STUDIA UBB CHEMIA, LX, 1, 2015 (p. 195-202)
(RECOMMENDED CITATION)

THEORETICAL EVALUATION OF THE AROMATIC CHARACTER OF AZA-PHOSPHA-CORONENES

RALUCA POP[a], MIRCEA DIUDEA[b*], MIHAI MEDELEANU[c], MIHAIELA ANDONI[a]

ABSTRACT. Three aza-phospha-compounds, derivatives of coronenes with N and P atoms in ortho, meta and para positions, were proposed. Their possible aromatic character was evaluated by means of local and global aromaticity indices like HOMA, NICS, PDI and HOMO-LUMO gap. The influence of the heteroatom has been discussed, all the results being compared to the ones obtained for coronene. Graphical representations of the Laplacian of electron density outline the influence of the heteroatoms on the aromaticity of the investigated compounds.

Keywords: *aromaticity, heterocyclic compounds, NICS index, ab initio.*

INTRODUCTION

During the last years, the design of new nanomaterials has known an increased interest. The demand for materials with new or improved properties resulted also in the studies regarding their precursors [1-3]. Most of them are compounds within the class of polycyclic aromatic compounds, most prominent examples being corranulene, coronene and sumanene. There are various studies that reported new nanomaterials based on the above-mentioned compounds [4,5].

Another area of interest within this domain is represented by the researches regarding the properties of hetero-aromatic compounds, most of them dealing with properties like aromaticity, conductivity or stability of the new compounds. There are known heterofullerenes with N and O atoms; recently, have published results regarding the design of new nanomaterials with O and S [6,7].

---

[a] *University of Medicine and Pharmacy "Victor Babeş" Timişoara, Faculty of Pharmacy, 2 Eftimie Murgu Square, 300041, Timişoara, România*

[b] *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 400028 Cluj, Romania*

[c] *University Politehnica of Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 300006, Timişoara, România*

* *Corresponding author: diudea@gmail.com*

In this regard, based on our previous studies of aromaticity of various flowers of type $[n:(p_1,p_2)]$ [8], we propose the evaluation of the aromatic character of some substituted coronene derivatives with N and P atoms. The structures are presented in Figure 1 below:

1,2-Aza-phospha-coronene 1,3-Aza-phospha-coronene 1,4-Aza-phospha-coronene

Figure 1. Structures **1-3** investigated during the present study

The differences among the three substitution types will be discussed. Due to the fact that there is no universal definition of aromaticity [9-11] , the geometric, magnetic and energetic properties of heterocompounds will be evaluated. In this regard, NICS(0) index [12] will be computed at the center of each 6-membered ring. Large negative values are the proof of a strong aromatic character. Also, HOMO-LUMO gap is a good measure of a stability of the compounds [14]. Highest differences between the energies of frontier HOMO and LUMO orbitals suggest an increased stability (and, thus, aromatic character). Bond length equalization [13], another characteristic of the aromatic compounds, will be evaluated. Electron density maps are presented for each of the investigated compounds.

RESULTS AND DISCUSSIONS

In order to evaluate the aromatic character of the aza-phospha-coronenes, various indices –NICS(0), HOMO-LUMO gap– have been computed. The results were compared to the ones obtained for coronene, which is considered a super-aromatic compound.

Bond length equalization deviation was calculated for each outer ring of the investigated compounds; results are presented in Table 1:

Table 1. Bond length equalization deviation (computed at HF/6-311+G)

	Bond length equalization deviation
Compounds	**Outer rings**
1,2	55.5%
1,3	58.8%
1,4	58.3%
Coronene	0.71%

The computations show that the presence of the N and P atoms lead to large differences between coronene and heterosubstituted derivatives. Among the three substitution types, the values are very close, so it is difficult to predict a hierarchy of local aromaticity of the outer cycles.
NICS (Nucleus-Independent Chemical Shift) index, that quantifies the absolute magnetic shielding at the center of a cyclic compound, has become one of the widely used descriptors of aromaticity. NICS values have been obtained using the GIAO approach [15] implemented in Gaussian 09 package [16] and are depicted in Table below:

