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Planar pentacoordinate carbon in $[XC_7H_2]^{2+}$ (X = Be and Mg) and its derivatives[†]

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Planar pentacoordinate carbon (ppC) atom is theoretically established here in $[XC_7H_2]^{2+}$ and $[XSi_2C_5H_2]^{2+}$, where X = Be and Mg, using density functional theory. Inclusion compounds with alkali and alkaline earth metal ions are identified with the monomer units of tri-cyclic C_7H_2 and $Si_2C_5H_2$ isomers with a planar tetracoordinate carbon (ptC) atom. While all alkali and some alkaline earth metals (Ca^{2+}, Sr^{2+}, and Ba^{2+}) stabilize the ptC isomer in both the cases, Be^{2+} and Mg^{2+} ions make a bond directly with the ptC atom and thus making it a ppC atom. Theoretical binding energies computed at the PBE0-D3/def2-TZVP level of theory are ∼ -9.68, -10.42, -5.85, and -5.47 eV for $[BeC_7H_2]^{2+}$, $[BeSi_2C_5H_2]^{2+}$, $[MgC_7H_2]^{2+}$, and $[MgSi_2C_5H_2]^{2+}$, respectively.

Nature prefers tetrahedral tetracoordination when four single bonds are made to carbon atom in a molecule.[1] Contrary to this eminent fact, Monkhorst first hypothetically proposed the idea of planar tetracoordination carbon (ptC) for a transition state geometry in a non-dissociative racemization process.[2] Hoffmann and co-workers suggested ways to stabilize the ptC atom[3] either through electronic effects by embedding the ptC into a $(4n + 2)\pi$ electron system or through mechanical strain by encapsulating the ptC atom in a cage like structure. Ever since, the concept of molecules with a ptC[4] atom became an inspiration to many chemists in various fields although it breaks one of the fundamental exemplars of organic chemistry - i.e., tetrahedral tetracoordinate carbon. Identification of pentaatomic molecules containing ptC atom (CAl_4^-, $CAl_3Si^{-/0}$, $CAl_3Ge^{-/0}$, CAl_4^{2-}, etc.,)[5] using anion photoelectron spectroscopy has given some momentum in the search of these molecules in the gas phase. Stabilization of ptC by hydrogenation, in the case of $CAl_4H^{-/0}$, has been reported in 2017.[6] It was demonstrated in the past that molecules with a ptC atom could be strongly stabilized by the cooperative influence of metal pairs (Zr/Al or Zr/Zr^+) of atoms.[7] In the solid state, a divanadium complex identified by Cotton and Miller,[8] was recognized later by Keese[9] that the crystallographic data of the complex indeed shows the ptC atom. Molecules with a planar hypercoordinate carbon (phC)[10] atom are also actively pursued as a logical extension to the idea of ptC. Because, apart from the chemical bonding perspective, interest in molecules with a ptC or phC atom stems from the fact that they could be used as potential new materials.[11]

The anomaly of carbon atom having a planar pentacoordination and at the same time being a global minimum was first reported by Schleyer and co-workers in CAl_5^+, which is a perfect pentagon with D_{5h} symmetry.[12] Majority of molecules with a ptC atom or a planar pentacoordinate carbon (ppC) atom satisfies the so-called “18 valence electrons (18 ves) rule”.[13] Following the latter strategy, Jimenez-Halla and co-workers predicted the neutral and anionic ppC molecules such as CAl_4Be and $CAl_3Be_2^-$.[10 b] Lu *et al.* analyzed the various isomers of $CAl_2Be_3^{2-}$ and $CAl_2Be_3Li^-$ and found that their global minima also contain ppC atom.[10 c] Zhang and Ding explored the potential energy surfaces (PESs) of CAl_4X^+ (X = Ga, In, and Tl) and concluded that only CAl_4Ga^+ alone contains a ppC atom.[10 d] By taking CBe_5^{4-} as the core unit and putting Li atoms as counter ions systematically, all clusters containing $CBe_5Li_n^{(4-n)-}$ (n = 1-5) were shown to retain the ppC atom.[10 e] Similar ideology was followed in predicting the ppC or quasi-ppC isomers of $CBe_5H_n^{(4-n)-}$ (n = 2-5),[10 f] $CBe_5X_5^+$ (X = Na, K, F, Cl, Br, Au),[10 g][10 h], CBe_5Y^- (Y = Al, Ga, In, and Tl) clusters.[10 i] CGa_5^+ derivatives containing ppC atoms as global minima were also predicted in the recent past.[10 j] Nevertheless,

