How to Accomplish a Square C(N)₄ Substructure of the Planar Tetracoordinate Carbon

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ABSTRACT: Nitrogen-based groups are usually not used as ligands to coordinate to the ptC atom. However, here we reported only nitrogen-based ligands to accomplish a theoretically successful square planar C(N)₄ substructure. The first difficulty in accomplishing a square ptC(N)₄ substructure is to conquer the tremendous strain from the planar to tetrahedral arrangements, and the second is to restrict it in a suitable system with the right symmetry. We designed several neutral molecules with the square ptC(N)₄ substructures, and the molecules were studied using the density functional theory method at the B3LYP/6-311++G(3df,3pd) and TPSSh/6-311++G(3df,3pd) level of theory. The results of this work show that the molecules are all real minima on the potential energy surface and successfully achieved the square ptC(N)₄ substructure in the theoretical method. The group orbitals among the square ptC(N)₄ arrangement in the D₄h symmetry have been discussed and used to investigate the bonding interactions among all atoms in the square ptC(N)₄ substructure. Usually, the ptC systems have 18 valence electrons, but the present ptC systems mentioned in this work have 24 valence electrons, which is unusual for ptC.

INTRODUCTION

The planar hypercoordinate carbon (phC), carbon, and its more than three donor atoms in the same plane, have been studied around five decades.¹ Among the phCs, most studies are on the planar tetracoordinate carbon (ptC). How could a ptC configuration be successfully achieved? In 1970, Hoffmann, Alder, and Wilcox suggested a strategy² to remove the 2pₐ lone pair of ptCs by σ-acceptor substituents or by aromatic delocalization and enhancing their σ electron-deficient bonding by σ-donors for stabilizing ptCs electronically. From then on, numerous ptCs have been reported theoretically and experimentally.³ According to the above strategy, most of the substituents attaching to ptCs are the electropositive and electron-deficient element-based groups, such as B⁺, Si⁺, Li⁺, and C⁺[x] and metal elements.⁴ Because nitrogen is an electron-rich element and more electronegative, it is a σ-acceptor not a σ-donor when bonding to ptC. Thus, nitrogen-based groups used as ligands to coordinate to the ptC atom are very rare. Nitrogen with metal Li as donor atoms to achieve the C(N)Lᵢ₂(ptC) substructure in a system of aromatic delocalization has been reported.⁵ To date, to our knowledge, only nitrogen-based groups as ligands to achieve a successful ptC, described as ptC(N)ₓ, have never been reported.

As we know, CH₄²⁺ is the simplest ptC species; the perpendicular carbon 2pₐ-orbitals in CH₄²⁺ are vacant, rather than being occupied. Based on the bonding model of CH₄²⁺, to remove the 2pₐ-π lone-pair electrons at the highest occupied molecular orbital (HOMO) of the ptC species using electron-deficient boron atoms as donor atoms and to use the "mechanical" design of alkaplane molecules,⁶ which restrict the ptC candidates in the strain cages, a family of neutral compounds called boraplanes was reported.³b Wang and Schleyer⁵a used two anionic −BH₂− groups to compensate the formal double-positive charges on the ptC substructure, such as two positive charges in CH₂⁺; the strategy was called the "charge-compensation" principle. They used the strategy to accomplish the more challenging ptC(C)₄ arrangements.⁶ In 2009, Wang reported several molecules containing a perfectly ptC(C)₄ substructure using the "charge compensation" and the "mechanical" strategies and stabilized the molecules in two ways: by using the electron delocalization in a three-dimensional π-conjugated system electronically and the strain of a rigid cage framework mechanically.⁵

Ordinarily, the "charge-compensation" and the "mechanical" strategies are useful approaches to achieve the ptC arrangements. However, the charge compensation by using the electron-deficient groups, such as BH₂, would be unworkable to achieve a ptC(N)₄ substructure. Because nitrogen is a more electronegative element and the central ptC atom is surrounded with four nitrogen atoms, removal of electrons from nitrogen or the central ptC atom would be very difficult.

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Therefore, to achieve a ptC(N)₄ substructure, the “mechanical” strategy by using the large strain of a very rigid cage framework to stabilize the ptC(N)₄ substructure is particularly important.

