

Aromaticity and electronic properties of Heterosuperbenzene (Heterohexabenzocoronene)

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Abstract A global electrophilicity parameter and the aromaticity of some heterocyclic polyaromatic hydrocarbons were evaluated on the basis of DFT calculations. The substitution of carbon atoms by nitrogen atoms dramatically changes the global electrophilicity of the molecules, with the fully substituted molecule being the most electrophilic with a reactivity very close to that of fullerene.

Keywords Aromaticity · DFT calculations · Heterosuperbenzene · Molecular simulations · Optoelectronic properties

Introduction

The hexagonal molecule hexa-peri-hexacoronene (HBC) **1** [1–3] has been particularly well studied due to its intrinsic symmetry, electronic behavior and aromaticity; these characteristics make it a special case among polyaromatic hydrocarbons. The HBC molecule consists of 42 carbon atoms joined in an arrangement of 13 six-membered rings. According to Clar's theorem [4, 5], a polyaromatic hydrocarbon can be represented by open rings and closed rings represented by circles—so called “aromatic sextets”—as long as circles are

not drawn in adjacent hexagons. Circles can be drawn in hexagons if the rest of the conjugated system has at least one Kekulé structure and the resultant formula contains the maximum number of circles. Therefore, in the case of HBC, these rules generate seven aromatic full electronic sextet alternate systems (see Fig. 1). There is a very strong electronic delocalization in the periphery of the species, which has been extensively studied because of its charge transport properties [3, 6]. For this and other reasons, HBC has been proposed as a graphite subunit model [1–3], and is the object of studies aiming to take advantage of its potential properties, such as electrical- or photo-conductivity [7].

Aromatic electrophilic substitution reactions do not proceed well in this molecule; however, substituted molecules have been synthesized by dehydrogenation of a hexaphenyl-benzene precursor [8, 9], with a preference for the substitution to occur precisely on those rings that complete the Clar's sextet.

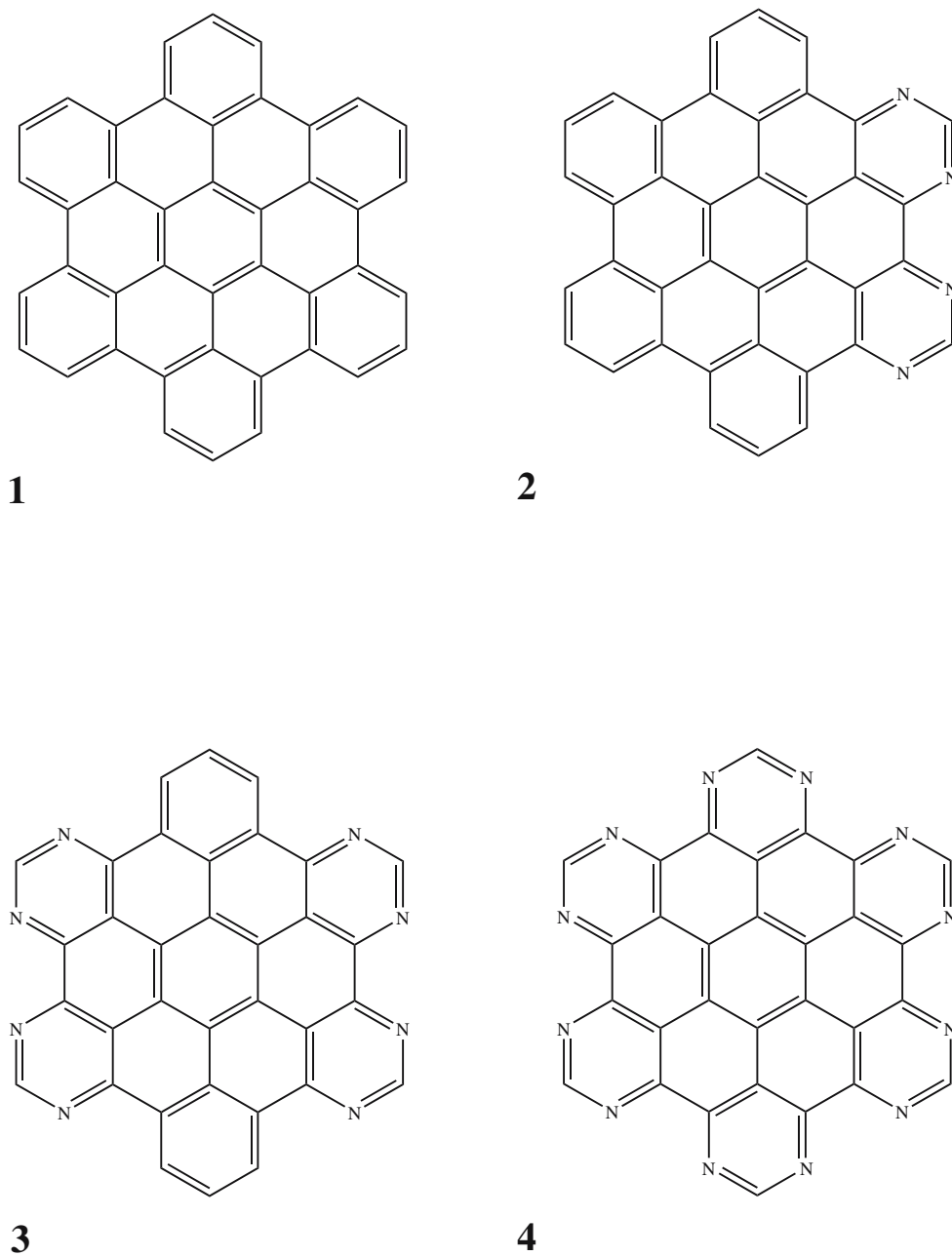
The heterocyclic analogue of **1**, heterohexabenzocoronene, has been prepared by Draper et al. [10, 11]. This molecule (**2** without substitution, **5** with *tert*butyl substituents, and **6** with CF_3 substituents) has four nitrogen atoms substituting carbon atoms in positions ortho to the contiguous fused ring and can be represented as shown in Fig. 2.

