Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Of

Double aromaticity in $BBe_6H_6^+$ cluster with planar hexacoordinate boron

Locating the global minima (GM) structure: ABCluster 2.0 version was used for the generation of the possible isomers. The size of the population was 50 and M06-2X/TZVP was used to get those structures. After harmonic frequency calculations at M06-2X/TZVP level, we found that 10 out of those 50 structures were local minima which on further re-optimization at M06-2X/Def2-TZVP lead to the last 6 local mimima. The remaining ones lead to either of the last 6 structures. We have not only generated some initial C1 structures but also some more symmetrical structures. However, most of the symmetrical ones lead to the global minima after optimization at M06-2X/Def2-TZVP level.

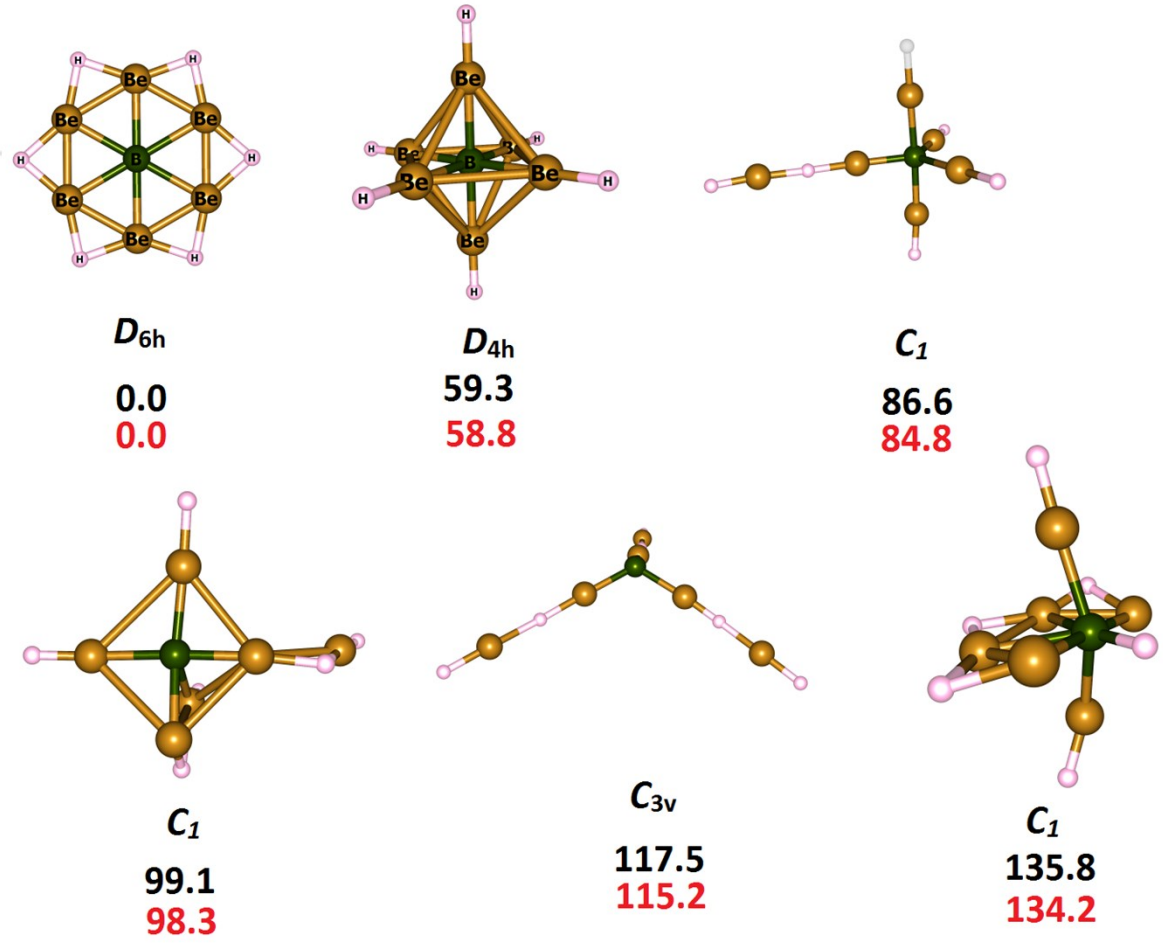

Fig S1. Optimized global minimum structure of $BBe_6H_6^+$ cluster along with five lowest lying isomers computed at M06-2X/TZVP level of theory. Zero point corrected relative energies (black font) at M06-2X/TZVP level and single point energies at CCSD/Def2-TZVP//M06-2X/TZVP (red font) are reported in kcal/mol.

