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Electronic Nature of the Aromatic Adamantanediyl Ions and its Analogues

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A estabilidade relativa do dicátion 1,3-desidro-5,7-adamantanediila é atribuída a sua aromaticidade tridimensional. Contudo, sua natureza eletrônica não é bem conhecida. A fim de entendê-la melhor, os di- e monocátions do adamantanodiil e alguns de seus análogos foram estudados utilizando a teoria de átomos e moléculas (AIM). Eles foram comparados com análogos de adamantano não-aromáticos. Os resultados de AIM indicam que a densidade eletrônica no centro da estrutura em gaiola e a média de todos os índices de deslocalização, envolvendo seus átomos cabeças-de-ponte são maiores em compostos aromáticos do que em não-aromáticos. A degenerescência energética dos átomos cabeça-de-ponte, a uniformidade e magnitude da carga compartilhada entre estes, distingue os dicátions 1,3-adamantila e 1,3-desidro-5,7-adamantanediila. Contudo, ambos são aromáticos, assim como o 1,3-desidro-5,7-diboroadamantano. O cátion 1,3-desidro-7-adamantila tem uma homoaromaticidade planar característica.

The relative stability of the 1,3-dehydro-5,7-adamantanediyl dication is ascribed to its tridimensional aromaticity. However, its electronic nature is not well known. In order to improve its understanding, dicationic and monocationic adamantanedyil species and some key analogues were studied by atoms in molecules (AIM) theory. They were compared to non-aromatic adamantane analogues. AIM results indicate that the density in center of the cage structure and the average of all delocalization indexes involving its bridged atoms are higher in aromatic than in non-aromatic compounds. Degeneracy in energy of the bridged atoms, uniformity and magnitude of their shared charge distinguish the dications 1,3-adamantyl and the 1,3-dehydro-5,7-adamantanediyl**.** However, both are aromatic as well as the 1,3-dehydro-5,7-diboroadamantane. The 1,3-dehydro-7-adamantyl cation has a characteristic planar homoaromaticity.

Keywords: adamantyl dication, adamantyl cation, degeneracy, delocalization index, ring density, aromaticity, tridimensional aromaticity, 1,3-dehydro-5,7-adamantanediyl dication

Introduction

Some cationic adamantanediyl species are relatively stable intermediates, e.g., Schleyer's 1,3-dehydro-5,7-adamantanediyl dication (Scheme 1). The adamantanediyl monocation is a stable species and can be synthesized from the 1-adamantanol and fluorosulfonic acid-antimony pentafluoride.[1] The adamantanediyl dication has not been observed as persistent long-lived species so far.[2] Ionization of 1,3-difluoroadamantane in superacids afforded only the monocation complex[3] $C_{10}H_{14}F\text{-}SbF_5$ (Scheme 1). Attempts of obtaining other adamantane-1,3-diyl dications were not successful.[4] However, the 1,3-dehydro-5,7-adamantanediyl dication (or 1,3,5,7-bisdehydroadamantane dication) is a stable species.[5] It exhibits shielded bridgehead carbons at δ 6.6 ppm with methylene carbon resonances appearing at δ 35.6 ppm which is characteristic of hypercoordinate carbocations.[5] Despite that 1,3,5,7-tetrasilaadamantane (Scheme 1) is easily obtained[6] from the 1,3,5-hexamethyl-1,3,5-trisilacyclohexane and $AlBr_3$, the 1,3-dehydro-5,7-tetrasilaadamantanediyl dication is not observed experimentally. However, it has a spherical homoaromaticity[7] which is another name for the tridimensional aromaticity.

A series of isoelectronic analogues of the adamantane and its dehydroadamantanes containing boron, nitrogen, and phosphorus atoms at bridgehead were studied and the three-

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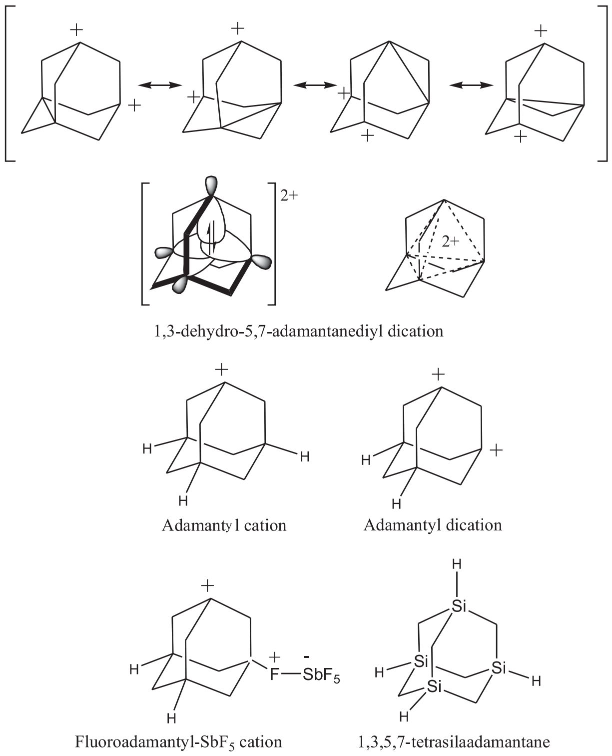


1,3-dehydro-5,7-adamantanediyl dication

Adamantyl cation

Adamantyl dication

Fluoroadamantyl-SbF$_5$ cation

1,3,5,7-tetrasilaadamantane

Scheme 1.

dimensional aromaticity is found to be general for 4c-2e electron systems.[8] The calculations of the isoeletronic boron and diboron analogues of the 1,8-dehydrohomoadamantanediyl-3,6-dication, $BC_9H_{12}^+$ and $B_2C_8H_{12}$, respectively, indicate that both have three-dimensional aromaticity.[9]

Despite that 1,3-dehydroadamantane undergoes addition reaction easily,[10] it is stable at low temperature and inert conditions. Hitherto, the 1,3-dehydro-5-adamantyl cation is not a long–lived stable ion but it is an intermediate in solvolysis of the 5-bromo-1,3-dehydroadamantane.[11] The density functional theory (DFT) study showed that the 1,3-dehydro-5-adamantyl cation has 20.0 kcal mol^{-1} stabilization due to trishomoaromatic interaction.[9] The 1,3-dehydro-5-boroadamantyl analogue has the same type of stabilization.[9]

The three-dimensional aromaticity of 1,3-dehydro-5,7-adamantanediyl dication is explained in terms of overlap among four p-orbitals in a tetrahedral fashion (Scheme 1) and its ^{13}C NMR spectrum has a single absorption (δ^{13}C 6.6 ppm) assigned for bridgehead carbons.[12] In order to understand the electronic nature of these systems we have performed AIM calculations of the 1,3-dehydro-5-7-adamantanediyl dication and its analogues.