The extended π conjugation of molecules such as **1** confers on them an electron acceptor character that can be very useful in the development of electronic and optoelectronic materials. It is expected that the inclusion of heteroatoms in such structures may help improve this characteristic, as was shown by Draper et al. [10, 11].

New structures containing more heteroatomic substituents have not been prepared; however, it is interesting to analyze potential changes in the aromaticity and reactivity of such molecules in order to design precursors of these interesting materials. To this end, the present theoretical study proposes

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Fig. 1 Molecules under study

the simulation of two new, very symmetrical structures, one with full lateral substitution of nitrogen atoms in the “phenanthrenoid” side fragments (3), and the other a fully substituted species (4).

Methods

All density functional (DFT) calculations were carried out with full geometry optimizations without symmetry constraints. Becke’s gradient corrections [12] for the exchange, and Perdew-Wang corrections for the correlation [13], were

used for optimization and total energy evaluation. The correspondent functional is BPW91, which has shown excellent performance in this kind of system [14, 15]. All calculations were performed using the 6-31-G** basis set. The version used was that included in the Gaussian03 code [16]. The bond lengths of the optimized structures were used for the HOMA (harmonic oscillator model of aromaticity) method [17–21] to study the aromaticity, as well as for NICS (nucleus independent chemical shifts)—a technique proposed by Schleyer [22] as an aromaticity index. Following the methodology of Schleyer, we obtained the absolute magnetic shielding at the center of the rings,

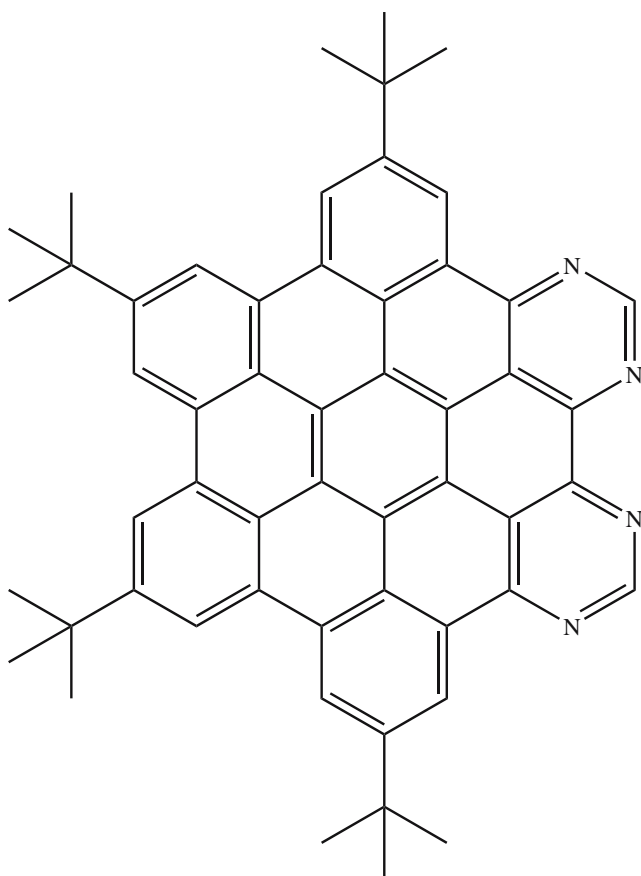


Fig. 2 Molecule prepared by Draper [10, 11]