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[†] Electronic Supplementary Information (ESI) is available: [Cartesian coordinates of the optimal geometries, total electronic energies, zero-point vibrational energies (ZPVEs), obtained at different levels are given]. See DOI: 10.1039/b000000x/

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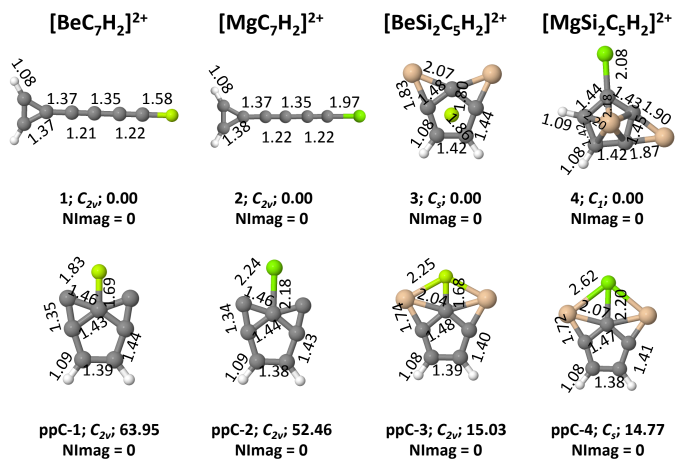

Fig. 1 Structures of $[XC_7H_2]^{2+}$ and $[XSi_2C_5H_2]^{2+}$ (X = Be and Mg) obtained at the PBE0-D3/def2-TZVP level. Putative global minima are shown at the top and structures exhibiting ppC atoms are shown at the bottom. Relative energies including ZPVE corrections are given in kcal mol^{-1}. Bond lengths are in Å.

it is worth noting here that the 18 ves rule for predicting ppC or ptC is a guide instead of a rule. Because, in CBe_4Li_4, the global minimum contains a ppC with 16 ves.[10k] Molecules with a ptC atom containing 20,[14] 19,[15] 17,[16] 15,[17] 16,[18] 14, and even as low as 12 valence electrons have been reported theoretically.[19] Here, we report both ptC and ppC molecules containing 20 valence electrons in $[XC_7H_2]^{2+}$ and $[XSi_2C_5H_2]^{2+}$. When X = Be and Mg, one could reach to ppC (see Fig. 1), whereas, when X = Ca, Sr, and Ba, they remained as ptC systems. In the case of $[XC_7H_2]^{+}$ and $[XSi_2C_5H_2]^{+}$ (where, X = Li, Na, K, Rb, and Cs), all systems remained as ptC systems. Our earlier theoretical work on C_7H_2 isomers predominantly focused on the low-lying region[20] and also identification of dissociation pathways where molecules with a ptC atom are involved as reactive intermediates.[21]