Computational Methods

Geometry optimization, vibrational analysis and the generation of the electronic density were obtained with GAUSSIAN 03 package.[13] The geometries were optimized in DFT level employing Becke three-parameter interchange functional[14] (B3) in conjunction with Lee-Yang-Parr[15] correlation functional (LYP) and the split valence basis set[16] 6-311++G**. Dehalogenation calculations were performed at the same level. All geometries were characterized as stationary points after vibrational analysis.

The AIM 2000 software[17] was used for charge density calculations from the electronic densities (ρ) obtained at B3LYP/6-311++G** level. NICS[18] (nucleus independent chemical shift) calculations were performed at GIAO/B3LYP/6-311++G** level at the geometric center of the cage.

Rationale

Within the molecular orbital theory (MO) the aromatic character of benzene is explained through delocalized orbitals. Nevertheless by using spin coupled from valence bond theory (SC), Gerratt and co-workers[19] established that all six ω electrons of benzene are localized and distorted symmetrically towards neighboring carbon atoms on each side and possess same energy and shape. Furthermore, from a more rigorous quantum mechanical standpoint,[20] benzene has no resonance[21] since there is not intersection of degenerate point group states. It means that benzene (D_{6h} symmetry) cannot be related to Kekulé (D_{3h} symmetry) or Dewar (D_{2h}) structures. In this case, benzene stability is ascribed to maximum overlap among six degenerate single-electron states.[22] Then, in modern valence bond theory (VB), the idea of aromaticity is based on the overlap and degeneracy of the single-electron states.[22]

The index used to study the aromaticity of adamantanediyl ions and its analogues in this work, D_3BIA, is inspired to the modern VB idea of aromaticity. The modern VB parameters of aromaticity can be associated with topological parameters. Then, it is possible to quantify aromaticity by AIM theory inspired on modern VB ideas of aromaticity. In the case of adamantanediyl ions and its analogues, the aromaticity from modern VB theory can be associated with the energy of atomic basins of the bridged atoms, the charge density in the cage critical point and the delocalization indexes involving the bridged atomic pairs of the cage (from AIM). The use of Kohn-Sham orbitals for the calculation of delocalization indices is a good approximation, although not strictly correct.

It is important to emphasize that the calculus of energy of an atomic basin is an one-electron integration over the whole atomic basin. Then, the AIM provides the energy value of the total energy of each atomic basin. Since degeneracy in Quantum Chemistry means same energy, the AIM can provide the information whether some atomic basins in a given molecular system are degenerate or not (see Electronic Supplementary Information for more details).

Results and Discussions

The studied species are depicted in Scheme 2. The AIM theory[23] is based on the analysis of the electronic density distribution, ρ(r), obtained from a quantum mechanical wavefunction. Although DFT does not generate a wave function, it yields a density matrix similar to that from a post-HF method such as MP2. Much information can be obtained from AIM such as the bond, cage and ring critical points and their respective eigenvalues (see electronic supplementary information).

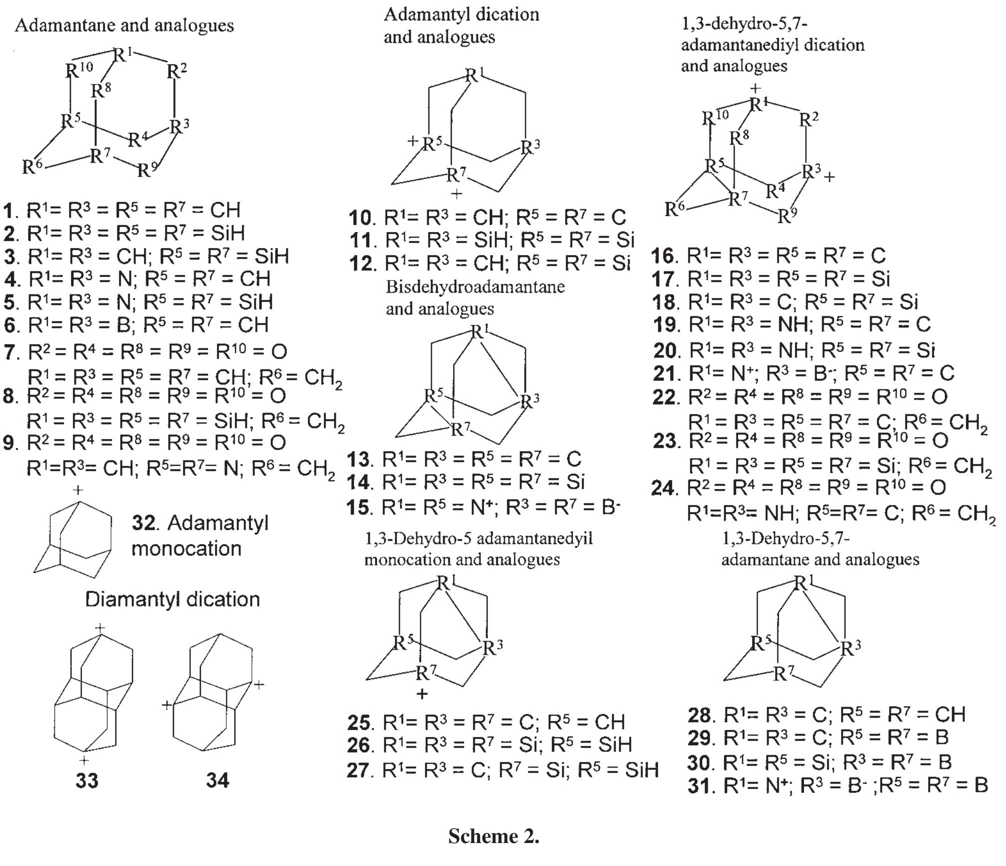
Table 1 contains the delocalization indexes and energy of bridged atoms (R^1, R^3, R^5 and R^7) of the species **1** to **32**, obtained from AIM theory. Their analysis allows the investigation of the electronic differences between aromatic and non-aromatic tridimensional systems. Table 1 also contains the point group symmetry of each studied species.

