

A CLAR-TYPE REGULARITY FOR DIANIONS OF BENZENOID HYDROCARBONS

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Phenanthreno-annelated anthracenes as well as their dianions are studied by means of molecular-orbital theory (at the AM1 level). The charge distribution in the dianions is highly non-uniform: the anthracene fragment bears roughly 50% more negative charge than the phenanthrene fragment(s). These findings point at the possibility to apply the concepts of Clar aromatic sextet theory to benzenoid dianions. Within the framework of this Clar-type model, phenanthreno-annelated anthracene dianions may be viewed as charged analogs of all-benzenoid hydrocarbons.

Keywords: Benzenoid dianions; phenanthreno-annelated anthracenes; Clar theory; all-benzenoid hydrocarbons

INTRODUCTION

The concept of all-benzenoid hydrocarbons [1, 2] represents the foundation of the Clar aromatic sextet theory [3, 4]. All-benzenoid hydrocarbons are characterized by a unique Clar formula, in which all π -electrons are grouped into aromatic sextets (indicated by drawing circles in the respective hexagons), and in which double bonds are absent. Such Clar formulas are known to provide a reasonably good description of the electronic structure, local aromaticity and physico-

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chemical behavior of the respective benzenoid molecules [3–5]. All-benzenoid hydrocarbons are chemically much less reactive and thermodynamically much more stable than other, isomeric, benzenoids [1–4].

The Clar model was designed for non-charged benzenoid systems, and has—so far—not been applied to ionic species. In this work we make an attempt into this direction. (Some preliminary observations on the rules governing cyclic conjugation in dianions of conjugated molecules, both benzenoid and non-benzenoid, were reported in [6].)

Dianions of the linear (1) and angular (2) phenanthreno-anthracene (see Fig. 1) have been synthesized by Rabinovitz *et al.* [7, 8]. The charge distribution in these dianions was estimated from their ^1H NMR spectra [7, 8]. It was found that the partitioning of the charge is highly non-uniform, a significant part of it being localized on the anthracene fragment. The authors of [8] describe this finding as “unusual”.

A Clar-theory-type reasoning applied to the dianions of 1 and 2 may be used to rationalize the above experimental results. Indeed, formula C_1 is the unique representation of the dianion of 1, in which all π -electrons except four are grouped into aromatic sextets (see Fig. 1). Such a formula requires that the remaining two pairs of π -electrons be

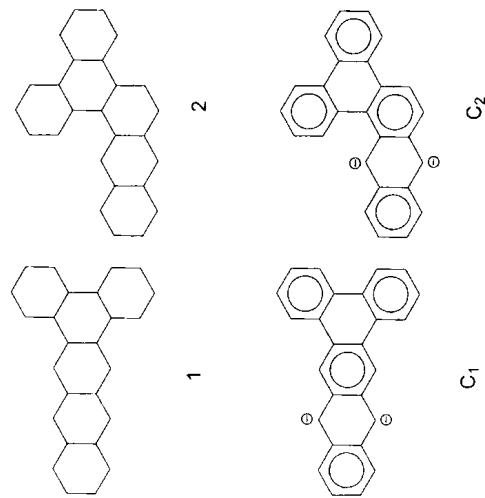


FIGURE 1 The two isomeric phenanthreno-anthracenes, namely dibenzo[*a,c*]naphthalene (1) and dibenzo[*b,g*]chrysene (2), and the Clar-type formulas C_1 , C_2 of their dianions; note the absence of double bonds in C_1 and C_2 .

located on the central hexagon of the anthracene fragment. In full analogy, formula C_2 is the Clar-type representation of the dianion of 2.

If such a model is chemically sound, then analogous excess of negative charge on the anthracene fragment should be expected also in the case of the dianions of the phenanthreno-annelated anthracenes 3–6, see Figure 2. These anions may also be viewed as “all-benzenoid” because each of them has a unique Clar-type formula without double bonds, with six full and two empty hexagons, and with two pairs of π -electrons located on the central hexagon of the anthracene fragment. For instance, C_3 and C_6 are the Clar-type representations of the dianions of 3 and 6, see Figure 2.

In order to test our model we have undertaken molecular-orbital studies of the benzenoid hydrocarbons 1–6 and of their dianions, aimed at establishing the charge distribution in them.