Table 2. Values of NICS(0) index (computed at HF/6-311+G)

	NICS(0) index	
Compounds	**Inner ring**	**Outer rings**
1,2	0.611	-1.110
1,3	2.565	-4.054
1,4	9.714	-1.440
Coronene	-0.009	-10.406

According to these results, all the central rings of the coronene and its heteroderivatives are non-aromatic; the outer rings of the 1,3-aza-phospha-coronene can be considered aromatic (but much weaker than the ones corresponding to coronene). It appears that the 1,3-substitution type leads to compounds with more pronounced aromatic character than 1,2- and 1,4-substitutions, respectively.

Another local index of aromaticity is the Para-Delocalization Index (PDI). PDI [17] is an electronic index of aromaticity computed within the "atoms-in-molecules" theory, which is employed for the evaluation of the aromatic character of 6-membered rings. It is computed as the average of the atoms situated in para positions within a benzenoid ring. Larger PDI values means a more pronounced aromatic character.

Table 3. Results of PDI index (computed at HF/6-311+G)

	PDI index	
Compounds	**Inner ring**	**Outer rings**
1,2	0.027	0.047
1,3	0.025	0.052
1,4	0.014	0.045
Coronene	0.024	0.056

The results presented in Table 3 outline the more pronounced aromaticity of the “petals” of heterocoronenes (also, as predicted by NICS values, the 1,3-substitution type is favored). The low value obtained for the inner cycle of the 1,4-aza-phospha-coronene can be attributed to the presence of the three N atoms.

In order to evaluate the stability of the structures **1-3**, HOMO-LUMO gaps have been computed. The results are closed to the ones obtained for coronene, showing that all the proposed heteroderivatives are stable (especially the compound where the N and P atoms are in ortho positions). Although there are no large differences among the HL values, it must be outlined that these results predict a different hierarchy of aromaticity (compared to the situations where local indices of aromaticity –NICS, HOMA, PDI- have been employed).

Table 4. HL gap (computed at HF/6-311+G)

Compounds	**HOMO-LUMO gap (eV)**	**Symmetry**
1,2	8.20	C_1
1,3	7.63	C_1
1,4	7.37	C_1
Coronene	8.95	D_{6h}

Another important parameter that characterizes the aromaticity is the electron density. We propose to estimate what is the influence of the N and P atoms on the electronic density of the vicinal C atoms. The results were compared to the ones obtained for coronene. The numbering of the C atoms is depicted in Figure 2:

