical relevance are discussed.

1. Introduction

In a recent paper [1] Knop, Müller, Szymanski, Nikolić and Trinajstić analysed the concept of fully–benzenoid hydrocarbons. One of their basic findings is that "the only truly fully–benzenoid hydrocarbon is benzene". This conclusion follows from the observation that in all other molecules that are fully–benzenoid in the sense of the Clar aromatic sextet theory [2], the bonds connecting the "full" hexagons are not essentially single [3]. Another way to express the same fact is to note that the (unique) Clar aromatic sextet formula of a fully–benzenoid hydrocarbon does not represent all Kekulé structures of the respective conjugated system. In other words, there are Kekulé

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structures in which the double bonds are located at the edges lying in empty hexagons. In [1] this fact is illustrated on the example of dibenzo[fg, op]naphthacene (see also below).

We mention in passing that the above property of fully–benzenoids was certainly known already to Clar and Zander [4,5a]. Some time ago, based on the same observation, Polansky and one of the present authors [6] found a combinatorial formula for the number of the "excess" Kekulé structures in a fully–benzenoid hydrocarbon. The fact that the "empty" rings in fully–benzenoids are not devoid of cyclic conjugation was also pointed out on several occasions [7–9].

The actual relation between Kekulé and Clar structures is not at all simple: in some cases the Clar formulas represent only a fraction of the Kekulé structures (as, for instance, in fully–benzenoid hydrocarbons), but in some other cases the Clar formulas represent all Kekulé structures with a certain degree of redundancy. This aspect of the theory of benzenoid molecules was first examined by Obenland, Schmidt and one of the present authors [10] and eventually outlined in detail in the book [5b].

Now, Knop et al. [1] establish that in benzenoid systems it is not possible to connect the full hexagons by essentially single bonds. Then they observe the important fact that such connections are possible between benzenoid fragments of larger size (= arenes), which straightforwardly leads to the new concept of "fully–arenoid hydrocarbons". As shown in [1] this class of benzenoid systems possesses a few remarkable properties and certainly deserves the attention of theoretical chemists.

By no means is the purpose of the present article to deny the significance of the results obtained in [1]. We, however, wish to point out another approach to the same problem. Needless to say that our research was strongly inspired by the work of Knop et al. [1].

2. On the Clar–Zander definition of fully–benzenoid hydrocarbons

The concept of fully–benzenoid (sometimes called all–benzenoid [5–7]) hydrocarbons was invented by Clar and Zander in 1958 [4] (see also [2,5a,11]). According to Clar and Zander [4], a benzenoid molecule is said to be fully–benzenoid if its aromatic sextet formula "contains benzenoid rings (each containing three double bonds) which are interlinked by quasi–single bonds". In other words, a fully–benzenoid system is divided into two types of domains: "full" and "empty", the "full" domains being hexagons, each containing an aromatic sextet (represented by an inscribed circle), and any two such "full" domains being disjoint. The "full" domains embrace all the vertices of the

respective system.

Below is depicted the usual Clar formula (I) of the fully–benzenoid hydrocarbon dibenzo[*fg,op*]naphthacene; in diagram II the four "full" domain are indicated by hatching.


I   II
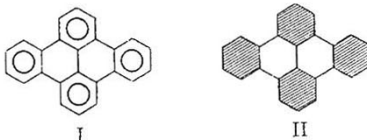
Precise graph–theoretic (i.e. structural) characterizations of fully–benzenoid hydrocarbons are available [12–15]. Herefrom we mention the following results:

1. A benzenoid graph B represents a fully–benzenoid hydrocarbon if and only if either (a) or (b) is obeyed.

    (a) All the vertices of B can be covered by disjoint hexagons.

    (b) B has a 2–factor, composed exclusively of 6–membered cycles.

2. If B is the molecular graph of a fully–benzenoid hydrocarbon, then the cover described under 1a and the 2–factor described under 1b are unique.

3. If B is the molecular graph of a fully–benzenoid hydrocarbon, then the number of its vertices (n) is divisible by six. Besides, $n/6$ is the number of "full" hexagons. The minimum value for $n/6$ is 3 apart from benzene itself $(n/6 = 1)$, which sometimes is included as the smallest (trivial) fully–benzenoid.

3. The extension of the Clar–Zander definition to fully–arenoid hydrocarbons

Following the same line of reasoning as outlined in the previous section, we may conceive the class of fully–arenoid hydrocarbons. Thus, a benzenoid system B is said to be fully–arenoid if it can be divided into two types of domains: "full" and "empty", the "full" domains being arenes (= Kekuléan benzenoids) and any two "full" domains being disjoint. The "full" domains embrace all the vertices of B.