In this work, the C_7H_2[21] and $Si_2C_5H_2$[22] isomers with a ptC atom are used as base units to make inclusion compounds. In C_7H_2, the ptC isomer is a local minimum lying 26.12 kcal mol^{-1} above the linear triplet isomer, heptatriynylidene (HC_7H), at the CCSD(T)/cc-pVTZ level of theory.[21] In $Si_2C_5H_2$, the ptC isomer is the global minimum.[23] Various structural isomers of $Si_2C_5H_2$ were explicitly explored elsewhere using both search algorithm and chemical intuition.[22] The ptC isomer of C_7H_2 was found to be kinetically stable using Born-Oppenheimer molecular dynamics (BOMD) simulations.[24] Isomerization pathways of C-C bonds connected to the ptC atom in C_7H_2 were also investigated by some of us in the past.[21] It was concluded that the overall isomerization pathway is exothermic. However, the minimum activation energy required for this molecule to undergo isomerization is 11.02 kcal mol^{-1} at the W1-F12 level. Isomerization pathways of C-C and Si-C bonds connected to the ptC atom in $Si_2C_5H_2$ were also investigated by us in the past and the minimum activation energy required now jumps to 30.51 kcal mol^{-1} and the overall reaction profile is endothermic unlike C_7H_2. Thus, it is concluded that the molecule is kinetically much more stable than the C_7H_2 ptC isomer.[25] On the basis of these past experiences, here, it is envisioned to make inclusion compounds with alkali and alkali-earth metal ions. In Fig. 1, we have shown the structures of $[XC_7H_2]^{2+}$ and $[XSi_2C_5H_2]^{2+}$ (X = Be and Mg) obtained at the PBE0[26]-D3[27]/def2-TZVP[28] level. Putative global minima are shown at the top and structures exhibiting five bonds to carbon are shown at the bottom. All the ppC structures turned out to be local minima when def2-TZVP basis set is used. However, $[BeC_7H_2]^{2+}$ (**ppC-1**) turned out to be a transition state geometry when Pople's basis set, 6-311++G(2d,2p), is used.[29]

Considering the ppC atoms in $[XC_7H_2]^{2+}$ and $[XSi_2C_5H_2]^{2+}$ (X = Be and Mg), we have explored the chemical space of these elemental compositions using both chemical intuition and the cluster building procedure implemented in the python program for aggregation and reaction (PyAR).[30] Modeling by intuition was done targeting for ptC and ppC based on similar reported molecules. The automated cluster building is done as follows: First, a diatomic molecule is generated from two randomly chosen atoms from C (or Si), H, and Be (or Mg). To the optimized geometry of these diatomic molecules, another randomly chosen atom is added following the procedure described elsewhere[31] to generate several (N) guess geometries. All these geometries are optimized and unique minima are chosen and further addition of random atoms are continued until the target chemical formula is reached. We have performed 10 different runs with N = 16 orientations for the these systems. The trial geometries were optimized using the ORCA program[32] interfaced with PyAR.[30,31] The initial geometry optimizations are carried out using PBE[33] functional with def2-SVP[28] basis set including Grimme's empirical dispersion corrections (D3)[27] with Becke-Johnson (BJ) damping[34] and resolution of the identity (RI) approximation. For brevity, various geometries obtained on these elemental compositions are shown in the ESI†.

Further, all geometry optimization and frequency calculations are also carried out at the PBE0[26]-D3/def2-TZVP[28] level. We have also used TPSSh[35] hybrid-meta functional including and excluding D3BJ corrections with the 6-311++G(2d,2p)[29] basis set. All these calculations are also repeated at the TPSSh-D3BJ/def2-TZVP level to compare the binding energy values in a reliable manner. In Table 1, the binding energies obtained are shown for all systems at four different levels. For Rb^{+}-, Cs^{+}-, Sr^{2+}-, and Ba^{2+}-chelated isomers, calculations are carried out with the LANL2DZ ECP (for metal ion alone)[36] when Pople's basis set is used. All electronic structure calculations are carried out with the Gaussian program package.[37] The topological analysis of electron localization function (ELF) and Laplacian of electron density were carried out for ppC geometries with Multiwfn program[38] using the wave function file generated by Gaussian program.[37] The color filled map of ELF is shown in Fig. 2. For brevity, the ELF values are given in ESI†(Table S1-S4). Through ELF analysis, one can confirm that the interaction between the central C atom (*i.e.,* the ppC atom) and four C (**ppC-1** and **ppC-2**) or two C and two Si atoms (**ppC-3** and **ppC-4**) is strong as the ELF values are close to 1 (covalent character). However, the interaction between central

Table 1 Binding energies (in eV) of $M^{+/2+}$-C_7H_2 and $M^{+/2+}$-$Si_2C_5H_2$ calculated at different levels.

