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Revisiting the Bonding of the Pentagonal-Pyramidal $C_6H_6^{2+}$ and $C_6(CH_3)_6^{2+}$ Dications

Luis E. Seijas,*[a] Rafael Almeida,[b] Luis Rincón, [c] Cesar Zambrano,[c] Vladimir Rodríguez, [d] Gabriel Merino,[e] and F. Javier Torres [a,c]

a. Escuela de Ingeniería Ciencia y Tecnología, Universidad del Rosario, Bogotá 11171, Colombia.

b. Laboratorio de Procesos Dinámicos en Química, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela

c. Grupo de Química Computacional y Teórica (QCT-USFQ), Departamento de Ingeniería Química, Universidad San Francisco de Quito, Diego de Robles y Vía Interoceánica, Quito 17-1200-841, Ecuador

d. Departamento de Matemática, Universidad San Francisco de Quito, Diego de Robles y Vía Interoceánica, Quito 17-1200-841, Ecuador

e. Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Física Aplicada, Km. 6 Antigua carretera a Progreso Apdo. Postal 73, Cordemex, 97310 Merida, MEXICO.

Supplementary material

TABLE S1. Results of the AIM analysis for the pentagonal-pyramidal benzene (R = H) and the hexamethylbenzene dications (R =CH_3). N, q, λ and δ are the population, charge, localization and delocalization indexes, respectively, associated to the different fragments shown in the first column of the Table. $\Delta(\Omega) = Z - \lambda(\Omega)$, where Z is the atomic number. For R^{Ap} and R^{Ring} the third row corresponds to the values for the substituent methyl group. The results were obtained from wavefunctions at MP2/6-311++G**. Results obtained from wB97XD/6-311++G** wave function are shown in parentheses.

	$N(\Omega)$	$q(\Omega)$	$\lambda(\Omega)$	$\Delta(\Omega)$	$\delta(\Omega,\Omega)$**/2**
C^{AP} R = H	6.0446	- 4.46 10^{-2}	4.3985	1.6015	1.6461
	(6.0586)	(- 5.89 10^{-2})	(4.0503)	(1.9497)	(2.0085)
C^{AP} R = CH_3	6.0375	- 3.75 10^{-2}	4.3000	1.7000	1.7374
	(6.0757)	(-7.57 10^{-2})	(3.9366)	(2.0634)	(2.1391)
C^{Ring} R = H	5.9708	2.92 10^{-2}	4.3048	1.6952	1.6660
	(5.9490)	(5.10 10^{-2})	(3.9862)	(2.0138)	(1.9627)
C^{Ring} R = CH_3	5.9980	1.90 10^{-3}	4.2394	1.7606	1.7586
	(5.9832)	(1.67 10^{-2})	(3.8940)	(2.1060)	(2.0892)
R^{Ap} R = H	0.6166	3.83 10^{-1}	0.2290	0.7710	0.3875
	(0.6487)	(3.51 10^{-1})	(0.1990)	(0.8009)	(0.4497)
R^{Ap} R= C	5.9000	1. 00 10^{-1}	4.1933	1.8067	1.7065
	(5.9807)	(1.92 10^{-2})	(4.0251)	(1.9749)	(1.9557)
R^{Ap} R= CH_3	8.5873	4.05 10^{-1}	5.4847	3.5153	--
	(8.6124)	(0.3876)	(5.0700)	(3.9300)	
R^{Ring} R = H	0.6969	3. 031 10^{-1}	0.2840	0.7160	0.4135
	(0.7094)	(2.96 10^{-1})	(0.2389)	(0.7611)	(0.4705)
R^{Ring} R=C	5.9226	7. 74 10^{-2}	4.1938	1.8062	1.7288
	(6.0092)	(-9.10 10^{-3})	(4.0343)	(1.9656)	(1.9748)
R^{Ring} (CH_3)	8.6757	3.24 10^{-1}	5.4778	3.5222	--
	(8.6790)	(3.21 10^{-1})	(5.1015)	(3.8985)	

Note: Results in parenthesis correspond to DFT wavefunction at wB97XD/6-311++G**

TABLE S2. Results for the average delocalization indexes between the apical carbon and one of the ring carbons, $\langle\delta(C^{AP},C^{Ring})\rangle$, between neighbor ring carbons, $\langle\delta(C^{Ring},C^{Ring})\rangle$, between the apical carbon and the R atom bonded to it (R= H,C), $\langle\delta(C^{AP},R)\rangle$, and between a ring carbon and the R a tom bonded to it, $\langle\delta(C^{Ring},R)\rangle$. The results were obtained from wavefunctions at MP2/6-311++G**. Results obtained from wB97XD/6-311++G** wave function are shown in parentheses.