The diagrams III–VI provide illustrative examples for the above definition; the "full" domains are indicated by hatching. The benzenoid systems VII and VIII are not fully–arenoid.

III   IV   V

VI   VII   VIII
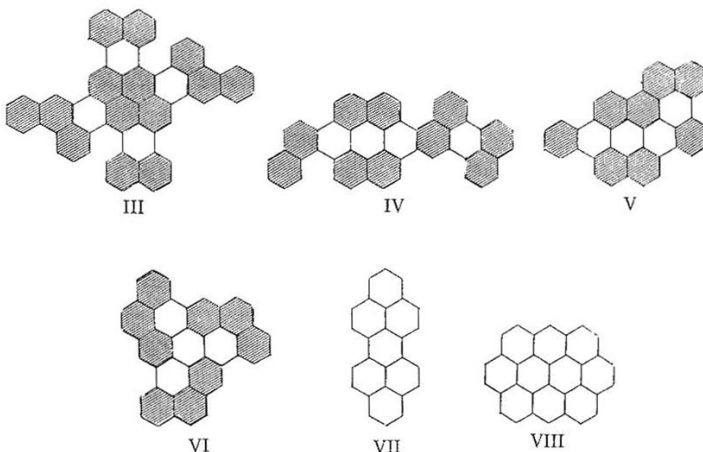
We observe that the arene–units forming the "full" domains may be mutually isomorphic (as in IV and VI), but need not (as in III and V). In particular, III can be viewed as composed of two naphthalene–, two phenanthrene– and one pyrene–unit; IV is composed of five naphthalene–units; V consists of two benzene–, one naphthalene– and one chrysene–unit; VI consists of three phenanthrene–units. We say that IV and VI are fully–naphthalenoid and fully–phenanthrenoid molecules, respectively, whereas III and V are mixed fully–arenoids.

Of the above examples, only III is a fully–arenoid in the sense of Knop et al. [1].

The following two special cases are evident from the above definition:

— The fully–arenoids in which all "full" domains are hexagons, are just the fully–benzenoid systems in the sense of Clar and Zander [4].

— The fully–arenoids in which all the bonds connecting the "full" domains are essentially single are fully–arenoid systems in the sense of Knop et al. [1].

Hence, our definition embraces as special cases both the fully–benzenoid hydrocarbons (as considered within the Clar aromatic sextet theory [2]) and all–arenoids (according to Knop et al.).

In what follows we will examine more carefully the simplest class of fully–arenoids other than the fully–benzenoid hydrocarbons. This class is formed by the

fully–naphthalenoid systems.

4. Fully–naphthalenoid hydrocarbons

According to the concept of "truly" fully–arenoid hydrocarbons [1], for each p, $p \geq$ 2, there exists just a single fully–naphthalenoid molecule with p naphthalene units. These are: perylene ($p = 2$), terrylene ($p = 3$, IX), quaterrylene ($p = 4$) etc. On the other hand, from our definition follows that there is a unique fully–naphthalenoid with p = 2 (perylene), but already ten fully–naphthalenoids with $p = 3$. These are IX–XVIII.
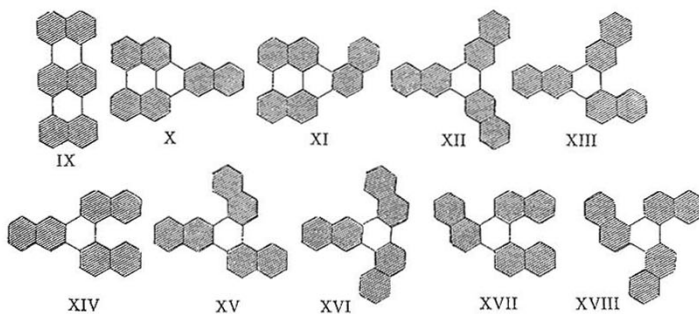
In complete analogy with the properties established for fully–benzenoid hydrocarbons (specified in section 2), we have the following results:

1. A benzenoid graph B represents a fully–naphthalenoid hydrocarbon if and only if either (a) or (b) is obeyed.

    (a) All the vertices of B can be covered by disjoint doublets of hexagons (= naphthalene units).

    (b) B has a 2–factor, composed exclusively of 10–membered cycles.

2. If B is the molecular graph of a fully–naphthalenoid hydrocarbon, then the cover described under 1a and the 2–factor described under 1b are unique.