The delocalization index (DI) is a measure of number of electrons that are shared or exchanged between two atoms or basins. The integration of the Fermi hole density through a pair density matrix leads to the localization index (LI) and the delocalization index[24] (DI). Although DFT does not yield a pair density matrix, the delocalization indexes from B3LYP are close to those from MP2 (see electronic supplementary information). It is important to emphasize that the delocalization index does not measure the delocalization of valence electrons over the whole molecular system.

In a previous work on benzene-like compounds it was shown the importance of some electronic parameters to determine their aromaticity.[25] These parameters were degeneracy of the atoms in the ring, density inside the ring and uniformity of delocalization index between atoms of the ring. All of these parameters are also analyzed in this work.

The bridged atoms of the adamantane **1** and the 3-dehydro-5,7-adamantanediyl dication **16** are degenerate and the delocalization indexes (or amount of shared charge density) among them are uniform in both molecules (0.039 in **1** and 0.280 in **16**). However, the delocalization indexes in **16** are seven-fold higher than those in **1**. As a consequence, the species **16** has 1.70e among the bridged atoms while the species **1** has only 0.23e.

The delocalization indexes among bridged atoms in adamantyl dication **10** are not uniform (0.079, 0.147 and 0.143) and the energy of its bridged atoms is not degenerate (Table 1). The degeneracy of bridged atoms, uniformity and magnitude of their delocalization indexes are the electronic features that distinguish the species **10** and **16.** They can be regarded as determinant factors for the relative stability of the 1,3-dehydro-5,7-adamantanediyl dication. One simi-


Adamantane and analogues

1. $R^1 = R^3 = R^5 = R^7 = CH$
2. $R^1 = R^3 = R^5 = R^7 = SiH$
3. $R^1 = R^3 = CH$; $R^5 = R^7 = SiH$
4. $R^1 = R^3 = N$; $R^5 = R^7 = CH$
5. $R^1 = R^3 = N$; $R^5 = R^7 = SiH$
6. $R^1 = R^3 = B$; $R^5 = R^7 = CH$
7. $R^2 = R^4 = R^8 = R^9 = R^{10} = O$
$R^1 = R^3 = R^5 = R^7 = CH$; $R^6 = CH_2$
8. $R^2 = R^4 = R^8 = R^9 = R^{10} = O$
$R^1 = R^3 = R^5 = R^7 = SiH$; $R^6 = CH_2$
9. $R^2 = R^4 = R^8 = R^9 = R^{10} = O$
$R^1 = R^3 = CH$; $R^5 = R^7 = N$; $R^6 = CH_2$

32. Adamantyl monocation

Diamantyl dication

33 **34**

Adamantyl dication and analogues

10. $R^1 = R^3 = CH$; $R^5 = R^7 = C$
11. $R^1 = R^3 = SiH$; $R^5 = R^7 = Si$
12. $R^1 = R^3 = CH$; $R^5 = R^7 = Si$

Bisdehydroadamantane and analogues

13. $R^1 = R^3 = R^5 = R^7 = C$
14. $R^1 = R^3 = R^5 = R^7 = Si$
15. $R^1 = R^5 = N^+$; $R^3 = R^7 = B^-$

1,3-Dehydro-5 adamantanedeyil monocation and analogues

25. $R^1 = R^3 = R^7 = C$; $R^5 = CH$
26. $R^1 = R^3 = R^7 = Si$; $R^5 = SiH$
27. $R^1 = R^3 = C$; $R^7 = Si$; $R^5 = SiH$

1,3-dehydro-5,7-adamantanediyl dication and analogues

16. $R^1 = R^3 = R^5 = R^7 = C$
17. $R^1 = R^3 = R^5 = R^7 = Si$
18. $R^1 = R^3 = C$; $R^5 = R^7 = Si$
19. $R^1 = R^3 = NH$; $R^5 = R^7 = C$
20. $R^1 = R^3 = NH$; $R^5 = R^7 = Si$
21. $R^1 = N^+$; $R^3 = B^-$; $R^5 = R^7 = C$
22. $R^2 = R^4 = R^8 = R^9 = R^{10} = O$
$R^1 = R^3 = R^5 = R^7 = C$; $R^6 = CH_2$
23. $R^2 = R^4 = R^8 = R^9 = R^{10} = O$
$R^1 = R^3 = R^5 = R^7 = Si$; $R^6 = CH_2$
24. $R^2 = R^4 = R^8 = R^9 = R^{10} = O$
$R^1 = R^3 = NH$; $R^5 = R^7 = C$; $R^6 = CH_2$

1,3-Dehydro-5,7-adamantane and analogues

28. $R^1 = R^3 = C$; $R^5 = R^7 = CH$
29. $R^1 = R^3 = C$; $R^5 = R^7 = B$
30. $R^1 = R^5 = Si$; $R^3 = R^7 = B$
31. $R^1 = N^+$; $R^3 = B^-$; $R^5 = R^7 = B$

Scheme 2.