As we know, isopagodane⁹ is a large-strain molecule with a very rigid cage framework. Because all structures in Figure 1 have two C⁴−C′⁴ bonds (Figure 1), the rigidities of their cage frameworks are more than those of the alkaplanes or the boraplanes,⁶ which have been reported to achieve ptC substructures. When a ptC(N)₄ substructure is placed in the center of isopagodane, the cage framework may struggle to conquer the strain from the planar to tetrahedral arrangements of C(N)₄. Based on the considerations, we placed a planar C(N)₄ substructure to take the place of the four carbon atoms in the center of isopagodane and found that isopagodane is a proper system with the right symmetry to achieve a square planar C(N)₄ substructure (abbreviated to sq-ptC(N)₄). Following this thought, four molecules 1–4 (Figure 1), derivatives of isopagodane, were constructed to accomplish the sq-ptC(N)₄ substructures or not.

## RESULTS AND DISCUSSION

**Bonding Interactions among the ptC Atom and Four Nitrogen Atoms in its Perimeter.** The molecules 1–4 are converged to the D₂d symmetry after the optimizations at the B3LYP/6-311+G(3df,3pd) and the TPSSH/6-311++G(3df,3pd)-D3(BJ) levels of theory (Figure 1). Thus, five atoms of C(N)₄, the central carbon, and four nitrogen atoms in its perimeter, form a perfectly square planar arrangement and all angles ζNCN = 90°. The smallest vibrational frequencies (Table 1) of 1, 2, and 3 are 177, 109, and 100 cm⁻¹ at the B3LYP/6-311+G(3df,3pd) level of theory and 169, 66, and 94 cm⁻¹ at the TPSSH/6-311+G(2dfp)-D3(BJ) level of theory, respectively; 4 has two imaginary vibrational frequencies at the two levels of theory. Therefore, all 1, 2, and 3 are true minima on the potential energy hypersurface, but 4 is not a stable molecule on the potential energy surface.

Boldyrev and Simons⁶ discussed the MOs of ptC with a D₂d structure. However, the systems containing the sq-ptC(N)₄ substructure studied in this work are all of the D₂d symmetry, which are different from the ptCs studied by Boldyrev and Simons.⁶ The D₂d irreps of all orbitals are different from those of the D₂d symmetry, and the shapes of the ligand group orbitals (LGO) are also different. Therefore, we studied the bonding interactions among the sq-ptC(N)₄ substructure.

Initially, we constructed the LGOs of the four nitrogen atoms in the perimeter using the D₂d irrep. The LGOs could be classified within the point group D₂d of the whole molecule, and the valence orbitals of the ptC atom also could be classified. The MO is then constructed by allowing interactions different from those of the D₂d symmetry, and the shapes of the ligand group orbitals (LGO) are also different. Therefore, we studied the bonding interactions among the sq-ptC(N)₄ substructure.

![Figure 1. Geometries of 1→4 with key parameters at the B3LYP/6-311+G(3df,3pd) and the TPSSH/6-311++G(3df,3pd)-D3(BJ) (in parentheses) levels of theory.](https://dx.doi.org/10.1021/acsomega.0c04876)

| molecule | 1 | 2 | 3 | 4 |
|----------|---|---|---|---|
| ES       | 1'A₁ | 1'A₁ | 1'A₁ | 1'A₁ |
| point group | D₂d | D₂d | D₂d | D₂d |
| freq/cm⁻¹ | 177 | 109 | 100 | 243 |
| EHOMO/eV  | −2.68(b₁) | −2.89(b₁) | −2.93(b₁) | −4.32(b₁) |
| ELUMO/eV  | −2.08(a₁) | −2.05(a₁) | −2.21(a₁) | −2.51(a₁) |
| ΔELUMO/eV | 0.60 | 0.84 | 0.72 | 1.81 |
| Q (ptC-2s) | 0.65 | 0.64 | 0.65 | 0.69 |
| Q (ptC-2p₁) | 1.60 | 1.61 | 1.66 | 1.71 |
| Q (ptC-2p₂) | 0.72 | 0.71 | 0.71 | 0.76 |
| Q (ptC-2p₃) | 0.72 | 0.71 | 0.71 | 0.76 |