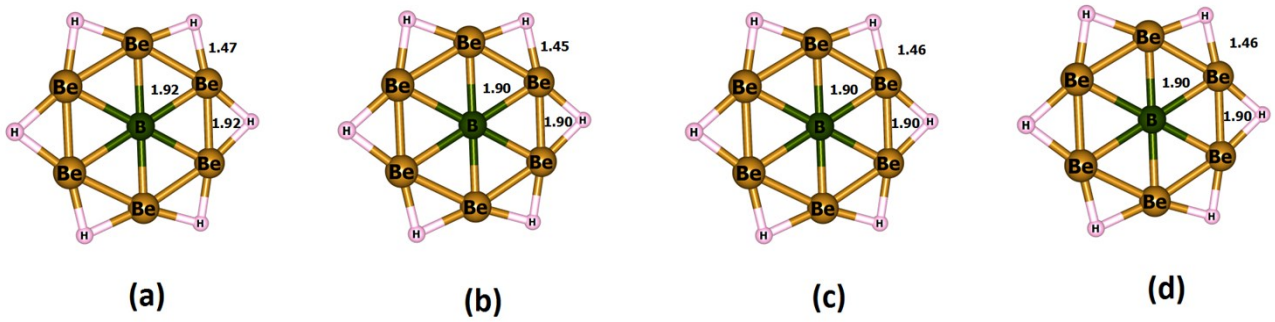

Fig S2. Optimized geometry of the global minimum of $BBe_6H_6^+$ cluster at (a) BP86, (b) B3LYP-D3, (c) MP2 and (d) CCSD levels of theory. Def2-TZVP basis set was used in all cases. Bond lengths are in Å.

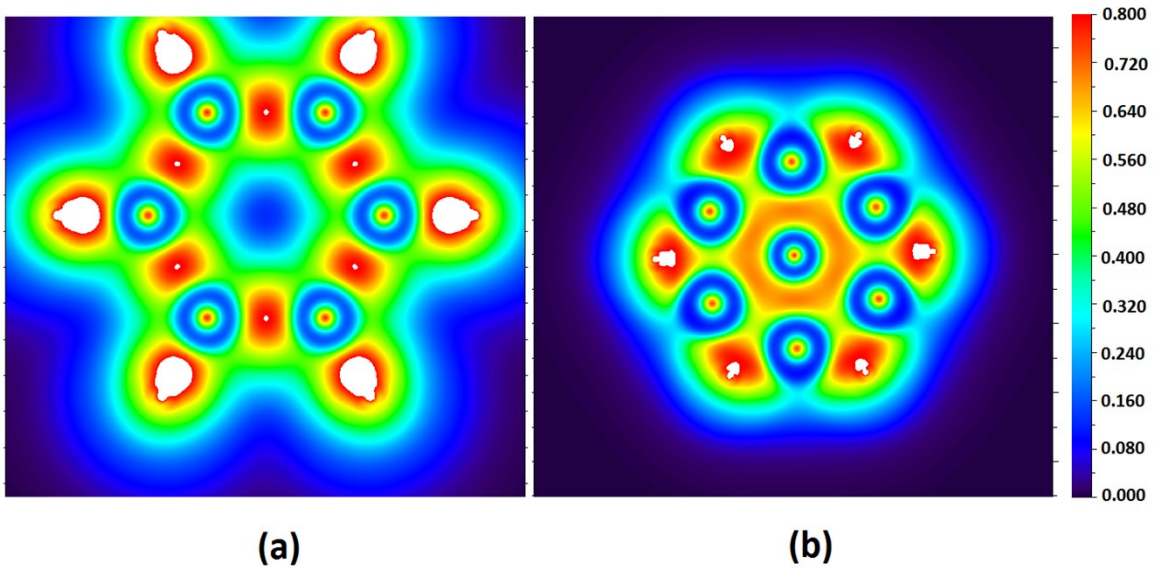

Fig S3. Localized orbital locator (LOL) plot for (a) benzene (C_6H_6) and (b) $BBe_6H_6^+$ cluster in the molecular plane showing similarity in topological feature of electron delocalization.