which is determined by the non-weighted mean of the heavy atom coordinates; these calculations were carried out at the 6-31+G* level as recommended by Schleyer.

The vertical ionization potentials (IP), electron affinities (EA) and global electrophilicity (ω) were calculated at the same level of theory. The IP's and EA's were taken from the HOMO–LUMO values obtained in the normal calculation, and ω was calculated according to reference [23] as $\mu^2/2\eta$, where μ is the chemical potential approximated as $-(IP+EA)/2$, and η is chemical hardness approximated as $(IP-EA)$.

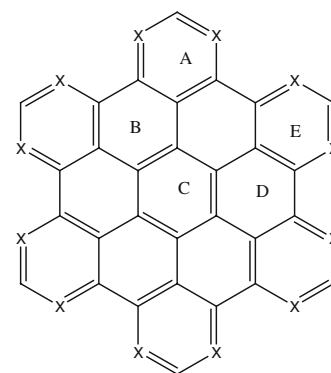
Results and discussion

Two analyses are presented: the first involves molecules in which the carbon aromatic rings on the corners of the structure are sequentially substituted by pyrimidine rings. Therefore, as mentioned above, molecule **1** is the fully carbon polyaromatic compound described by Müllen and colleagues [8, 9], **2** constitutes the framework of the molecule prepared by Draper et al. [10, 11] without *tert*-butyl substituents, while **3** and **4** are idealized pyrimidine substituted species. The second analysis compares molecule **2** with molecule **5**, which corresponds to the *tert*-butyl

substituted molecule prepared by Draper; this latter analysis is focused on the study of the electronic influence of the *tert*-butyl group. The molecules under study are shown in Figs. 1 and 2.

First, an analysis of aromaticity for each ring in each molecule was carried out using both the HOMA and NICS methods. The aromaticity results for all cases are shown in Fig. 3.

The results are not conclusive because the aromaticity is more or less the same for all cases, but this analysis is useful as it shows good agreement with Clar's model since the alternation of large aromaticity values with lower ones is evident as can be seen in rings A, C and E for the large aromaticity, and the B and D rings for lower aromaticity. Indeed, the same analysis was made on the reported X-ray structure of **1** [24], yielding similar values (A=0.922, B=



Comp.	HOMA				
	A	B	C	D	E
1	0.974	0.841	0.949	0.840	0.974
2	0.960	0.834	0.925	0.839	0.966
3	0.996	0.838	0.952	0.831	0.963
4	0.989	0.859	0.994	0.860	0.988
5	0.982	0.873	0.968	0.871	0.973

Comp.	NICS				
	A	B	C	D	E
1	-8.70	-1.71	-12.10	-1.69	-8.38
2	-6.08	-1.81	-12.21	-1.9	-8.59
3	-6.27	-1.77	-12.18	-1.97	-8.32
4	-6.86	-1.62	-12.51	-1.67	-6.75
5	-6.55	-1.58	-12.18	-1.61	-9.22

Fig. 3 Aromaticity values obtained using harmonic oscillator model of aromaticity (HOMA) and nucleus independent chemical shifts (NICS) for all molecules. Ring A has heteroatom substitution in compounds 2–5

Table 1 Global electrophilicity of the molecules under study

Compound	ω
1	1.790
2	2.936
3	3.397
4	3.998
5	2.504

0.868 and $C=0.969$). Unfortunately, these procedures do not provide much information about the π delocalization. Therefore, it is important to carry out other kinds of analysis.

The global electrophilicity index shows which compounds have the capacity to accept electrons (Table 1).