Table 1. Electronic States (ES); Point Groups; the Smallest Frequencies Freq (in cm⁻¹); Energies of HOMO and LUMO; Occupations Q of Valence Orbitals 2s, 2p₁, 2p₂, and 2p₃ of the ptC Atoms in 1→4 at the B3LYP/6-311++G(3df,3pd) Level of Theory

Symmetry of HOMO and LUMO is given in parentheses. ΔELUMO is the energy gap between HOMO and LUMO.
Various nitrogen atoms are 0.62, 0.51, 0.45, and 0.54 at the TPSSh/6-311++G(3df,3pd) level of theory. The planar C(N)4 arrangement in the center of the isopagodane-like structure is perfectly square. Usually, the planar C(N)4 arrangement in the center of the isopagodane-like structure is perfectly square. Usually, the planar C(N)4 arrangement in the center of the isopagodane-like structure is perfectly square. Usually, the planar C(N)4 arrangement in the center of the isopagodane-like structure is perfectly square. Usually, Figure 3. Frontier orbitals of 1−4 (MO contour values are 0.05 (e/Å²)) at the B3LYP/6-311++G(3df,3pd) level of theory.

Additionally, according to the group orbitals of the sq-ptC(N)4 substructure (Figure 2), such as 1a1 and 1b2 group orbitals, there must be net bonding interactions among the four atoms in the perimeter in the sq-ptC(N)4 arrangement. Total Wiberg bond indexes of every nitrogen atom with other three nitrogen atoms are 0.62, 0.51, 0.45, and 0.54 (Table 2) at the B3LYP/6-311++G(3df,3pd) level of theory and 0.61, 0.51, 0.45, and 0.54 at the TPSSh/6-311++G(3df,3pd)-D3(BJ) level of theory of 1−4, respectively, which make the sq-ptC(N)4 arrangement more rigid than expected. This is one of reasons to accomplish the sq-ptC(N)4 substructure in a neutral molecule.

Actually, the MOs in Figure 2 are not real MOs of the whole molecule; they could be considered as group orbitals of the sq-ptC(N)4 substructure. These group orbitals might interact with valence orbitals of other atoms except the atoms in the sq-ptC(N)4 substructure to form real MOs. However, there should be a number of real MOs predominantly possessing the group orbitals of the sq-ptC(N)4 substructure. For example, the HOMO and lowest unoccupied molecular orbital (LUMO) of 1−4 predominantly possess the b2 and a1 group orbitals, respectively (Figure 3).

**Accomplishing the sq-ptC(N)4 Substructure.** To accomplish a sq-ptC(N)4 substructure, except to conquer the huge strain from the planar to tetrahedral configuration, the importance is to constrain a sq-ptC(N)4 arrangement in a proper system with the right symmetry. We have found the right system: an isopagodane-like structure with D2h symmetry. In this system, the planar C(N)4 arrangement in the center of the isopagodane-like structure is perfectly square. Usually, the “charge-compensation” strategy and the “mechanical” strategy are used to accomplish a ptC substructure. As we know, nitrogen is a more electronegative element and the central ptC atom is surrounded by four nitrogen atoms in the sq-ptC(N)4 arrangement; removal of electrons from nitrogen or central ptC atom would be very difficult. Thus, the “charge-compensation” strategy is not suitable for accomplishing a sq-ptC(N)4 substructure. Therefore, the “mechanical” strategy using the large strain of a very rigid cage framework to stabilize the sq-ptC(N)4 substructure is particularly important.

Verification of the “mechanical” strategy is important for achieving the sq-ptC(N)4 substructure, so we computed the planar C(N)4 with the D2h symmetry at the B3LYP/6-311++G(3df,3pd) level of theory. The planar C(N)4 with the D2h symmetry has two imaginary frequencies, which is not a minimum. The result described above reveals that the “mechanical” strategy is important for achieving the sq-ptC(N)4 substructure.