	$\langle\delta(C^{Ring},C^{Ring})\rangle$	$\langle\delta(C^{Ring},R)\rangle$	$\langle\delta(C^{AP},C^{Ring})\rangle$	$\langle\delta(C^{AP},R)\rangle$
R = H	0.9374	0.7569	0.5066	0.7056
	(1.0945)	(0.8538)	(0.6282)	(0.8090)
R = CH_3	0.9014	0.8755	0.4661	0.8596
	(1.0501)	(1.0185)	(0.5808)	(1.0071)

Note: Results in parenthesis correspond to DFT wavefunction at wB97XD/6-311++G**

TABLE S3. Results of the AIM analysis for the optimized models $[(C_5R_5)R^{AP}H]^m$ (R= H, CH_3; R^{ap} = B, Be; m = +1, 0), results in parenthesis correspond to R = CH_3. N, q, λ and δ are the population, charge, localization, and delocalization indexes, respectively, associated to the different fragments shown in the first column of the Table. $\Delta(\Omega) = Z - \lambda(\Omega)$, where Z is the atomic number. For R^{ap} and C^{ring}. The results were obtained from wavefunctions at MP2/6-311++G**.

	$N(\Omega)$	$q(\Omega)$	$\lambda(\Omega)$	$\Delta(\Omega)$	$\delta(\Omega,\Omega)/2$
R^{AP} = B	3.1643	1.8357	2.2803	2.7197	0.8840
	(3.2128)	(1.7871)	(2.2983)	(2.7017)	(0.9145)
R^{AP} = Be	2.3669	1.6331	2.0169	1.9831	0.3499
	(2.3762)	(1.6237)	(2.0174)	(1.9826)	(0.3589)
C^{ring} (R^{AP}= B)	6.2159	-0.2159	4.4507	1.5493	1.7652
	(6.24202)	(-0.2455)	(4.4212)	(1.5788)	(1.8191)
(R^{AP} = Be)	6.2065	-0.2065	4.4430	1.5570	1.7636
	(6.2382)	(-0.2382)	(4.4394)	(1.5606)	(1.7988)
H^{ap} (R^{AP} =B)	1.5758	-0.5758	1.1444	-0.1444	0.4314
	(1.5871)	(-0.5871)	(1.1516)	(-0.1516)	(0.4355)
H^{ap} (R^{AP} = Be)	1.8351	-0.8351	1.5621	-0.5621	0.2730
	(1.8228)	(-0.8228)	(1.5401)	(-0.5401)	(0.2827)
R^{ring} (R^{ap} = B)	0.8361	0.1689	0.3851	0.6149	0.4510
	(5.8836)	(0.1164)	(4.1366)	(1.8634)	(1.7469)
R^{ring} (R^{ap}= Be)	0.9530	0.0470	0.4745	0.5255	0.4785
	(5.8718)	(0.1282)	(4.1095)	(1.8905)	(1.7623)

TABLE S4. Results of the AIM analysis for the pentagonal-pyramidal benzene (R = H) and the hexamethylbenzene dications (R =CH_3) with a change in the angle a. N, q, λ and δ are the population, charge, localization and delocalization indexes, respectively, associated to the different fragments shown in the first column of the Table. , where Z is the atomic number. For R^{Ap} and R^{Ring}. The results were obtained from wavefunctions at MP2/6-311++G**.