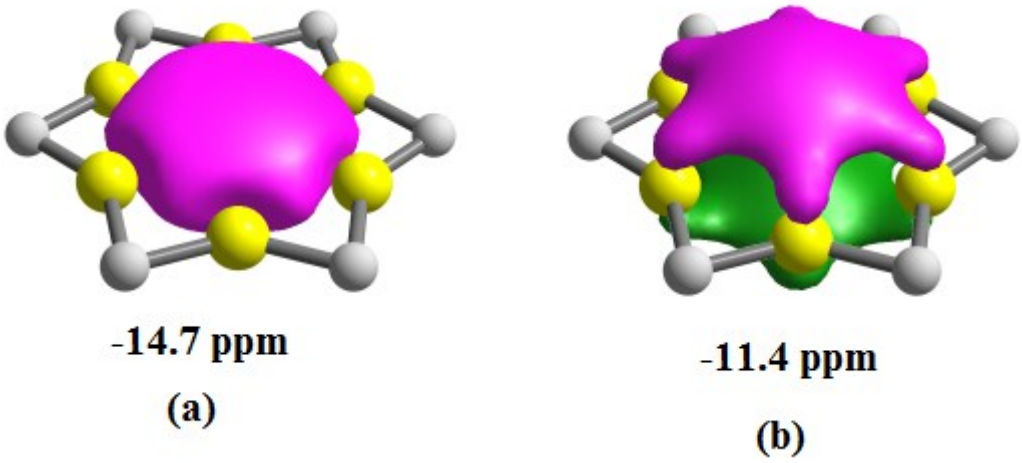

Fig S4. CMOs with maximum diamagnetic contribution to (a) σ and (b) π aromaticities, obtained through CMO-NICS analysis at the Be-B-Be ring centre.

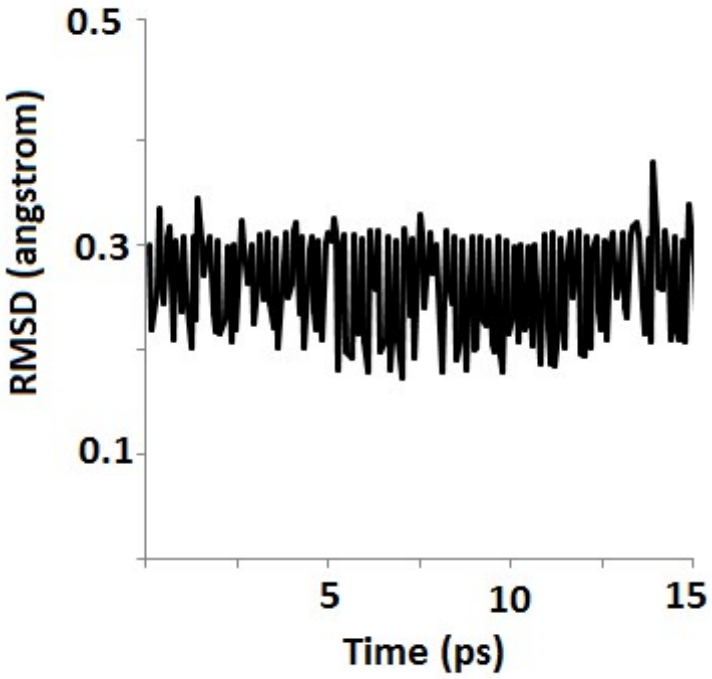

Fig S5. Plot of RMSD (Å) versus time (ps) obtained from BOMD simulation (M06-2X/TZVP) at 398K.

Table S1. QTAIM and ELF parameters of $BBe_6H_6^+$ cluster. Electron density at bond critical point (ρ), laplacian of electron density ($\nabla^2\rho$), total electronic energy density, *H*(r) and ELF value (η) at the bond and ring critical point. Para-delocalization index (PDI) and aromatic fluctuation index (FLU) of Be_6 ring of $BBe_6H_6^+$ cluster and benzene (for comparison) are also shown. All values are in a.u.

Bond	**Ring**	**ρ**	$\nabla^2\rho$	***H*(r)**	**η**	**PDI**	**FLU**
Be-Be		0.063	-0.032	-0.033	0.612		
B-Be		0.070	0.189	-0.025	0.183		
	Be-B-Be	0.061	0.062	-0.029	0.262		
	Be-H-Be	0.032	0.041	-0.021	0.211		
	Be_6					0.08	0.00
	Benzene, C_6H_6					0.10	0.00

Cartesian coordinates of the optimized global minimum of $BBe_6H_6^+$ cluster at different levels of theory along with the lowest vibrational frequency (ν_{min}) in cm^{-1}.