Using the “mechanical” strategy, the more rigid molecules 1−3 (Figure 1) were proposed as the candidates to accomplish the neutral molecules with the sq-ptC(N)4 substructures and singlet states. Molecules 1−3 have been studied by using the DFT method at the B3LYP/6-311++G(3df,3pd) and TPSSh/6-311++G(3df,3pd)-D3(BJ) levels of theory. The computa-
tional results show the rigidity around the sq-ptC(N)_4 substructure in molecules 1–3 than expected. In the structures of 1–3, the lengths of N2–C3 (see the labels in Figure 1, the same below) and their equivalent bonds, 1.452, 1.455, and 1.439 Å at the B3LYP/6-311++G(3df,3pd) level of theory and 1.448, 1.455, and 1.440 Å at the TPSSh/6-311++G(3df,3pd)-D3(BJ) level of theory for 1, 2, and 3, respectively, are shorter than that of the N–C bond in methyamine CH3NH2 (1.471 Å).10 Thus, the “mechanical” strength or rigidity of 1–3 is strong; the tetrahedral substructures of C(N)_4 in 1–3 are less stable than the planar one, so 1–3 are all stable molecules on the potential energy surfaces.

Molecule 4 (Figure 1, a isomer of 2) is another example which shows the importance of the rigidity in the sq-ptC(N)_4 substructure. The longer C3–Si4, Si4–Si4′, and their equivalent bonds result in the more loose structure of 4 and the longer C1–N2 than those in 1–3 (Figure 1); the tetrahedral substructure of C(N)_4 in 4 is more stable than the planar one; therefore, 4 is not a stable molecule on the potential energy surface. According to the computational result, the difference in energy between the planar and the tetrahedral substructures of C(N)_4 in 4 (the smallest vibrational frequency of 4 with the tetrahedral substructure of C(N)_4 is 189 cm⁻¹) is 101 kJ·mol⁻¹ at the B3LYP/6-311G(d,p) level of theory.

According to the discussion above, the “mechanical” strategy to accomplish the sq-ptC(N)_4 arrangement should include the following considerations: (1) improving the bonding interactions among the five atoms of the sq-ptC(N)_4, (2) strengthening N2–C3 and its equivalent bonds, and (3) shortening C4–C4′ and its equivalent bonds. Therefore, the greater “mechanical” rigidity and the lower destabilized planar geometries of C(N)_4 are the main reasons for accomplishing the sq-ptC(N)_4 substructure in a neutral molecule.

Characterization of C–N and Other Bonds. In order to study unusual bonding features of the sq-ptC(N)_4 substructure, the quantum theory of atoms in molecules (QTAM)11,12 was used in this work. In QTAM, the CPs and their properties are important for studying the bond characterization. When n, b, r, and c are used to express numbers of nuclear, bond, ring, and cage CPs, they satisfied the Poincare–Hopf relationship:12 n = b + r + c = 1. All CPs of 1–4 have been searched by using the Multiwfn program.17 They all satisfied the Poincare–Hopf relationship (Figure 4). The properties of CPs, electron densities ρ(r_c), Laplacian of electron densities V^2ρ(r_c), total electronic energy densities E_b(r_c), and the ellipticity ε of all bonds in the cage skeletons of 1–4 were calculated at the TPSSh/6-311++G(3df,3pd)-D3(BJ) level of theory (Table 3).

In the extraordinary bonding features of the sq-ptC(N)_4 substructure of 1–4, all C1–N2 bonds are typical covalent bonds based on the classification,13 but C3–Si5 in 2, C3–Ge5 in 3, and C3–Si4 in 4 are strongly polar bonds on the basis of V^2ρ(r_c)s, which corresponds to the NBO charges in Table 2. Except for the above strongly polar bonds, all other bonds in the cage skeletons of 1–4 are typical covalent bonds based on the classification.13 Moreover, the ellipticities ε (Table 3) reveal that all C1–N2 bonds have large π bonding interactions. Additionally, N2–C3 and its equivalent bonds in 2 and 3 have large π bonding interactions.

There are some weak interactions between C1 and C4 (or its equivalent atoms) in 1–3, but 4 has no weak interactions (Figure 4). The CPs’ properties between the C1 and C4, the

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c04876)  
Figure 4. Critical points and the bond paths of 1–4. Balls are atoms. Small spheres of orange, yellow, and green correspond to bond, ring, cage CPs, respectively. Brown lines denote bond paths.