Table 1. Delocalization index among bridged atoms, energy of bridged atoms and point group symmetry of the species **1** to **32**

Entry	Delocalization index						Energy / au				Point group symmetry
	R^1-R^3	R^1-R^5	R^1-R^7	R^3-R^7	R^3-R^5	R^5-R^7	R^1	R^3	R^5	R^7	
1	0.039	0.039	0.039	0.039	0.039	0.039	-38.06	-38.06	-38.06	-38.06	Td
2	0.007	0.007	0.007	0.007	0.007	0.007	-288.81	-288.81	-288.81	-288.81	C_1
3	0.038	0.016	0.016	0.016	0.016	0.008	-37.91	-37.91	-289.04	-289.04	Cs
4	0.107	0.068	0.068	0.068	0.068	0.041	-55.21	-55.21	-38.07	-38.07	C_1
5	0.119	0.034	0.034	0.034	0.034	0.009	-55.06	-55.07	-289.04	-289.04	Cs
6	0.026	0.033	0.033	0.033	0.033	0.045	-24.10	-24.10	-38.01	-38.01	Cs
7	0.022	0.023	0.023	0.023	0.023	0.045	-37.18	-37.18	-37.50	-37.50	Cs
8	0.008	0.006	0.006	0.006	0.006	0.006	-288.55	-288.55	-288.46	-288.44	Cs
9	0.049	0.045	0.045	0.045	0.045	0.091	-37.54	-37.55	-54.37	-54.37	C_1
10	0.079	0.147	0.147	0.147	0.147	0.143	-38.01	-38.01	-38.13	-38.13	Cs
11	0.023	0.023	0.024	0.023	0.023	0.011	-288.89	-288.82	-288.90	-288.82	C_1
12	0.056	0.061	0.061	0.061	0.061	0.033	-37.92	-37.92	-289.10	-289.10	C_1
13	0.825	0.081	0.082	0.082	0.082	0.829	-38.12	-38.12	-38.12	-38.12	C_1
14	0.102	0.070	0.086	0.106	0.146	0.091	-288.99	-289.15	-289.16	-288.99	C_1
15	0.073	0.144	0.073	0.031	0.069	0.069	-55.14	-24.11	-55.15	-24.11	C_1
16	0.280	0.280	0.280	0.280	0.280	0.280	-38.09	-38.10	-38.09	-38.09	C_1
17	0.097	0.096	0.096	0.097	0.097	0.096	-288.97	-288.97	-288.97	-288.97	C_1
18	0.153	0.140	0.140	0.140	0.140	0.183	-289.22	-289.22	-38.02	-38.02	Cs
19	0.065	0.085	0.085	0.085	0.085	0.836	-38.13	-38.13	-55.21	-55.21	Cs
20	0.010	0.019	0.019	0.019	0.019	0.068	-288.99	-288.99	-55.07	-55.07	Cs
21	0.147	0.254	0.253	0.107	0.107	0.184	-55.20	-24.12	-38.10	-38.10	C_1
22	0.137	0.158	0.158	0.158	0.158	0.248	-37.03	-37.03	-37.41	-37.41	C_1
23	0.151	0.119	0.118	0.118	0.119	0.057	-288.55	-288.55	-288.66	-288.66	C_1
24	0.046	0.060	0.060	0.060	0.060	0.804	-54.47	-54.47	-37.61	-37.61	C_1
25	0.410	0.071	0.410	0.410	0.071	0.071	-38.12	-38.12	-38.04	-38.12	C_1
26	0.155	0.019	0.155	0.155	0.019	0.019	-289.03	-289.03	-288.82	-289.03	C_1
27	0.217	0.034	0.217	0.217	0.034	0.028	-38.03	-38.03	-289.03	-289.33	C_1
28	0.855	0.062	0.062	0.062	0.062	0.036	-38.15	-38.15	-38.04	-38.04	C_1
29	0.319	0.113	0.113	0.113	0.113	0.041	-38.12	-38.12	-24.12	-24.12	C_1
30	0.228	0.055	0.055	0.055	0.055	0.026	-289.28	-289.28	-24.04	-24.04	C_1
31	0.103	0.103	0.103	0.029	0.029	0.029	-55.19	-24.11	-24.11	-24.11	C_1
32	0.112	0.112	0.112	0.053	0.053	0.053	-38.16	-38.04	-38.04	-38.04	Cs

larity between the species **10** and **16** is that their positive charge is distributed among the hydrogen atoms, as one can see in Figure 1.

The relative stability of the 1,3-dehydro-7-adamantyl cation **25** is experimentally known.[3] It is suggested that the species **25** (Figure 1) has homoaromaticity among R^1, R^3, and R^7 bridged atoms (see Table 2) since they are nearly degenerate. Besides, the delocalization indexes among these atoms have high magnitude and uniformity.

When bridgehead carbon atoms are substituted by silicon atoms, such as in **2**, **11**, **17** and **26**, it is noteworthy that their respective delocalization indexes decrease significantly (Table 2). All other electronic features remain the same when comparing the silicon derivatives with their carbon analogues **1**, **10**, **16** and **25**, respectively. Bridged silicon atoms in **17** are nearly degenerate and the delocalization indexes among them are nearly uniform. However, the magnitude of these delocalization indexes is almost three-fold smaller than that from **16**. The same occurs with **26** in comparison to **25**.

In **3**, **12**, **18** and **27**, only two carbon bridged atoms are replaced by silicon ones. This change decreases

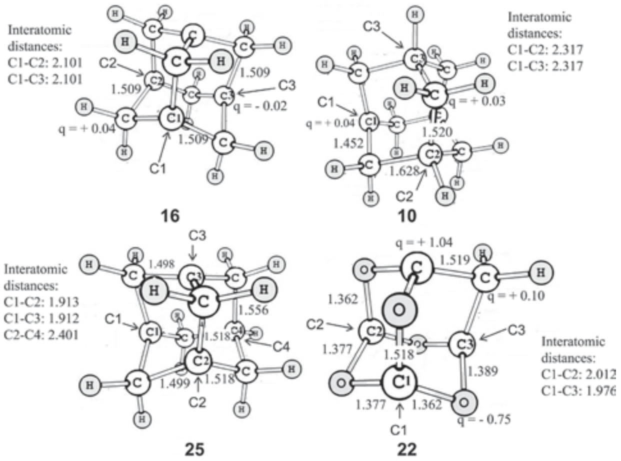


Figure 1. Bond lengths, interatomic distances (Å) and atomic charge (in atomic units) of 1,3-dehydro-5-7-adamantanediyl dication **16**, 1,3-adamantyl dication **10**, 1,3-dehydro-7-adamantyl cation **25** and oxy-species **22**.

degeneracy of their bridged atoms due to a decrease on the symmetry of their respective species. In **3** and **18** there is no uniformity of delocalization indexes involving the bridgehead atoms. The exception is the species **27**. As to the magnitude of delocalization indexes, **3**, **12**, **18** and **27** have higher values than those from their respective analogues **2**, **11**, **17** and **26**.