3. If B is the molecular graph of a fully–naphthalenoid hydrocarbon, then the number of its vertices (n) is divisible by ten. Besides, $n/10$ is the number of "full" naphthalene–units. The minimum value of $n/10$ is 2 apart from naphthalene itself ($n/10 = 1$), which may be included as the smallest (trivial) fully–naphthalenoid.

The concept of fully–naphthalenoid hydrocarbons implies numerous open questions. First of all, how many such systems exist for a given number p of naphthalene–units? Is it possible to give a non–trivial structural characterization of these molecules?

In the case of fully–benzenoid hydrocarbons various theoretical methods [7–9] indicate that the extent of cyclic conjugation in "full" hexagons is much greater than in "empty" hexagons. It is plausible to expect that similar regularities will be found also in the case of fully–naphthalenoids. An extra complication here is that fully–naphthalenoids possess three types of naphthalene units: Those with two "full" hexagons, those with one "full" and one "empty" hexagon and (in some cases) those with two "empty" hexagons. Research in this direction is under way.

5. Some remarks

The newly introduced class of fully–arenoid hydrocarbons provides a sound generalization of both the concept of fully–benzenoids and of the recently proposed "truly" fully–arenoids [1]. Whereas the structural features of fully–benzenoids are understood to a great extent [12–14], a complete structural characterization of fully–arenoids is a problem that remains to be solved in the future. At this moment we don't even know how to efficiently recognize fully–arenoid molecules. The fact that a benzenoid species is a fully–arenoid is verified by constructing its appropriate cover. One should, however, note that this cover needs not to be unique, as illustrated by means of XIX, XX and XXI.

XIX   XX   XXI
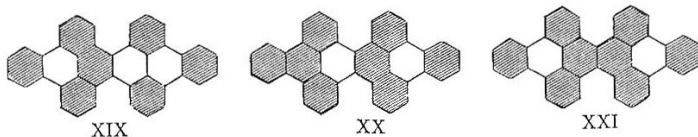
If, on the other hand, the benzenoid system considered is not fully–arenoid (as is the case with VII and VIII), then this fact can be verified only by a trial–and–error testing of all possible covers, which may be a quite tedious task.

The enumeration of fully–arenoid hydrocarbons and their classification with respect to the number and type of "full" domains is another challenging problems that

awaits elaboration.

6. Some chemical applications of the concept of fully–arenoid molecules

Although the main goal of this paper is to provide the conceptual and structural foundation for the definition of the class of fully–arenoid molecules, it is worth noting that this definition enables a better understanding of the various π–electron properties of benzenoid hydrocarbons and, in particular, a better insight into their conjugation modes. As known [2], the conjugation modes determine the basic features of the electron spectra of a benzenoid compound. Besides, these modes have experimentally observable effects on the proton n.m.r. spectrum, geometry and chemical reactivity of the respective molecules.

In order to illuminate some chemical aspects of our definition, we examine here the effects of various cycles on the thermodynamic properties of fully–arenoids.

A convenient method for the calculation of these energy–effects was developed within the framework of the Hückel molecular–orbital approximation. (For details of this approach see [16,17]; for some recent applications to benzenoid systems see [18–22].)

Every cycle Z in a polycyclic conjugated molecule G has a certain contribution to the HMO total π–electron energy, denoted by $ef = ef(G,Z)$. In what follows, the ef–values are expressed in the units of the HMO carbon–carbon resonance integral β, where β is negative–valued. Consequently, $ef > 0$ means thermodynamic stabilization; the larger $ef(G,Z)$ is, the larger is the contribution of the cycle Z to the enthalphy of the conjugated system G. It is clear that $ef(G,Z)$ measures the intensity of cyclic conjugation in the molecule G, along the cycle Z.

Studies of cyclic conjugation in fully–naphthalenoid hydrocarbons were reported elsewhere [22]. Here we present some characteristic results for fully–anthracenoid systems.

Consider first the molecule XXII which is fully–anthracenoid in the sense of both Knop's [1] and our definition. The three anthracene–units of XXII are separated by essentially single bonds.