| molecule | bond | ρ(r_c) | V^2ρ(r_c) | E_b(r_c) | ε |
|----------|------|-------|-----------|----------|---|
| 1        | C1–N2 | 0.233 | −0.358   | −0.259   | 0.564 |
| N2–C3    | 0.260 | −0.691 | −0.306   | 0.062   |
| C3–C4    | 0.225 | −0.460 | −0.166   | 0.046   |
| C3–C5    | 0.238 | −0.526 | −0.189   | 0.030   |
| C4–C4′   | 0.221 | −0.433 | −0.160   | 0.010   |
| C1–C4′   | 0.052 | 0.130 | −0.009   | 7.680   |
| C1–N2    | 0.230 | −0.338 | −0.255   | 0.648   |
| N2–C3    | 0.255 | −0.615 | −0.290   | 0.140   |
| C3–C4    | 0.222 | −0.442 | −0.163   | 0.077   |
| C3–Si5   | 0.116 | 0.141 | −0.073   | 0.079   |
| C4–C4′   | 0.206 | −0.377 | −0.140   | 0.002   |
| C1–C4′   | 0.053 | 0.123 | −0.009   | 65.82   |
| C1–N2    | 0.228 | −0.335 | −0.250   | 0.619   |
| N2–C3    | 0.265 | −0.670 | −0.313   | 0.130   |
| C3–C4    | 0.226 | −0.460 | −0.168   | 0.072   |
| C3–Ge5   | 0.119 | −0.014 | −0.070   | 0.038   |
| C4–C4′   | 0.204 | −0.367 | −0.137   | 0.004   |
| C1–C4′   | 0.054 | 0.123 | −0.010   | 101.1   |
| C1–N2    | 0.216 | −0.321 | −0.210   | 0.333   |
| N2–C3    | 0.272 | −0.719 | −0.331   | 0.099   |
| C3–Si4   | 0.107 | 0.099 | −0.066   | 0.109   |
| C3–C5    | 0.230 | −0.485 | −0.177   | 0.042   |
| Si4–Si4′ | 0.098 | −0.170 | −0.053   | 0.023   |

The ellipticities ε of BCPs of Some Bonds in 1–4 at the TPSSh/6-311+G(3df,3pd)-D3(BJ) Level of Theory

*Labels of atoms of 1–4 are given in Figure 1. *Weak interactions are only in 1–3.
$ρ(r_j)$s (0.052−0.054 au), the $E_1^s(r_j)$s (−0.009 to −0.010 au), and the $V^2ρ(r_j)$s (0.123−0.130 au) (Table 3) coincided with the typical weak interactions.14 The weak interactions may be one of the reasons for achieving the sq-ptC(N)$_4$ substructure.

**Simulations of IR Spectra.** To characterize the neutral molecules with the square ptC(N)$_4$ arrangements by IR or Raman spectroscopy in the future, the vibrational frequencies of 1−3 have been calculated at the B3LYP/6-311+G-(3df,3pd) level of theory. The reducible representation of vibrational frequencies of 1−3 are reduced on the basis of the $D_{2d}$ symmetry as follows

$$
\Gamma_{\text{vib}} = 17A_1\text{(IR/R)} + 12A_2 + 12B_1\text{(R)} + 18B_2\text{(IR/R)} + 29E\text{(IR/R)}
$$

of which $B_1$ is only Raman-active, and $A_1$, $B_2$, and $E$ are all infrared- and Raman-active. $A_2$ is neither infrared- nor Raman-active.

The vibrational frequencies of 1−3 at the B3LYP/6-311+G-(3df,3pd) level of theory have been used to simulate the IR spectra (Figure 5). 1−3 with the square ptC(N)$_4$ substructures could be characterized using the simulated IR spectra.