From AIM electronic analysis, bisdehydro-1,3,5,7-adamantane **13** and the 1,3-dehydro-5,7-adamantane **28** do not have tridimensional aromaticity since the delocalization indexes among their bridged atoms are not uniform. Moreover, they are smaller than those from **16** (except for the DI´s between C-C bonds). The non-stability of bisdehydro-1,3,5,7-adamantane[8] is probably due to its anti-aromatic 4n-electron character. The bridged silicon analogue of **13**, bisdehydro-1,3,5,7-tetrasilaadamantane **14**, has no Si-Si bonds (Figure 2b). However, its delocalization indexes are not so much different than those from **18** which has only 2 electrons among bridged atoms.

In oxy-species **7**, **8**, **22** and **23** there is no degeneracy of bridged atoms and uniformity of delocalization indexes among them. By comparing oxy-species with bridged carbon atoms (**7** and **22**) with their analogues **1** and **16**, one can see that the magnitude of the DI´s decreases significantly in **7** and **22** due to the higher electronegativity of the oxygen atom. However, this does not happen with oxy-species with bridged silicon atoms (**8** and **23**) when comparing to their analogues **2** and **17** (Table 1). The effect of oxygen atoms in **22** can be seen in Figure 1 where its bridged carbon atoms are positively charged while in **16** the corresponding bridged carbon atoms are negatively charged. Likewise, it is expected that **22** and **23** have smaller aromaticity with respect to their respective analogues **16** and **17**.

The dicationic diazo-analogues **19** and **20** have very small delocalization indexes values among bridged atoms in comparison to **16** and **17**, respectively. The species **19** and **20** probably do not have tridimensional aromaticity since their delocalization indexes among bridged atoms are equivalent with those from neutral analogues **4** and **5**, respectively (Table 1). However, in **19**, there exists a bond between bridged carbon atoms, while in **20** no similar bond exists between bridged silicon atoms. The diazo-oxy-derivative **24** has the smallest delocalization indexes values within the dicationic aromatic oxy-analogues (**22**, **23** and **24**) and it is probably the least aromatic one.

The dicationic **21**, containing one boron, one nitrogen and two carbon bridged atoms, has delocalization indexes among bridged atoms higher than those from **19** and **20**. Then, **21** is probably more aromatic than **19** and **20**, as it is confirmed by its NICS value in Table 2.

The molecular graphs of **14** and **19** show interesting aspects. In **14** (Figure 2a) both σ bonds between silicon atoms are broken after its optimization. Moreover, the delocalization indexes among R^1, R^3, R^5 and R^7 are not uniform. In **19** (Figure 2b) the two sp^2 carbon atoms make a bond after geometry optimization as it can be seen in the delocalization index between them (DI=0.836, in Table 1) and the density of this bond critical point (ρ=0.21a.u.). All other delocalization indexes among R^1, R^3, R^5 and R^7 are just little higher than those from **4**, which agrees with the small NICS value of **19** (Table 2). Nevertheless, no bond is made between silicon atoms in **20**.

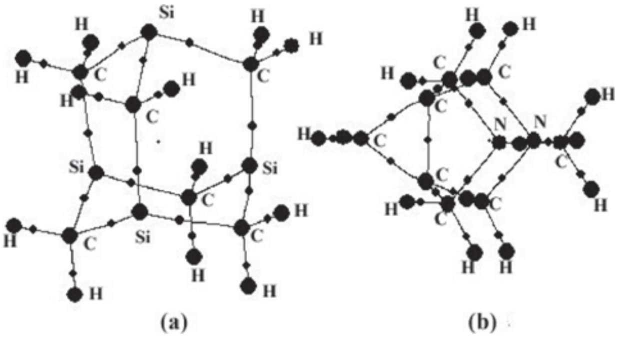


Figure 2. Molecular graph from AIM of the species **14** (a) and **19** (b).

Interestingly, in the neutral compound **29**, electropositive boron atoms attract electrons from bridgehead carbon atoms and generate reasonable delocalization indexes among bridged carbon and boron atoms. By comparing with compound **6**, where DI´s among bridged carbon and boron atoms is only 0.033, it is possible to see how effectively boron atoms distribute electrons from bridged carbon atoms in **29** (Table 1). This can be verified by comparing C-C atomic distances between **28** (1.562 Å) and **29** (2.110 Å) in Figure 3. The latter has a much larger distance which represents a delocalization

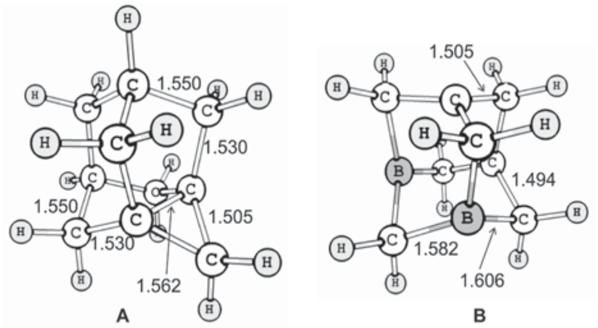


Figure 3. Selected atomic and interatomic distances (Å) of the species **28** (A) and **29** (B).

of this σ C-C bond. Then, **29** can be regarded as tridimensional aromatic species, as supported by its NICS value of -38.80 (Table 2). Although less effectively, boron atoms also provoke distribution of the electrons of the bridged silicon in **30**. Optimized structures of the species **1, 2, 4, 6, 7, 10, 11, 13, 15, 16, 17, 19, 21, 22, 25** and **26** are shown in the electronic supplementary information.