The energy–effects of the six–membered cycles of XXII are: $ef(\text{XXII},\mathbf{a}) = 0.0936$, $ef(\text{XXII},\mathbf{b}) = 0.0488$, $ef(\text{XXII},\mathbf{c}) = 0.0320$, $ef(\text{XXII},\mathbf{d}) = 0.0874$, $ef(\text{XXII},\mathbf{e}) = 0.0397$. Because of symmetry, $ef(\text{XXII},\mathbf{a}) = ef(\text{XXII},\mathbf{a'})$, $ef(\text{XXII},\mathbf{c}) = ef(\text{XXII},\mathbf{c'})$, etc.
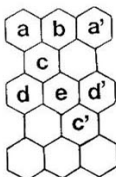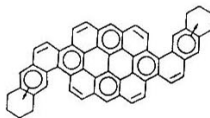
XXII

The full hexagons of XXII have a significantly larger *ef*–value (average: 0.0763) than the empty hexagons (average: 0.0320), showing that the gross part of the conjugation is located in the anthracene units. (Note, however, that the conjugation in the "empty" hexagons is far from being negligible.) The same phenomenon is seen even better, if one considers the energy–effects of the 14–membered cycles: ef (XXII,a+b+a') $= 0.0154$, ef (XXII,d+e+d') $= 0.0115$, ef (XXII,a+c+e) $= 0.0006$, ef (XXII,b+c+d) $= 0.0009$, ef (XXII,c+e+c') $= 0.0002$. Hence, the conjugation along the perimeter of the anthracene–units of XXII is almost two orders of magnitude stronger than the conjugation along other 14–membered cycles.

The above data show that the dominant conjugation modes in XXII are those within the anthracene–units. This, of course, is no surprise whatsoever and is in harmony with the classical (Kekulé–structure–based) theories of conjugation [1,5]. The following two examples indicate that the conjugation induced by the fully–arenoid character of certain benzenoids may be at variance with the predictions of the classical approaches.
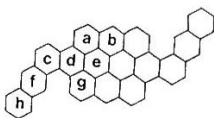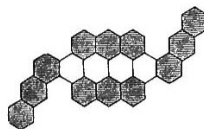

XXIII   XXIIIa   XXIIIb

For the six–membered cycles of XXIII we calculated: ef (XXIII,a) $= 0.0590$, ef (XXIII,b) $= 0.0563$, ef(XXIII,c) $= 0.0547$, ef(XXIII,d) $= 0.0502$, ef(XXIII,e) $= 0.0337$, ef (XXIII,f) $= 0.0756$, ef (XXIII,g) $= 0.0581$, ef (XXIII,h) $= 0.1037$. We see that the

cyclic conjugation is relatively large in hexagons which according to our model are full
(**a,b,c,f,g,h**) and relatively small in hexagons which within the fully–arenoid–concept are
considered as empty (**d,e**), although the differences are not dramatic. The Clar formulas
of XXIII possess aromatic sextets in both full and empty hexagons (cf. diagrams XXIIIa
and XXIIIb). In particular, hexagon **d** is full in the Clar formula XXIIIa, but is empty in
the fully–arenoid formula XXIIIb. The opposite is true for the hexagons **a** and **c**. The
calculated *ef*–values of **a**, **c** and **d** clearly indicate that the predictions of the Clar model
are violated in favour of our fully–arenoid concept.

A similar conflict between Clar theory and the fully–arenoid picture occurs in the
case of the benzenoid system XXIV, cf. XXIVa and XXIVb.

XXIV   XXIVa   XXIVb
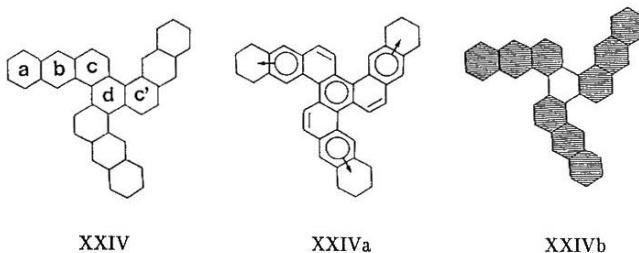
Here ef (XXIV,**a**) = 0.1022, ef (XXIV,**b**) = 0.0745, ef (XXIV,**c**) = 0.0559, ef
(XXIV,**d**) = 0.0652, and we are faced with a kind of compromise between XXIVa and
XXIVb. Indeed, hexagon **d** has a (slightly) larger effect than hexagon **c**, in agreement
with the Clar theory. On the other hand, the average energy–effect of the full hexagons
of XXIVb is 0.0755, exceeding that of the empty hexagon **d**.

The importance of the conjugation modes, implied by formula XXIVb is seen
much clearer from the energy–effects of the 14–membered cycles: ef (XXIV,**a+b+c**) =
0.0145, ef (XXIV,**b+c+d**) = 0.0041, ef (XXIV,**c+d+c'**) = 0.0010. Again, the perimeters
of the anthracene–units have considerably stronger conjugation effects than other cycles
of the same size.

The examples discussed above show that the concepts put forward in this work
have chemical significance and may lead to interesting chemical applications.

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