For the future experimental characterization, several important vibrational bands of 1−3 are discussed here. For 1, (i) the strongest IR spectroscopic signal is at 2874 cm$^{-1}$, the asymmetric C4−H stretching vibrational mode; (ii) two strong vibrational modes are at frequencies of 2986 cm$^{-1}$, the symmetric C3−H stretching vibrational mode, and 2982 cm$^{-1}$, the asymmetric C3−H stretching vibrational mode, respectively; (iii) four intermediate modes are present at frequencies of 641 cm$^{-1}$, the C1 up−down wagging vibrational mode, 746 cm$^{-1}$, the C4−C4′ up−down wagging vibrational mode, 807 cm$^{-1}$, the C5−H bending vibrational mode, and 3028 cm$^{-1}$, the asymmetric C5−H stretching vibrational mode, respectively. For 2, (i) the strongest IR signal appears at 2862 cm$^{-1}$, the asymmetric C4−H stretching vibrational mode; (ii) three strong modes are at frequencies around 946 cm$^{-1}$, the Si5−H bending vibrational mode, 2145 cm$^{-1}$, the asymmetric Si5−H stretching vibrational mode, and 3008 cm$^{-1}$, the asymmetric C3−H stretching vibrational mode, respectively; (iii) three intermediate modes appear at frequencies around 775 cm$^{-1}$, the C1 up−down wagging vibrational mode, 797 cm$^{-1}$, the Si5−H wagging vibrational mode, and 2215 cm$^{-1}$, the asymmetric Si5−H stretching vibrational mode, respectively. For 3, (i) the strongest IR signal is at 2015 cm$^{-1}$, the symmetric Ge5−H stretching vibrational mode; (ii) two strong frequencies are at around 2852 cm$^{-1}$, the asymmetric C4−H stretching vibrational mode, and 3013 cm$^{-1}$, the asymmetric C3−H stretching vibrational mode, respectively; (iii) three vibrational intermediate modes are at frequencies around 780 cm$^{-1}$, the C1 up−down wagging vibrational mode, 845 cm$^{-1}$, the Ge5−H bending vibrational mode, and 2090 cm$^{-1}$, the asymmetric Ge5−H stretching vibrational mode, respectively.

**CONCLUSIONS**

As an electron-rich and more electronegative element, nitrogen-based groups are usually not used as ligands to coordinate with the ptC atom. Whereas, here, we reported the successfully theoretical ptCs only using nitrogen-based ligands. The singlet neutral molecules 1−3 with square planar C(N)$_4$ substructures have been studied at the B3LYP/6-311+G(3df,3pd) and the TPSSh/6-311++G(3df, 3pd)-D3(BJ) levels of theory. Usually, the ptC systems have 18 valence electrons, but the present ptC systems mentioned in this work have 24 valence electrons, which is unusual for ptC. The conclusions of this work could be summarized as follows:

1. We proposed the MOs of the sq-ptC(N)$_4$ arrangement at the $D_{2d}$ symmetry according to the method of deriving the MOs of the planar methane $^{2a,2i}$ and used the results to study the bonding interactions among the sq-ptC(N)$_4$ substructures. The computed Frontier orbitals are in accordance with our proposed MOs. The characterization of the HOMOs and the low Koopmans’ ionization potentials of 1−3 have been discussed based on our proposed MOs.

2. The “charge-compensation” strategy not suitable for the sq-ptC(N)$_4$ has been discussed. The “mechanical” strategy is important to design the neutral molecule with the sq-ptC(N)$_4$ substructure. Therefore, through the large strain of a very rigid cage framework to stabilize the ptC(N)$_4$ substructure is a key way to achieve the sq-ptC(N)$_4$ substructure.

3. The nature of the extraordinary bonding interactions among the sq-ptC(N)$_4$ arrangements has been discussed using the quantum theory of atoms in molecules. The
C–N bonds in the nonclassical structures of the sq-pC(N)4 arrangement are typical covalent bonds with some π bonding interactions.

(4) The computational vibrational frequencies of 1–3 are used to simulate their IR spectra (Figure 5). 1–3 with the square ptC(N)4 substructures could be characterized using the simulated IR spectra.

The conclusions of this work could be used to accomplish more planar polycordinate carbon or other elements.