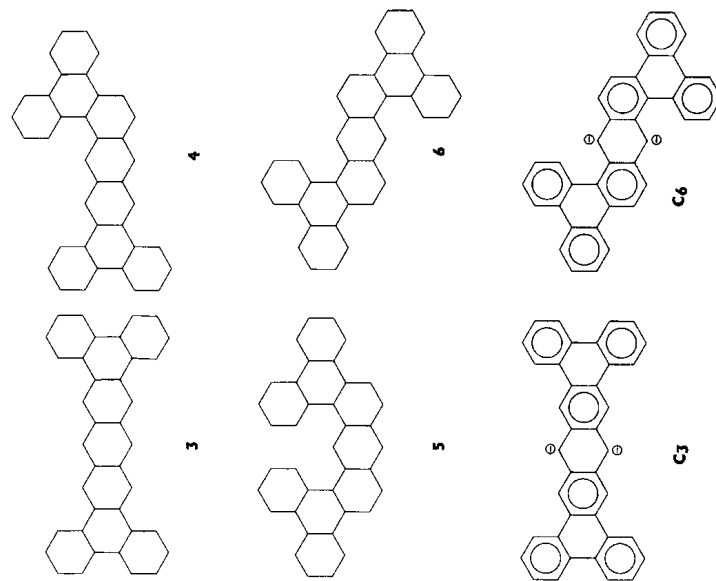


FIGURE 2 The four isomeric benzenoid hydrocarbons obtained by attaching phenanthrene units to both ends of an anthracene fragment, and the Clar-type formulas of two of their dianions.

DETAILS OF CALCULATION

The geometries and charge distributions of the molecules **1–6** and, separately, of their dianions were determined by the AM1 method (using a MOPAC 7.0 package) [9–11], employing full geometry optimization and imposing no a priori symmetry constraints. The structures of the compounds were built with PCMODEL 4.0 [12, 13] and were saved as MOPAC files for AM1 semiempirical calculations.

For illustrative purposes, in Figures 3–6 are shown the calculated geometries of the molecules **3** and **5** and of their dianions, as well as the charge distribution in the dianions. Analogous results for the systems **1**, **2**, **4** and **6** together with other computational details are available from the authors upon request.

RESULTS AND DISCUSSION

In Table I are presented the charges of the anthracene and phenanthrene fragments of **1–6** and their dianions. These are obtained by summing the charges of all atoms of the respective fragment; for the carbon atoms shared by two fragments half of the charge is attributed to one, and half to the other fragment.

In neutral molecules **1–6** the charge distribution found is essentially uniform, with the phenanthrene fragment(s) bearing a small negative charge. This feature is to be expected, because **1–6** are typical representatives of alternant hydrocarbons, to which the pairing theorem applies [14].

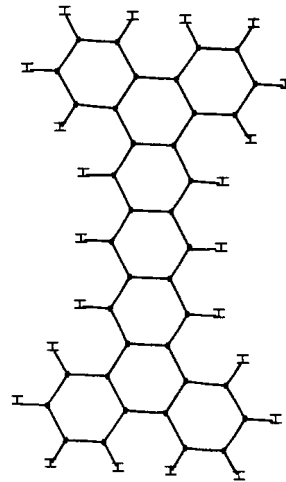


FIGURE 3 Geometry of the benzenoid hydrocarbon **3**; both the neutral molecule and its dianion (see Fig. 4) are found to be perfectly planar, possessing a D_{2h} symmetry.

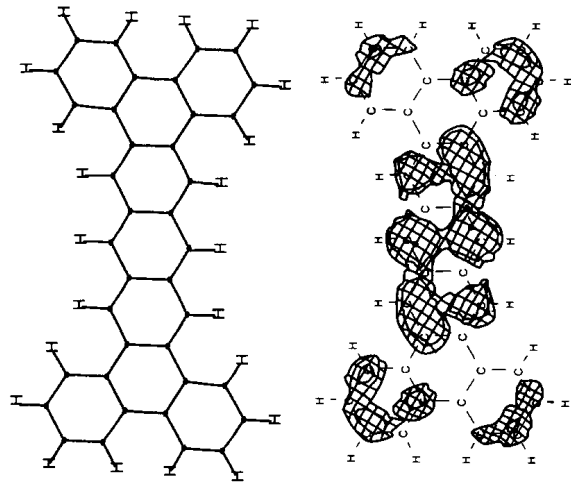


FIGURE 4 Geometry of the dianion of **3** and the charge distribution in it; the geometries of the dianion and the neutral molecule (see Fig. 3) are almost identical.

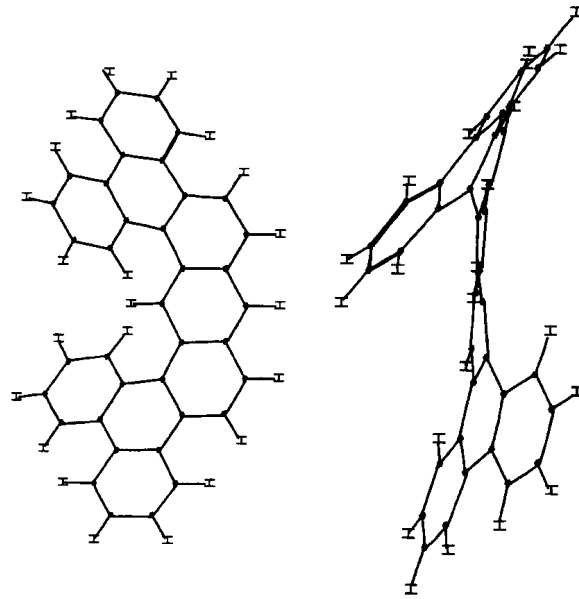


FIGURE 5 Geometry of the benzenoid hydrocarbon **5**.