Species	TPSSh	TPSSh-D3BJ	PBE0-D3	TPSSh-D3BJ
	6-311++G(2d,2p)		def2-TZVP	
Li^+-C_7H_2	-1.83	-1.90	-1.86	-1.90
Na^+-C_7H_2	-1.40	-1.47	-1.46	-1.48
K^+-C_7H_2	-1.10	-1.17	-1.17	-1.18
Rb^+-C_7H_2	-0.93	-1.00	-1.07	-1.07
Cs^+-C_7H_2	-0.83	-0.91	-0.99	-0.98
Be^{2+}-C_7H_2	-9.72[a]	-9.80[a]	-9.68	-9.74
Mg^{2+}-C_7H_2	-5.76	-5.86	-5.85	-5.90
Ca^{2+}-C_7H_2	-4.38	-4.48	-4.42	-4.51
Sr^{2+}-C_7H_2	-3.20	-3.30	-3.78	-3.83
Ba^{2+}-C_7H_2	-2.79	-2.89	-3.31	-3.35
Li^+-$Si_2C_5H_2$	-1.22	-1.31	-1.19	-1.27
Na^+-$Si_2C_5H_2$	-0.71	-0.81	-0.72	-0.79
K^+-$Si_2C_5H_2$	-0.43	-0.53	-0.46	-0.52
Rb^+-$Si_2C_5H_2$	-0.30	-0.39	-0.40	-0.44
Cs^+-$Si_2C_5H_2$	-0.24	-0.33	-0.36	-0.39
Be^{2+}-$Si_2C_5H_2$	-10.46	-10.56	-10.42	-10.51
Mg^{2+}-$Si_2C_5H_2$	-5.46	-5.58	-5.47	-5.56
Ca^{2+}-$Si_2C_5H_2$	-3.55	-3.68	-3.49	-3.65
Sr^{2+}-$Si_2C_5H_2$	-2.04	-2.16	-2.78	-2.89
Ba^{2+}-$Si_2C_5H_2$	-1.59	-1.71	-2.26	-2.37

[a] Be^{2+}-C_7H_2 geometry is a transition state at this level.

C and Be or Mg atoms shows less covalent character though ppC is preserved.

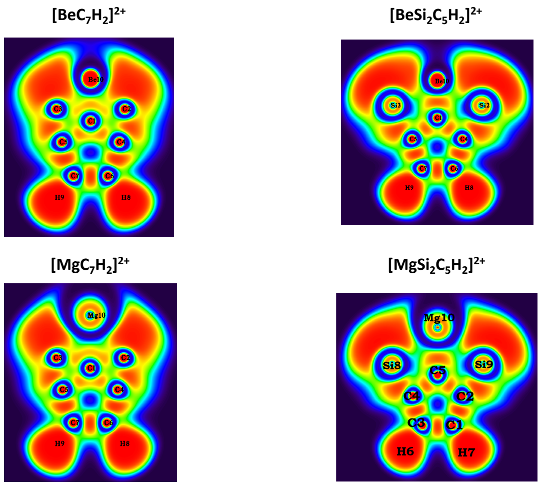
$[BeC_7H_2]^{2+}$ $[BeSi_2C_5H_2]^{2+}$
$[MgC_7H_2]^{2+}$ $[MgSi_2C_5H_2]^{2+}$

Fig. 2 Color filled map of ELF for ppC structures obtained at the TPSSh-D3BJ/6-311++G(2d,2p) level.

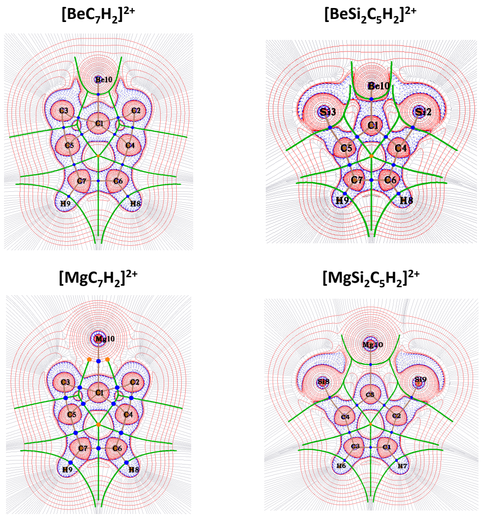
$[BeC_7H_2]^{2+}$ $[BeSi_2C_5H_2]^{2+}$
$[MgC_7H_2]^{2+}$ $[MgSi_2C_5H_2]^{2+}$

Fig. 3 Contour map of the Laplacian of Electron Density ($\nabla^2\rho(r_c)$) with the bond paths for ppC structures obtained at the TPSSh-D3BJ/6-311++G(2d,2p) level.