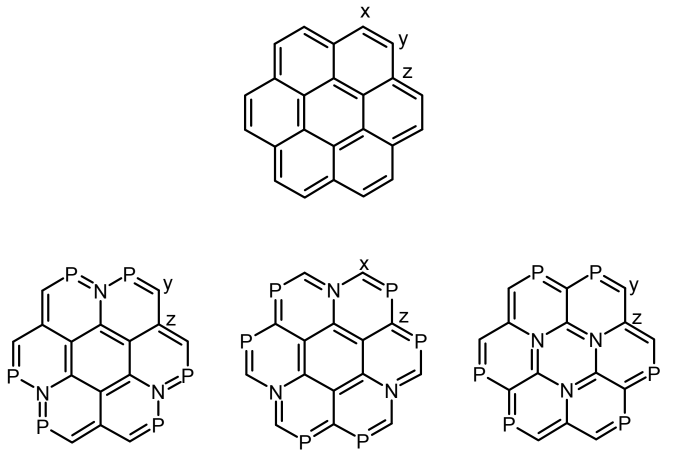


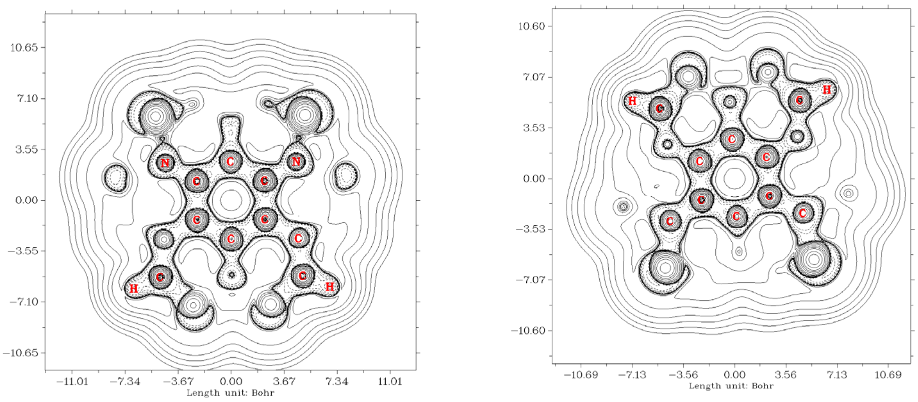
Figure 2. Carbon atoms numbering for the computations of electronic density in a specific point of the cyclic compounds

Table 5. Electron density computed for the outer C atoms (HF/6-311+G)

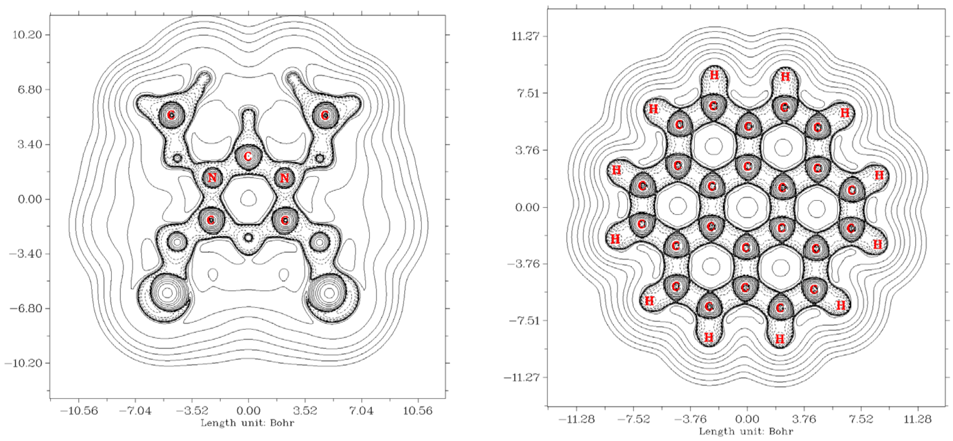
Electron density (a.u.)	x	y	z
1,2	-	$0.1196\cdot10^{3}$	$0.1196\cdot10^{3}$
1,3	$0.1197\cdot10^{3}$	-	$0.1197\cdot10^{3}$
1,4	-	$0.1196\cdot10^{3}$	$0.1196\cdot10^{3}$
Coronene	$0.1195\cdot10^{3}$	$0.1195\cdot10^{3}$	$0.1195\cdot10^{3}$

The results outline that there is no significant difference on the electron density of the C atoms due to the presence of N and P. Also, the results cannot predict a differentiation among the three substitution types.

Another possibility for evaluating the aromatic character of compounds **1-3** is the analysis of the Laplacian of electron density [18]. The maps for each compound (and coronene) are depicted in Figure 3 and clearly show the influence of the heteroatoms. It can be observed that the presence of the N and P atoms disrupt the electron delocalization within the coronene derivatives.



1,2-Aza-phospha-coronene 1,3-Aza-phospha-coronene



1,4-Aza-phospha-coronene Coronene

Figure 3. Graphical representation of Laplacian of electron density, ∇^2 ρ(r), for the aza-phospha-coronenes and coronene, respectively.