α			128.3°		
	$N(\Omega)$	$q(\Omega)$	$\lambda(\Omega)$	$\Delta(\Omega)$	$\delta(\Omega,\Omega)/2$
C^{ap}	6.0254	-0.0254	4.3740	1.6260	1.6514
C^{ring}	5.9632	0.0368	4.2934	1.7066	1.6697
H^{ap}	0.6327	0.3673	0.2414	0.7586	0.3913
H^{ring}	0.7059	0.2941	0.2907	0.7093	0.2907
α			135.5		
C^{ap}	6.0181	-0.0182	4.3692	1.6308	1.6489
C^{ring}	5.9684	0.0316	4.2976	1.7024	1.6708
H^{ap}	0.6309	0.3691	0.2401	0.7599	0.3907
H^{ring}	0.7019	0.2981	0.2886	0.7114	0.4133

TABLE S5. Results for the average delocalization indexes between the apical Atom Rap in the isoelectronic models $[(C_5R_5)R^{AP}H]^m$ (R= H, CH_3; R^{AP} = B, Be; m = +1, 0), results in parenthesis correspond to R = CH_3 and one of the ring carbons, $\langle\delta(R^{AP},C^{Ring})\rangle$, between neighbor ring carbons, $\langle\delta(C^{Ring},C^{Ring})\rangle$, between the apical atom R^{ap} and the H atom bonded to it, $\langle\delta(R^{AP},C^{Ring})\rangle$, and between a ring carbon and the atom bonded to it, $\langle\delta(C^{Ring},R)\rangle$. The results were obtained from wavefunctions at MP2/6-311++G**.

R^{AP}	$\langle\delta(C^{Ring},C^{Ring})\rangle$	$\langle\delta(C^{Ring},R)\rangle$	$\langle\delta(R^{AP},C^{Ring})\rangle$	$\langle\delta(R^{AP},H)\rangle$
B	1.0993	0.8210	0.2451	0.6237
	(1.0475)	(0.8829)	(0.2329)	(0.6147)
Be	1.1364	0.8591	0.0810	0.2853
	(1.0840)	(0.8895)	(0.0816)	(0.2793)