Thus, to establish the pentacoordinate nature of carbon in $[XC_7H_2]^{2+}$ and $[XSi_2C_5H_2]^{2+}$ (X = Be and Mg) systems further, we have analyzed the topology of electron density ($\rho(r_c)$) for the ppC isomers based on the Quantum Theory of Atoms in Molecules (QTAIM).[39] To analyze the topology of electron density ($\rho(r_c)$), contour plots of the Laplacian of electron density ($\nabla^2\rho(r_c)$) along with bond paths and critical points for ppC isomers are shown in Fig. 3. Generally, low value of electron density ($\rho(\mathrm{r_c})$) and positive value of Laplacian electron density ($\nabla^2\rho(\mathrm{r_c})$) at BCP indicate a "closed shell type of bonding"[40], whereas a high value of $\rho(\mathrm{r_c})$ and negative value of $\nabla^2\rho(\mathrm{r_c})$ represents covalent interaction.[39] To get further insight into this result, Lagrangian kinetic energy density $\mathrm{G(r_c)}$, electron energy density $\mathrm{H(r_c)}$, the ratio of $-\mathrm{G(r_c)/V(r_c)}$, the ratio of $\mathrm{G(r_c)}/\rho(r_c)$ should also be accounted. If, $\nabla^2\rho(\mathrm{r_c}) > 0$, and $\mathrm{H(r_c)} < 0$, then the bonding is partly covalent type, as suggested by Cremer and Kraka,[40] which is reflected in the case of BCP (C1-Be10) for **ppC-1** system, as shown in Table

S1 (ESI†).

If, $-G(r_c)/V(r_c) > 1$, then it indicates purely non-covalent type of interaction[41], which is reflected in the Table S2 (ESI†), at BCP (C3-Mg10) for the **ppC-2** system. But, if this ratio of $-G(r_c)/V(r_c)$ falls in the range of 0.5 to 1.0, then it can be said that, there will be a partial covalent character.[41] This is reflected in case of all values of $-G(r_c)/V(r_c)$ (see Table S1-S4 (ESI†). These results ensure that for all cases, there are partial covalent character except for BCP (C3-Mg10) as discussed earlier. To check the covalency, another parameter is utilized called the ratio of $G(r_c)/\rho(r_c)$.[42] When the ratio is less than one, then it clearly indicates the presence of some degree of covalent bond, which is shown in Table S2 (ESI†). If the ratio of $G(r_c)/\rho(r_c) >> 1$, then this should be referred as "closed shell type of interaction", which is reflected in the case of BCP (C4-Si8 and C2-Si9 for **ppC-4** system.

"Open shell interaction" can be classified when $-V(r_c) > G(r_c)$ to give a negative value of $H(r_c)$, with $G(r_c)/\rho(r_c) < 1$, but > 1 for closed shell interaction,[42 c] which is shown in Table S4 (ESI†). In case of BCP (C2-Si9) and BCP(C4-Si8), low value of $(\rho(r_c))$ (0.139) and positive value of $(\nabla^2\rho(r_c))$ (0.346) have observed and in case of both of them, $-V(r_c) > G(r_c)$ which gives negative value of $H(r_c)$ (-0.094) with $G(r_c)/\rho(r_c)$ (1.294) > 1. This clearly indicates that, for **ppC-4** system, these two BCPs have closed shell type of interaction.

As it can also be seen in Table S3 (ESI†) that, at BCP (Si2-C4) and BCP (Si3-C5) for **ppC-3**, negative value of $V(r_c)$ predominates over the positive value of $G(r_c)$, which gives overall $H(r_c)$ a negative value (-0.09), with $G(r_c)/\rho(r_c)$ (1.254) > 1. Moreover, for these two BCPs, $(\rho(r_c))$ is low (0.314) with positive $(\nabla^2\rho(r_c))$ (0.314), which actually establish the "closed shell type of bonding interaction". All these bonding analyses clearly indicate the pentacoordinate nature of carbon in these four systems.