Another important analysis from AIM theory is the Laplacian of the charge density, $\nabla^2\rho$. It is defined as the sum of the three principal curvatures of the function at each point of the space. However, it is a convenient convention to use the negative of the Laplacian, L(r), rather than the Laplacian itself. Then, $L(r) = -\nabla^2\rho$. The density is a locally concentrated in those regions where $L(r)>0$, since $\nabla^2\rho(r)<0$ when $\rho(r)$ is a local maximum. Likewise, the density is a locally depleted in those regions where $L(r)<0$, since $\nabla^2\rho(r)>0$ when $\rho(r)$ is a local minimum.[24]

In Figure 4, it is depicted the negative of the Laplacian curves in a plane that passes through three bridged carbon atoms of **10** and **16**. It is possible to see that the negative of the Laplacian distribuition region in the 1,3-dehydro-5,7-adamantanediyl dication (**16**) where $L(r)<0$ encompasses the three bridged carbons atoms. This represents a uniform charge density distribution over these atoms and indicates an interaction among them. In case of the 1,3 adamantyl dication (**10**), there exists no $L(r)<0$ Laplacian distribution region encompassing the three bridged carbons and it indicates absence of significant interaction among them.

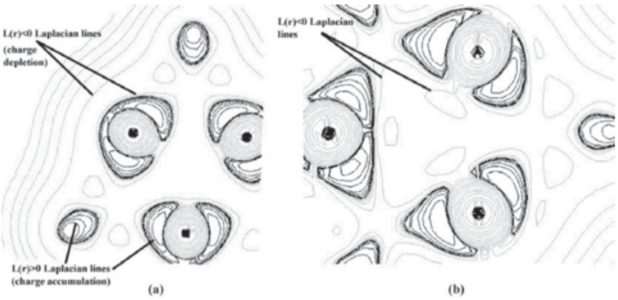


Figure 4. Contour maps of the Laplacian distribution of the electronic charge density for the 1,3-dehydro-5-7-adamantanediyl dication (a) and 1,3 adamantyl dication (b) in the plane that contains three bridged carbon atoms. The gray curves are related to charge depletion, while the black lines are charge concentration.

The AIM study of the diamantyl dications **33** and **34** provides a different electronic nature between them (see Figure 5). The former was prepared and characterized but the latter was not obtained.[26] In the 4,9-diamantyl dication **33** there are three considerable delocalization indexes (DI= 0.117) linking each positively charged carbon atom (C1 and C8) and its corresponding bridgehead carbon atoms (C2 to C7). In the 1,6-diamantyl dication **34**, there exists just one considerable delocalization index (DI=0.168) and two delocalization indexes immediately inferior (DI=0.085) For **33**, the delocalization indexes are uniform and for **34** the delocalization indexes are not.

In Figure 6, one can see that the atomic distances between each positively charge carbon atom and its vicinal carbon atom is uniform in **33** (1.462 Å) and non-uniform

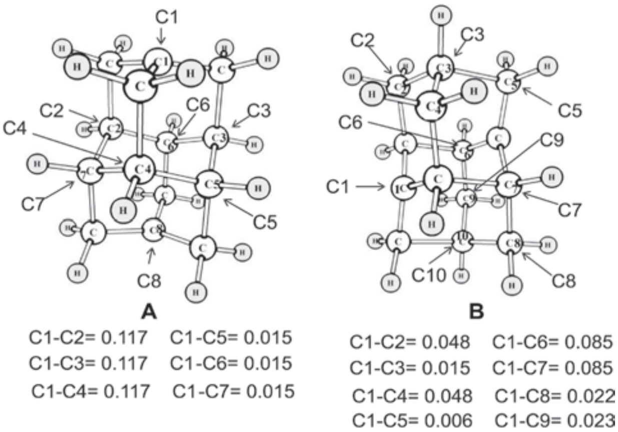


Figure 5. Delocalization indexes between positively charge carbon atoms and non-vicinal carbon atoms in the species **33** (A) and **34** (B)."

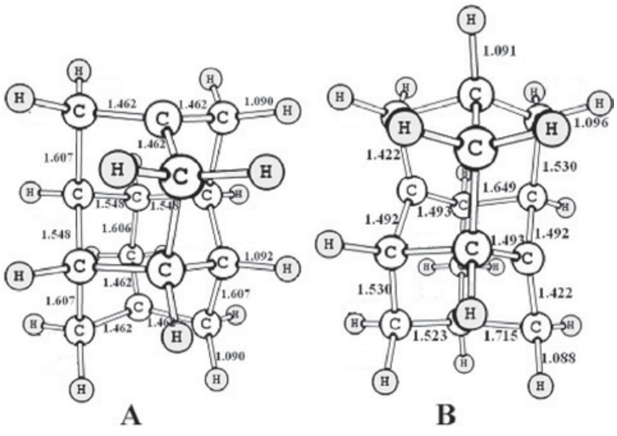


Figure 6. Atomic distances (Å) of the species **33** (A) and **34** (B).

in **34** (1.492, 1.493 and 1.422 Å). These results are in consonance with the uniformity of the delocalization indexes of each corresponding species mentioned above.

We proposed the D_3BIA index which is based on the density in the ring, the degeneracy and the delocalization index of atoms in the ring[21] and it is inspired to the modern VB idea about aromaticity as mentioned before. (see Electronic supplementary information).

The rationale on the index D_3BIA was influenced by modern VB studies on the aromaticity and the particularities of some aromatic compounds.[21] The similarities of the results between AIM and spin coupled wave function (SC) encouraged us to use the former since it provides important and complementary information. The coherence between the AIM and SC can be noticed from their results for benzene (see Electronic supplementary information).

There are some multi-center delocalization indexes proposed to measure aromaticity, for example, the six-center delocalization index[27] (SCI) and Fermi hole density delocalization index[28] (FDDH). However, it is important to emphasize that these multi-center indexes are based on MO approach of aromaticity, *i.e.*, the delocalization of orbitals in the aromatic molecules.[29] On the other hand, the D3BIA index is inspired to a different approach - the spin-coupled (SC) of the modern VB theory. The focus of SC study on the aromaticity is not the delocalization of the molecular orbital over the aromatic molecule since it was demonstrated that π single-electron orbitals are localized in each sp^2 carbon atom in the case of benzene.[19] The focus of modern VB study on aromaticity is the degeneracy and the overlap of the single-electron orbitals and these are the VB paremeters that inspired the formula of D3BIA index in atoms in molecules theory.