M06-2X/Def2-TZVP, ν_{min} = 87.8

	X	Y	Z
Be	0.116784000	-1.909947000	-0.028508000
Be	-1.596208000	-1.056731000	0.025465000
Be	-1.713677000	0.853889000	-0.003064000
Be	-0.116792000	1.910436000	-0.023546000
Be	1.596066000	1.056498000	0.018412000
Be	1.714007000	-0.854153000	-0.000663000
H	-1.521592000	2.297749000	-0.023974000
H	1.229565000	2.466640000	-0.006783000
H	2.750092000	0.168697000	0.010006000
H	1.521420000	-2.297854000	-0.026669000
H	-1.229240000	-2.466659000	-0.003848000
H	-2.749988000	-0.168685000	0.015519000
B	0.000036000	0.000026000	-0.000243000

BP86-D3/Def2-TZVP, ν_{min} = 104.2

	X	Y	Z
Be	0.117054000	-1.915044000	-0.027134000
Be	-1.600292000	-1.059547000	0.024018000
Be	-1.718172000	0.856219000	-0.002290000
Be	-0.117038000	1.915538000	-0.022348000
Be	1.600100000	1.059277000	0.017277000
Be	1.718507000	-0.856449000	0.000056000
H	-1.536201000	2.319881000	-0.021844000
H	1.241806000	2.490459000	-0.008631000

H	2.777420000	0.170728000	0.008001000
H	1.536059000	-2.319978000	-0.024516000
H	-1.241441000	-2.490494000	-0.005695000
H	-2.777355000	-0.170712000	0.013851000
B	0.000026000	0.000029000	0.001358000

B3LYP-D3/Def2-TZVP, ν_{min} = 74.3

	X	Y	Z
Be	0.115238000	-1.885648000	-0.027338000
Be	-1.575538000	-1.043242000	0.023098000
Be	-1.691582000	0.843056000	-0.003273000
Be	-0.115273000	1.885947000	-0.022707000
Be	1.575587000	1.043116000	0.015892000
Be	1.691775000	-0.843254000	-0.001444000
H	-1.511171000	2.281983000	-0.021583000
H	1.221376000	2.449817000	-0.006540000
H	2.732547000	0.167818000	0.009720000
H	1.511049000	-2.282048000	-0.024108000
H	-1.221176000	-2.449817000	-0.003873000
H	-2.732410000	-0.167851000	0.014924000
B	0.000049000	0.000028000	-0.000664000

MP2/Def2-TZVP, ν_{min} = 91.0

	X	Y	Z
Be	-0.085280000	-1.901057000	0.025133000
Be	1.603982000	-1.024955000	-0.025478000
Be	1.689624000	0.876849000	0.001912000
Be	0.085324000	1.901417000	0.020445000
Be	-1.603829000	1.024788000	-0.021240000

Be	-1.689808000	-0.877059000	-0.002959000
H	1.486410000	2.326773000	0.022214000
H	-1.271898000	2.450736000	0.003213000
H	-2.758433000	0.124104000	-0.014734000
H	-1.486265000	-2.326817000	0.022558000
H	1.271712000	-2.450752000	0.002469000
H	2.758391000	-0.124064000	-0.015702000
B	0.000007000	0.000018000	-0.002253000

CCSD/Def2-TZVP, ν_{min} = 94.0

	X	**Y**	**Z**
Be	0.086079000	-1.901021000	-0.025133000
Be	-1.603551000	-1.025629000	0.025478000
Be	-1.689992000	0.876139000	-0.001912000
Be	-0.086123000	1.901381000	-0.020445000
Be	1.603399000	1.025461000	0.021240000
Be	1.690176000	-0.876349000	0.002959000
H	-1.487387000	2.326148000	-0.022214000
H	1.270869000	2.451270000	-0.003213000
H	2.758381000	0.125263000	0.014734000
H	1.487242000	-2.326193000	-0.022558000
H	-1.270682000	-2.451286000	-0.002469000
H	-2.758339000	-0.125223000	0.015702000
B	-0.000007000	0.000018000	0.002253000