We have analyzed the bonding nature of all four ppC systems (**ppC-1**, **ppC-2**, **ppC-3**, and **ppC-4**) further using the Adaptive Natural Density Partitioning (AdNDP) approach[43,44], which is shown in Fig. 4. In case of **ppC-1** system, we have found two 3c-2e π bonds with occupation number (ON) of 1.954 $|e|$ each and two 4c-2e σ bonds with occupation number (ON) of 1.937 $|e|$ each. In case of **ppC-2** system, there are two 3c-2e π bonds with occupation number (ON) of 1.960 $|e|$ each and two 4c-2e σ bonds with occupation number (ON) of 1.944 $|e|$ each. For **ppC-3** system, one 3c-2e σ bond is found with an ON of 1.983 $|e|$, two 3c-2e σ bonds with an ON of 1.969 $|e|$ (Figs. 4 b and 4 c), two 3c-2e σ bonds with an ON of 1.963 $|e|$ (Figs. 4 d and 4 e), one 3c-2e σ bond with an ON of 1.929 $|e|$ (Fig. 4f), two 3c-2e π bonds with an ON of 1.912 $|e|$ (Figs. 4 g and 4 h) each. In case of **ppC-4** system, there are total five 3c-2e bonds. Out of these five bonds, two 3c-2e π bonds have ON of 1.934 $|e|$ (Figs. 4 a and 4 b), one 3c-2e σ bond with an ON of 1.912 $|e|$ (Fig. 4 c), one 3c-2e π bond with ON of 1.901 $|e|$ (Fig. 4 d), and one 3c-2e σ bond with ON of 1.901 $|e|$ (Fig. 4e). Overall, one could conclude that all ppC systems examined here exhibit dual aromaticity (σ and π).

To estimate the bond order between two atoms, including the orbital overlap, the Mayer bond order (MBO)[45] has been used as a quantum mechanical tool. We have analyzed the MBO using Multiwfn program[46] for the four ppC systems at the PBE0-D3/def2-TZVP level of theory (for details please see ESI†). In case of $[BeC_7H_2]^{2+}$ (**ppC-1**), MBO of C1-Be10 is 0.357, while in case of **ppC-2**, the value is 0.124. For **ppC-3** (C1-Be10) and **ppC-4** (C5-Mg10), the MBO values are 0.917 and 0.516, respectively (see ESI†). From these results, we can conclude that, for **ppC-1**, **ppC-2**, **ppC-4**, there exist partial single bond character and for **ppC-3**, the bond is intermediate between a double bond and a single bond.

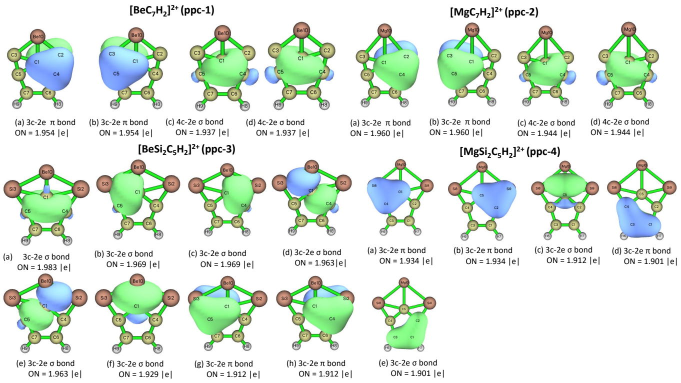

Fig. 4 AdNDP bonding analysis of ppC isomers obtained at the PBE0-D3/def2-TZVP level of theory.

At the PBE0-D3/def2-TZVP level, the four different ppC systems (**ppC-1** to **ppC-4**) are 63.95, 52.46, 15.03, and 14.77 kcal mol^{-1} above the corresponding global minimum geometries, respectively (see Fig. 1). All the ppC geometries are found to be local minima. Thus, it is better to check the kinetic stability of these molecules. To achieve this goal, we have carried out ab initio MD simulations using the atom-centered density matrix propagation (ADMP) method[47] at 1 atm pressure and 298 K for 1000 fs. In Fig. 5, we have depicted the evolution of energy (in a.u) for each ppC structure up to 1000 fs. The oscillation in energy is quite steady and the geometry is not breaking apart, which suggests that these molecules are kinetically stable.