Here, it is possible to appreciate a significant difference. Firstly, all of these compounds are good electrophiles—comparing these results with those of benzene evaluated using the same theoretical conditions (0.854), all the values are large. Furthermore, all the heterocyclic molecules are more electrophilic than HBC **1** and the values increase with the number of substituents. Molecule **4** is the best electrophile (3.998); this value resembles that of fullerene (C_{60}), which is 4.262 (calculated using the same theoretical conditions). Fullerene is known as a very strong electrophile [25].

An important feature to consider is the possible application of these substances in optoelectronic devices. It has been suggested that **2** might be suitable for LED applications [10]. Many substances have now been shown to behave as organic light-emitting diodes (OLEDs) [26, 27].

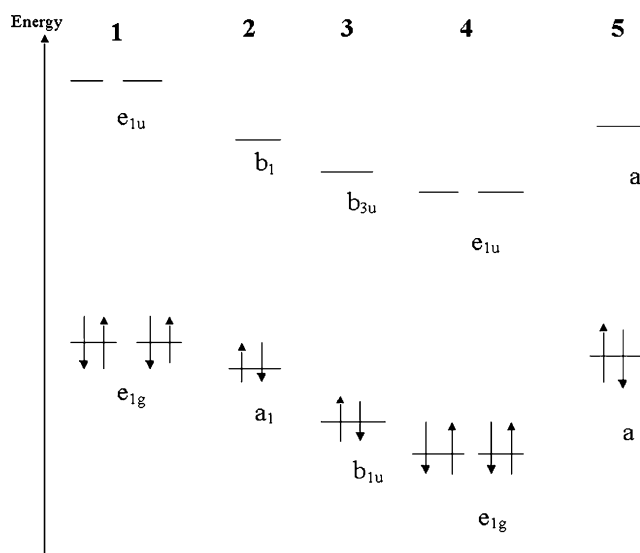
One of the main characteristics of molecules that are good targets for this application is a narrow gap between HOMO and LUMO, indicating semiconductor behavior, and the best efficiency in commercial devices is found when this gap occurs in the visible spectrum of light emission (1.59–3.18 eV). The HOMO–LUMO energy gaps for the molecules under study are shown in Table 2.

These results show that the only molecule with a behavior suitable as a medium-gap semiconductor is **2**, as was predicted by Draper [10, 11], although **5** is a possibility and this is the only previously synthesised compound. The progressive inclusion of groups of N atoms opens the gap until, with molecule **4**, the gap is similar to that of HBC.

The molecular orbital diagram for all analyzed molecules is shown in Fig. 4. Molecules **1** and **4** show the degenerated

Table 2 HOMO–LUMO energy gaps of the molecules under study

Compound	HOMO	LUMO	Δ
1	-5.396	-1.79	3.606
2	-5.883	-2.726	3.157
3	-6.479	-3.102	3.337
4	-7.260	-3.584	3.676
5	-5.673	-2.411	3.262

**Fig. 4** Molecular orbital diagrams for the molecules under study

sets that arise from analysis of the D_{6h} point group to which they belong. Molecules **2** and **3** belong to the C_{2v} and D_{2h} point groups, respectively, whereas molecule **5** has no symmetry (C_1 point group). The molecular orbital energy gap (Δ) is similar in all cases; however, molecule **2** is the only one situated in the visible region suitable for LED. Nevertheless, many commercial LEDs are not made of pure substances—in several cases doping is carried out in order to modify the gap to fit a specific application [28, and references therein]. In this sense, all the molecules under study are good targets for this type of development.

One more calculation was carried out in order to illustrate this point. Since the substituents on the rings can help to modify the gap, an analogue of **5** containing CF_3 substituents instead of the *tert-butyl* fragments was calculated. This new compound, **6**, shows a gap of 3.347 eV. Again, not totally suitable as an LED but very close, and potentially a good target as part of a doped pair.

Conclusions

The aromaticity, reactivity and electrical properties of heterocyclic derivatives of HBC **1** have been studied theoretically. The progressive substitution of nitrogen atoms in place of carbon atoms produces electroactive imines with different behavior depending on the number of sets of nitrogen atoms substituted. All these compounds are aromatic and exhibit the expected behavior for alternative, more aromatic, rings as predicted by the Clar model. Compound **2**, and its substituted analogue **5**, are better electrophiles than HBC; however, the more substituted species **3** and **4** are the best electrophilic agents, with **4** being almost as good an electrophile as fullerene. On the other hand, the relationship between the frontier orbitals indicates that molecules **2** and **5** may be good candidates

for semi-conductors and optoelectronic materials, whereas **3** and **4** are less likely to be useful.

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