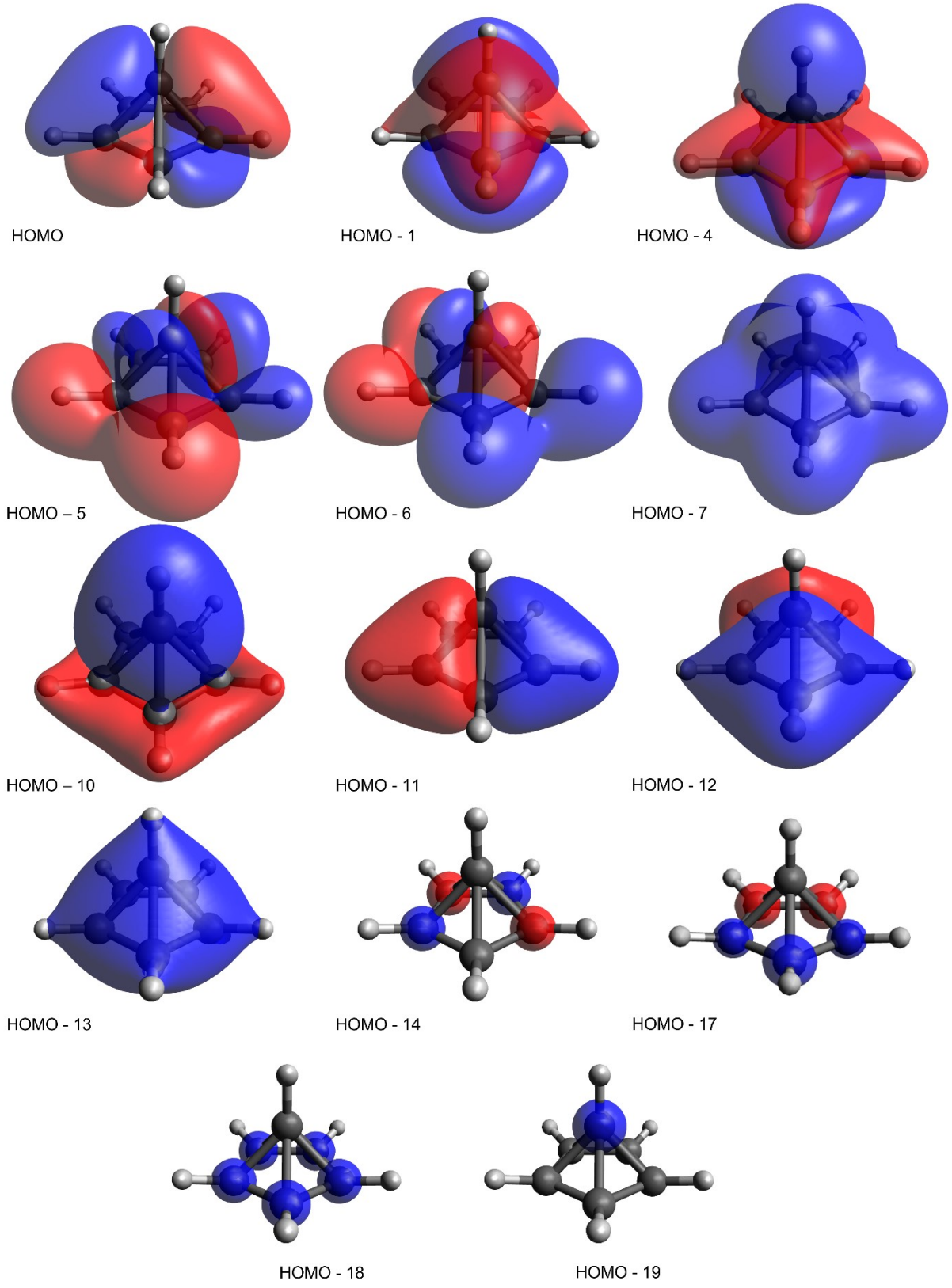

FIGURE S1. Subgroup of orbital belonging to irreducible representations A1 and E1

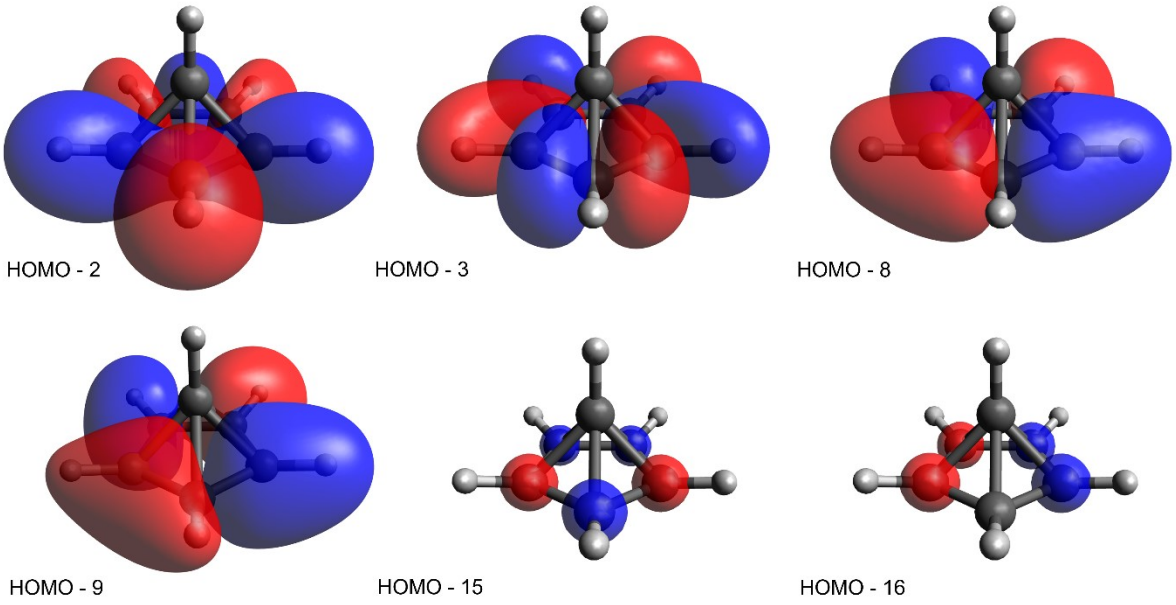

FIGURE S2. Subgroup of orbital belonging to irreducible representation E2.