The electron density in the aromatic site can be understood in terms of the density in the region involving the bridged atoms. Then, the density factor is the density in the center of the cage structure and the magnitude of the delocalization indexes among bridged atoms or mean delocalization index $\overline{DI}$.

The degree of the degeneracy (δ) is derived from the energies of the atomic basins of the bridged atoms (from AIM theory).

The uniformity of delocalization indexes among bridged atoms is another important electronic feature found in the tridimensional aromatic species (Table 1).

The proposed D_3BIA formula is:

$$D_3BIA = \rho(3,+3) \bullet (\overline{DI}) \bullet DIU \bullet \delta \qquad (1)$$

The degree of degeneracy is regarded to be maximum (δ=1) when energy difference is smaller than 0.009 a.u.

The AIM provides a delocalization index for each bond between vicinal atoms.[19] The mean delocalization index ($\overline{DI}$) can be related to the magnitude of the single-electron states interaction (or overlap).

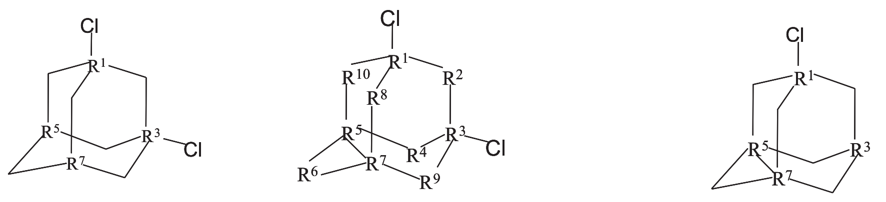
The delocalization index uniformity (DIU) among bridged atoms is given by equation 2:

$$\mathrm{DIU} = 100 - \frac{100\sigma}{(\overline{\mathrm{DI}})} \qquad (2)$$

Where σ is mean deviation and ($\overline{DI}$) is mean DI of the ring.

In Table 2, one can see the D_3BIA values for all aromatic and non-aromatic species (**1** to **32**). It was also performed NICS of the species **1** to **32**. Their NICS values are depicted in Table 2 and it is calculated from a probe (berkelium) in the center of adamantyl cage.[7,5] Since all the studied species do not have π orbitals, the use of a dissected NICS, e.g. CMO-NICS method, is unnecessary.[30] Because the species **33** and **34** are structurally different from other species, their D_3BIA´s have not been calculated.

From the 1,3-dehydro-5,7-dichloro-adamantane, the 1,3-dichloro-adamantane, the 1,3-dehydro-5-chloro-adamantane and their analogues (Scheme 3) it is possible to calculate the stability of the species **10-12**, **16**, **18**, **21-23** and **25-27** by means of the equations 3 and 4.



35. R^1=R^3=CCl; R^5=R^7=CH
36. R^1=R^3=SiCl; R^5=R^7=SiH
37. R^1=R^3=SiCl; R^5=R^7=CH

38. R^1=R^3=CCl; R^5=R^7=C
39. R^1=R^3=Si; R^5=R^7=Si
40. R^1=R^3=SiCl; R^5=R^7=C
41. R^1=R^3=CCl; R^5=N^+ ;R^7=B^-
42. R^2=R^4=R^8=R^9=R^{10}=O
R^1=R^3=CCl; R^5=R^7=C; R^6=CH_2
43. R^2=R^4=R^8=R^9=R^{10}=O
R^1=R^3=SiCl; R^5=R^7=Si; R^6=CH_2

44. R^1=CCl; R^3=CH; R^5=R^7=C
45. R^1=SiCl; R^3=SiH; R^5=R^7=Si
46. R^1=SiCl; R^3=SiH; R^5=R^7=C

Scheme 3.

Table 2. Density of (3,+3) critical point [ρ (3,+3)], mean delocalization index ($\overline{DI}$), delocalization index uniformity (DIU) among bridged atoms, degree of degeneracy (δ), D_3BIA, NICS and free energy variation of the dehalogenation reaction ($\Delta G_{(dehalogenation)}$) of the species **1** to **32**

Entry	ρ (3,+3) / au	$\overline{DI}$	DIU	δ	$D_3BIAx10^2$	NICS	$\Delta G_{(dehalogenation)}$ / (kcal mol^{-1})
1	0.012	0.039	100	1	4.68	-0.38	-
2	0.007	0.007	100	1	0.49	-0.63	-
3	0.009	0.018	64.24	0.5	0.52	-0.90	-
4	0.014	0.070	82.38	0.5	4.04	2.38	-
5	0.010	0.044	43.18	0.5	0.95	1.78	-
6	0.015	0.034	88.99	0.5	2.27	-12.62	-
7	0.018	0.026	76.73	0.5	1.79	3.27	-
8	0.012	0.006	91.23	0.5	0.33	0.24	-
9	0.017	0.053	76.45	0.5	3.44		-
10	0.020	0.135	86.17	0.5	11.63	-19.31	384.97
11	0.011	0.021	83.99	0.5	0.97	-6.42	397.59
12	0.013	0.055	86.49	0.5	3.09	-9.07	419.74
13	0.044	0.330	0.32	1	0.46	1.91	-
14	0.012	0.100	82.19	0.5	4.93	23.53	-
15	0.020	0.076	70.59	0.5	5.36	-12.70	-
16	0.046	0.280	100	1	128.8	-46.47	355.34
17	0.021	0.096	99.48	1	20.05	-36.35	365.37
18	0.024	0.149	91.67	0.5	16.39	-29.08	375.27
19	0.023	0.207	1.39	0.5	0.33	-10.90	-
20	0.009	0.026	45.02	0.5	0.53	-0.87	-
21	0.033	0.175	68.63	0.5	19.82	-37.52	364.20
22	0.053	0.169	84.56	0.5	37.87	-36.81	513.71
23	0.015	0.114	83.38	0.75	10.69	-19.55	491.86
24	0.030	0.182	14.19	0.5	3.87	-6.31	-
25	0.031	0.240	29.52	0.75	16.47	-29.76	110.83
26	0.014	0.087	21.84	0.75	1.99	-15.93	127.35
27	0.018	0.124	25.70	0.5	2.87	-22.30	131.17
28	0.023	0.190	16.79	0.5	3.67	-9.90	-
29	0.030	0.135	54.76	0.5	11.09	-38.80	-
30	0.021	0.079	37.13	0.5	3.08	-29.32	-
31	0.027	0.066	43.94	0.75	5.87	-27.85	-
32	0.015	0.082	64.24	0.75	5.93	-8.58	-