Binding energies have been computed to analyze the strength of the ptC and ppC systems in $[XC_7H_2]^{+/2+}$ and its derivatives. They are shown in Table 1 at four different levels and they reflect the following trend: (i) as the ionic radii increases down the group, binding energy decreases; (ii) due to higher-charge (+2), alkali earth metal ions binding energies are higher than alkali metal ions; (iii) within their respective groups, the smaller ions, Li^+ and Be^{2+} exhibit higher stabilization of ptC and ppC atom, respectively, than the larger ions; (iv) with empirical dispersion corrections, the binding energies are slightly higher for all cases, however, the overall changes are not drastic; and (v) whether we use def2-TZVP or 6-311++G(2d,2p) basis set, the change in binding energy values are moderately small.

As far as experimental viability of these ppC molecules are concerned, it is noted here that dications are, in general, hard to synthesize and isolate compared to dianions.[48] Unfortunately, all the dianions/anions of these ppC molecules either turned out to be a second-order or third-order saddle-points.†Therefore, we turned our attention to neutralizing them using counter ions such as Cl^- or OH^-. In these cases, we found that the counter ions stabi-

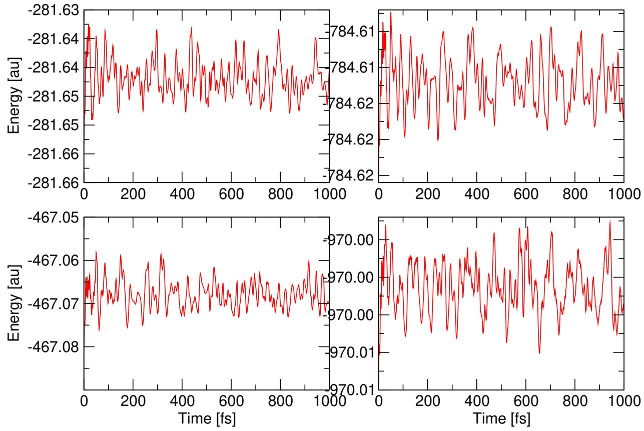

Fig. 5 Energy evolution of ppC structures at 298 K for 1000 fs obtained from the ab initio molecular dynamics simulations carried out at the TPSSh-D3BJ/6-311++G(2d,2p) level.

lize the ptC moiety through non-bonded interactions and there is no ppC in these structures. Therefore, we note that it will be a challenging task to synthesize and isolate these molecules as dications.

In summary, inclusion compounds using alkali and alkaline earth metal ions with the ptC isomer of C_7H_2 and $Si_2C_5H_2$ are theoretically identified containing ptC and ppC atoms. Among the alkali metal ions, Li^+ stabilizes the ptC-moiety better than other ions in the group. As far as alkali earth metal ions are concerned, Be^{2+} stabilizes the isomer more with a binding energy of -9.68 eV (**ppC-1**). The binding energy for **ppC-3** was found to be higher ($\sim$ 10.42 eV) than **ppC-1**, which could be due to strong 3c-2e σ bonds when silicon atoms are involved. Despite the fact that beryllium is toxic, it could be effectively used to stabilize the ptC atom and eventually making a ppC atom. Like Be^{2+} ion, the Mg^{2+} ion also makes pentacoordination with the carbon atom and thus converts from a ptC atom into a ppC atom (**ppC-2** and **ppC-4**) in both C_7H_2 and $Si_2C_5H_2$, and these ppC-moieties are also found to be minima at all levels. The binding energies for $[MgC_7H_2]^{2+}$ $[MgSi_2C_5H_2]^{2+}$ compounds are almost half of what it had been estimated for Be^{2+}-compounds. However, it is worth mentioning here that magnesium compounds are easy to make considering the safety aspects in the laboratory than beryllium compounds.

Conflicts of interest

This project is conceived by VST. Electronic structure calculations are done by all the authors. Results are analyzed and discussed by all the authors. The original draft is written by VST and reviewed by AA. The authors declare no competing financial interest and no further conflicts to declare.

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