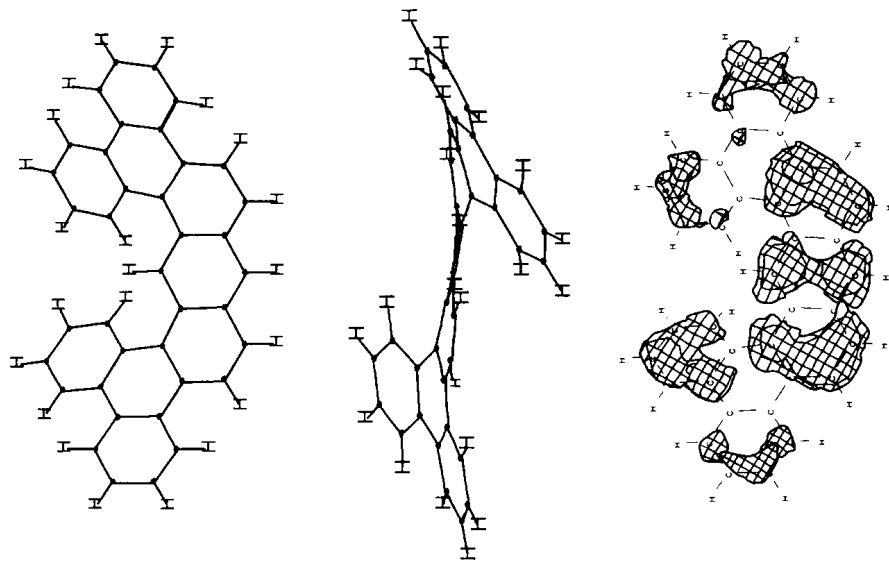


FIGURE 6 Geometry of the dianion of **5** and the charge distribution in it; note that the non-charged molecule **5** (see Fig. 5), and especially its dianion, are pronouncedly non-planar and non-symmetric.

From Table I is seen that the non-uniformity of the charge distribution of the dianions of phenanthreno-annulated anthracenes is a general phenomenon and is basically in agreement with the Clar-type model. In the case when two phenanthrene fragments are attached, the excess of charge on anthracene is 50–60% (relative to *one* phenanthrene unit). If only one phenanthrene fragment is attached this excess is 74% (when the annelation is linear) or 33% (when the annelation is angular). In all examples studied, linear annelation is noticeably more efficient in “attracting” the negative charge to the anthracene fragment.

TABLE I Charges of the anthracene and phenanthrene fragments in the benzenoid hydrocarbons **1–6** and their dianions; “left” and “right” refers to the diagrams depicted in Figure 2

hydrocarbon	anthracene fragment	phenanthrene fragment
1	+0.010	-0.010
2	+0.005	-0.005
3	+0.011	-0.006
4	+0.012	-0.007
		left
5	+0.054	-0.005
		right
		left
		right
6	+0.008	-0.031
		-0.024
		-0.004
dianion		
1	-1.270	-0.730
2	-1.140	-0.860
3	-0.895	-0.553
4	-0.857	-0.560
		left
5	-0.877	-0.583
		right
		left
		right
6	-0.861	-0.554
		-0.569

The Clar-type structural formulas (e.g., those depicted in Figs. 1 and 2) must not be understood as providing a complete description of the electronic structure of the respective dianion: they only indicate the *dominant* mode of cyclic conjugation and the π -electron charge distribution caused by it. (Recall that in the Clar model σ -electron effects are fully disregarded [3]). In particular, it would be a gross oversimplification to expect that the negative charge in the dianions of **1–6** is located solely or predominantly on the two central carbon atoms of the anthracene fragment. Our calculations show that, nevertheless, these carbon atoms bear a significant portion of the negative charge, but that certain other atoms are highly charged as well (cf. Figs. 4 and 6). Anyway, the fact that the negative charge predominantly accumulates on the anthracene fragment (contrary to electrostatic repulsion which would direct it towards the peripheral phenanthrene units) confirms that the Clar model pinpoints the most important features of the electron configuration of the benzenoid anions examined.

Another argument supporting the Clar-type model of dianions follows from the study of the LUMO levels of the neutral hydrocarbons and the HOMO levels of the dianions. These are given in Table II.

TABLE II The lowest unoccupied molecular-orbital (LUMO) energy levels of anthracene and of the benzenoid hydrocarbons 1–6, and the highest occupied molecular-orbital (HOMO) energy levels of their dianions; all values are in *eV*

<i>molecule</i>	<i>LUMO energy of hydrocarbon</i>	<i>HOMO energy of dianion</i>
anthracene	−0.840	2.628
1	−1.158	1.386
2	−1.085	1.242
3	−1.370	0.359
4	−1.264	0.496
5	−1.167	0.558
6	−1.181	0.415

From Table II we see that both energy levels are significantly lowered when a phenanthrene unit is attached to anthracene, and are further decreased by means of a second phenanthrene unit. This implies that the ease of the formation of the dianion (i.e., its stability) increases by the introduction of phenanthrene side groups. Again, linear annelation has a stronger effect than angular annelation.

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