CONCLUSIONS

Three aza-phospha-coronenes (with heteroatoms in ortho, meta and para positions, respectively) have been proposed. Their aromatic character was evaluated by means of magnetic, energetic and geometric criteria, using both local and global descriptors of aromaticity. All the structures are believed to be stable, taking into the account the values of HOMO-LUMO gap, close to the one corresponding for coronene. In this regard, and also when taking into account the values of electronic descriptors like PDI, it can be said that the heteroatoms don't have a significant contribution. Instead, values of local indices like NICS and bond length equalization deviation clearly show a decrease of the aromatic character together with the presence of heteroatoms. Among the studied compounds, the 1,3-substitution type appears to be favored (according to NICS and PDI values). Graphical representation of the Laplacian of electron density outlines the influence of the heteroatoms on the aromatic behavior of the compounds.

COMPUTATIONAL DETAILS

All the computations have been performed at HF/6-311+G level of theory. All the structures have been optimized, no imaginary frequencies being obtained. The geometries of all the aza-phospha-coronenes are non-planar. All the computations have been performed with the Gaussian 09W program; exceptions are the electron density calculations and the graphical representation of the Laplacian of electron density, which have been obtained by means of Multiwfn 3.3.4 software [19].

ACKNOWLEGMENTS

This work was supported by a grant of the Romanian Ministry of Education, CNCS – UEFISCDI, project number PN-II-RU-PD-2012-3-0102.

REFERENCES

[1]. J.Z. Wen, H. Richter, W.H. Green, J.B. Howard, M. Treska, P.M. Jardin, J.B. Vander Sande, J. Mater. Chem. **2008**, *18*, 1561.

[2]. H. Takehara, M. Fujiwara, M. Arikawa, M.D. Diener, J.M. Alford, Carbon **2005**, *43*, 311.

[3]. B. Saha, S. Irle, K. Mokoruma, J. Chem. Phys. **2010**, 132, 224303.

[4]. Q. Zhang, H. Peng, G. Zhang, Q. Lu, J. Chang, Y. Dong, X. Shi, J. Wei, J. Am. Chem. Soc. **2014**, *136*(13), 5057-5064.

[5]. S. Sanyai, A.K. Manna, S.K. Pati, Chem. Phys. Chem. 2014, 15(5), 885-893.

[6]. G.V. Baryshnikov, R.R. Valiev, N.N. Karaush, B.F. Minaev, Phys. Chem. Chem. Phys. **2014**, *16*, 15367.

[7]. G.V. Baryshnikov, B.F. Minaev, N.N. Karaush, V.A. Minaeva, RSC Adv. **2014**, *4*, 25843.

[8]. M.V. Diudea, A.E. Vizitiu, T. Beu, A. Bende, C.L. Nagy, D. Janezic, J. Mol. Struct.: THEOCHEM **2009**, *904*, 28.

[9]. Krygowski, T.M.; Cyrañski, M.K. Chem. Rev. **2001**, *101*, 1385-1419.

[10]. Katritzky, A.R.; Jug, K.; Oniciu, D.C. Chem. Rev. **2001**, *101*, 1421-1449.

[11]. A. Acocella, R.W.A. Havenith, E. Steiner, P.W. Fowler, L.W. Jenneskens, Chem. Phys. Lett. **2002**, *363*, 64.

[12]. Schleyer, P.v.R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N.J. J. Am. Chem. Soc. **1996**, *118*, 6317.

[13]. J. Aihara, Bull. Chem. Soc. Japan **2004**, *77*(12), 2179-2183.

[14]. Y. Ruiz-Morales, J. Phys. Chem. A **2002**, *106*(46), 11283-11308.

[15]. Chesnut, D.B.; Moore, K.D., J. Comput. Chem. **1985**, *10*, 648.

[16]. Gaussian 09, Revision B.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

[17]. J. Poater, X. Fradera, M. Duran, M. Sola, Chem. Eur. J. **2003**, *2*, 400.

[18]. C. Foroutan-Nejad, S. Shahbazian, P. Rashidi-Ranjbar, Phys. Chem. Chem. Phys. **2010**, *12*, 12630-12637.

[19]. Lu, T.; Chen, F.J. Comp. Chem. **2012**, *33*, 580.