**COMPUTATIONAL DETAILS**

Because DFT is the preferred method for investigating species with ptC atoms, the B3LYP hybrid density functionals and TPSSh hybrid functional using the TPSS functionals with Grimme’s D3 dispersion correction with the damping function were used in this study. The basis sets used in this work are 6-311G(d,p), 6-311+G(2df,p), and 6-311++G(3df,3pd). The full geometry optimizations and frequencies’ computations of all systems reported in this paper were run at the B3LYP/6-311G(d,p) level of theory to characterize structures first, and then, all geometries were reoptimized at the B3LYP/6-311G(d,p) level of theory and the TPSSh/6-311++G(3df,3pd)-D3(Bj) levels of theory. Based on the reoptimized geometries, frequencies and natural bond orbital analyses also recomputed at the B3LYP/6-311+G(3df,3pd)-D3(Bj) level of theory. To understand the interactions between valence orbitals of sq-pC(N)4 and other atoms in the molecules, the net charges, Wiberg bond indexes, and species with ptC atoms, the B3LYP hybrid density functional17 with Grimme’s D3 dispersion correction with the damping function were used in this study. The basis sets used in this work are 6-311G(dp), 6-311+G(2df,p), and 6-311++G(3df,3pd). The full geometry optimizations and frequencies’ computations of all systems reported in this paper were run at the B3LYP/6-311G(dp) level of theory to characterize structures first, and then, all geometries were reoptimized at the B3LYP/6-311G(dp) level of theory and the TPSSh/6-311++G(3df,3pd)-D3(Bj) levels of theory. Based on the reoptimized geometries, frequencies and natural bond orbital analyses also recomputed at the B3LYP/6-311+G(3df,3pd)-D3(Bj) level of theory. The critical points and their properties were also calculated using the net charges, Wiberg bond indexes, and species with ptC atoms as analogues of planar methane. Chem. Soc. Rev. 1999, 28, 367–371. (d) Keese, R. Carbon Flatland: Planar Tetracordinate Carbon and Fenesranes. Chem. Rev. 2006, 106, 4787–4808. (e) Merino, G.; Méndez-Rojas, M. A.; Vela, A.; Heine, T. Recent advances in planar tetracordinate carbon chemistry. J. Comput. Chem. 2007, 28, 362–372. (f) McGrath, M. P.; Radom, L. Alkaphanes: A Class of Neutral Hydrocarbons Containing a Potentially Planar Tetracordinate Carbon. J. Am. Chem. Soc. 1993, 115, 3320–3321. (g) Yañez, O.; Vázquez-Espinal, A.; Báez-Greze, R.; Rabanal-León, W. A.; Osorio, E.; Ruiz, L.; Tunado, W. Carbon rings decorated with group 14 elements: new aromatic clusters containing planar tetracordinate carbon atom as analogues of planar methane. Chem. Soc. Rev. 2019, 43, 6781–6785. (i) Thirumooorthy, K.; Thimmakondu, V. S. Flat crown ethers with planar tetracordinate carbon atoms. Int. J. Quantum Chem. 2020, No. e26479. (j) Thirumooorthy, K.; Cooksy, A. L.; Thimmakondu, V. S. Si3C2H2 isomers - search algorithms versus chemical intuition. Phys. Chem. Chem. Phys. 2020, 22, 5865–5872. (k) Thimmakondu, V. S.; Thirumooorthy, K. Si3C2H2 isomers with a planar tetracordinate carbon or silicon atom(s). Comput. Theor. Chem. 2019, 1157, 40–46. (l) Thirumooorthy, K.; Karton, A.; Thimmakondu, V. S. From High-Energy C–H Isomers with A Planar Tetracordinate Carbon Atom to An Experimentally Known Carbene. J. Phys. Chem. A 2018, 122, 9034–9064. (m) Xu, J.; Zhang, X.; Yu, S.; Ding, Y.-h.; Bowen, K. H. Identifying the Hydrogenated Planar Tetracordinate Carbon: A Combined Experimental and Theoretical Study of CALH and CALH–. J. Phys. Chem. Lett. 2017, 8, 2263–2267. (n) Ebner, F.; Greb, L. Calix[4] pyrrole Hydridosilicate: The Elusive Planar Tetracordinate Silicon Imparts Striking Stability to Its Anionic Silicon Hydride. J. Am. Chem. Soc. 2018, 140, 17409–17412. (2) (a) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. Planar tetracordinate carbon. J. Am. Chem. Soc. 1970, 92, 4992–4993. (b) Hoffmann, R. The theoretical design of novel stabilized systems. Pure Appl. Chem. 1971, 28, 181–194. (3) (a) Li, J.; Hoffman, R. Ca3Al2Si6: An inorganic structure analogous to but not isoelectronic with polyacene. J. Phys. Chem. 1988, 92, 887–893. (b) Wang, Z.-X.; Schleyer, P. V. R. A new strategy to achieve perfectly planar carbon tetracordination. J. Am. Chem. Soc. 2004, 126, 13837–13845.
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