$$Cl–R–CL \rightarrow R^{+2} + 2Cl^{-} \qquad (3)$$

R= Adamantyl or its analogues; or 1,3-dehydroadamantyl or its analogues

$$R–Cl \rightarrow R^{+} + Cl^{-} \qquad (4)$$

R= 1,3-Dehydroadamantyl or its analogues

The energetics of all studied species are depicted in Electronic supplementary information. The free energy variation values of the dehalogenation of the species **10-12**, **16-18**, **21-23** and **25-27** are shown in Table 2.

From Table 2 one can see that the non-aromatic species **1** to **12** have the same electronic characteristics: small density in (3,+3) critical point (the density in centre of the cage structure) and small values of mean delocalization index among bridged atoms. One exception is the 1,3-adamantyl dication **10**, for not having two electrons distributed among bridged carbon atoms and still having a reasonable mean delocalization index value (0.135) and density in (3,+3) critical point (0.020 a.u.).

All non-aromatic species (**1** to **15** and **28** to **32**) have low D_3BIA. However, **10** and **29** have reasonable D_3BIA´s (Table 2) because their density in (3,+3) critical point and their values of mean delocalization index among bridged atoms are not small. There exists an apparent tendency for interaction between bridged atoms. In the 1,3-adamantyl dication **10**, there is no available electrons as it happens in its parent the 1,3-dehydro-5,7-adamantanediyl dication **16**, but it uses sigma electron density to generate interaction among its bridged atoms. On the other hand, **29** has two electrons between bridged carbon atoms but it has no positive charge as the aromatic species **16**. However, its bridged electropositive boron atoms draw the electron density towards them and this provokes a reasonable distribution of electron density among all bridged atoms (Tables 1 and 2). Then, **29** has tridimensional aromaticity.

The species **19** and **20** are not regarded aromatic ones since their D_3BIA´s are very low. The species **19** has quite small delocalization index uniformity and **20** has small density in (3,+3) critical point and small values of mean delocalization index among bridged atoms (Table 2).

In spite of not having tridimensional aromaticity the 1,3-dehydro-7-adamantyl cation **25** has a high D_3BIA (16.47). The species **25** has a characteristic planar homoaromaticity.

When analyzing its planar aromaticity, by exclusion of methine bridged carbon and the density in (3,+3) critical point, it is considered a three-membered planar ring among the other bridged carbons where its $\overline{DI} = 0.410$, its DIU = 100 and its $\delta = 1$. Then, its planar D_3BIA is higher than that shown in Table 2.

Free energies of dehalogenation reactions of **10-12**, **16-18**, **21-23** have been used to confirm the coherence of the D_3BIA values (Table 2). Despite there is no good correlation between them, it is possible to verify that the smaller the free energy of dehalogenation the higher is the D_3BIA. The smallest $\Delta G_{(dehalogenation)}$ value is for the 1,3-dehydro-5-7-adamantanediyl dication **16**. $\Delta G_{(dehalogenation)}$ values of **10** to **12** are higher for than those from **16**, **17**, **18** and **21**. All of these $\Delta G_{(dehalogenation)}$ values fit to their relation with D_3BIA. For example, **10**, with D_3BIA=11.63, has $\Delta G_{(dehalogenation)}$ value (384.97 kcal mol^{-1}) higher than those from the species **18** (D_3BIA=16.39, $\Delta G_{(dehalogenation)}$=375.27 kcal mol^{-1}) and **21** (D_3BIA=19.82 , $\Delta G_{(dehalogenation)}$= 364.20 kcal mol^{-1}). However, $\Delta G_{(dehalogenation)}$ value of **22** does not fit in the analyzed group, according to its D_3BIA. Moreover, one can see that NICS values somewhat support all of these tendencies described above (Table 2).

Within monocationic species **25** to **27**, there seems to be a reasonable relation between D_3BIA and $\Delta G_{(dehalogenation)}$ values, where the 1,3-dehydro-7-adamantyl cation **25** (D_3BIA=16.47) has the smallest $\Delta G_{(dehalogenation)}$ value (Table 2).

Conclusions

The electronic interaction among bridged atoms is decisive in tridimensional aromaticity, along with uniformity of the delocalization index involving bridged atoms and their degeneracy. The density in the center of the cage [(3,+3) critical point] and the mean delocalization index values among bridged atoms are distinguished between tridimensional non-aromatic and aromatic species: non-aromatic species have small $\rho(3,+3)$ and $\overline{DI}$ values while aromatic ones have high $\rho(3,+3)$ and $\overline{DI}$ values. The degeneracy of the bridged atoms, the uniformity and the magnitude of their delocalization indexes are the electronic features that distinguish the dications **10** and **16.** However, the 1,9 diamantyl dication **10** has tridimensional aromaticity as well as the 1,3-dehydro-5,7-diboroadamantane **29**.

The positive charge is mainly distributed among the hydrogen atoms and the bridged atoms remain negatively charged in the dicationic and monocationic aromatic species.

Supplementary Information

This supplementary material shows the atoms in molecules theory, the rationale on D_3BIA, benzene and resonance, delocalization index and basis set dependence, the quantum atom, similarities between NICS and D_3BIA, comparison of the delocalization indexes between MP2 and B3LYP computed energy values of the species **1** to **46**, optimized structures of the species **1**, **2**, **4**, **6**, **7**, **10**, **11**, **13**, **15**, **16**, **17**, **19**, **21**, **22**, **25** and **26** and their bond lengths, and internal coordinates of optimized structures. This material is available free of charge at http://jbcs.sbq.org.br, as PDF file.

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