Structural and magnetic properties of small symmetrical and asymmetrical sized fullerene dimers

Sandeep Kaur, Amrish Sharma, Hitesh Sharma and Isha Mudahar

1 Department of Physics, Punjabi University, Patiala, India
2 Department of Applied Sciences, IKG Punjab Technical University, Kapurthala, India
3 Department of Basic and Applied Sciences, Punjabi University, Patiala, India
4 Author to whom any correspondence should be addressed.
E-mail: sandeep_rs16@pbi.ac.in, amrish99@gmail.com, hitesh@ptu.ac.in and dr.ishamudahar@gmail.com

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Abstract

Magnetism in carbon nanostructures is of high scientific interest, which could lead to novel magnetic materials. The magnetic properties of symmetrical and asymmetrical sized small fullerene dimers ($C_n$ for $n \leq 50$) have been investigated using spin polarized density functional theory. The interaction energies depict that small fullerene cages form stable dimer structures and symmetrical sized fullerene dimers are found more stable than asymmetrical sized dimers. The dimerization of fullerene cages in different modes leads to change in their magnetic properties. The non-magnetic fullerene cages become magnetic after formation of dimer ($C_{20}-C_{20}, C_{24}-C_{24}, C_{32}-C_{32}, C_{40}-C_{40}, C_{20}-C_{24}, C_{40}-C_{44}$ and $C_{44}-C_{50}$), whereas the magnetism of magnetic fullerenes is enhanced or lowered after dimerization ($C_{28}-C_{28}, C_{36}-C_{36}, C_{24}-C_{28}, C_{28}-C_{32}, C_{32}-C_{36}$ and $C_{36}-C_{40}$). The individual cages of dimer structures show ferromagnetic interactions amongst them and resultant magnetic moment strongly depends on the type of inter-connecting bonds. The magnetism may also be explained based on distortion of carbon cages and change in the electron density of states in dimer configuration. The calculations presented show strong possibility of experimental synthesis of small fullerene based magnetic dimers.

1. Introduction

The non-IPR (isolated pentagon rule) fullerenes or small fullerenes ($C_n$, $n < 60$) are interesting to study as they exhibit significant structural, electronic and magnetic properties, owing to their high curvature and fused adjacent pentagons [1–5]. The fullerenes have been widely studied in recent years and they have been explored for emerging potential applications in various areas of research such as nano-electronics, molecular devices, spin-electronics etc [6–8]. The applications of these fullerenes in the field of chemical catalysis [9] and pharmaceutics [10] have also become important by virtue of their particular properties like high chemical reactivity and small diameter.

In past, carbon based systems have become increasingly interesting due to their significant magnetic properties and they can be considered as a possible magnetic materials [11]. The origin of carbon based ferromagnetism has been reported due to the dislocations, vacancies and impurity atoms [12]. Till date, various attempts have been made to study the magnetic properties of small and larger fullerene cages [13–15]. Synthesis of ferromagnetic polymerized fullerenes has been treated by photo assisted oxidation, which show magnetization of order $10^{-3} \mu_B$ per $C_{60}$ [16]. There is an introduction of strong magnetism in the fullerene cages when they are endohedrally doped [14, 15, 17]. When the transition metals are encapsulated inside small carbon cages, the magnetic behavior of small cages is altered, which furnish a novel possibility to control the magnetic properties of carbon systems [17]. A theoretical and experimental study on carbon clusters show that their magnetic moment can be significantly enhanced by appropriately choosing their size, geometry and composition [18].
Apart from this, the fullerene cages also have ability to form dimer structures. The formation of C₆₀ dimer has been confirmed by mechanochemical synthesis experimentally using high speed vibration miling technique [19]. It is found that the stability of C₆₀ dimer is comparable to that of two C₆₀ molecules and the results are in agreement with theoretical calculations [20]. The dimer structures of fullerene cages can also be obtained through combination of either functionlized fullerenes or bifunctional cycloadditions to C₆₀ fullerene cages [21]. Thermal reactions of C₆₀/C₆₀O/C₆₀O₂ system lead to the formation of other dimeric fullerene derivatives such as C₁₂₀O₂ and C₁₉₉ [22]. The sulfur containing fullerene derivative C₁₁₂O has been formed by thermolysis of C₁₄₂O in the presence of sulfur [23]. Scanning tunneling microscopy and low-energy electron diffraction studies on polymerized C₆₀ studies reveal that annealing of the electron-beam-modified surfaces restores the fullerene lattice [24]. The heating of dimerized C₆₀ structures at high temperature restores the fullerenes to their pristine state [18, 24]. Some more experiments have been performed to produce the carbon bridged dimers like C₁₂₁ and C₁₂₂, which could be used as the basic units of fullerene chain structures [25–29].

The existence of C₆₀ dimer was also reported theoretically in metastable phases of MC₆₀ (M = K, Rb, Cs) [30] and the dimerization can occur in different phases like dumb-bell [31], peanut and capped nanotubes [32]. The conductance of the dimer can be tuned with doping as a result of which it become more versatile in molecular electronics [33]. The magnetic properties of C₆₀ dimer indicate the presence of strong magnetic field at cage centers of the dimer and the addition of C-bridges change the behavior of magnetic field. The fullerene dimers connected through BN hexagons alter the behavior of magnetic field inside the cages [34]. Ab initio calculations show that unpaired electrons of C₅₉ and C₅₉N are delocalized over C₆₀ molecule in C₅₉N–C₆₀, hetrodimer [33]. Nucleus independent chemical shift and nuclear magnetic resonance studies have reported the magnetic properties of C₅₉BN dimer and the results reveal that the dimerization of fullerene cages causes the major changes in magnetic properties [35]. C₃₆ cage can also form strong inter cage bonds and may be a hexavalent building block for fullerene compounds like dimers and polymers [36]. A computational study [37] on C₃₆ shows the dimerization of the cage, but the experimental existence of dimer is not yet confirmed. The endohedral derivatives of C₃₆ dimer are also expected to exist with their unique properties, making it useful for molecular devices [38]. However, no systematic study on small fullerene dimers has been reported yet. Because of the limited study on dimer structures, we are reporting for first time a systematic study on symmetrical and asymmetrical sized small fullerene dimers. The motivation for considering asymmetrical sized dimers comes from the experimental existence of carbon nanobuds, which are also a combination of asymmetrical sized nanostructures [39].

In the present work, we employed the first principle calculations on the dimers of small fullerene cages (Cₙₜ, n ≤ 50) based on density functional theory. Since C₆₀ dimer has significant properties, so it is interesting to study the interaction between small fullerene cages, which adds a new dimension to dimer properties.

2. Computational details

All the calculations were performed using Spanish Initiative for electronic simulation with thousands of atoms computational code, which is based on density functional theory [40]. The Perdew, Burke and Ernzerhof functional combined with double-ζ polarized basis set were used for the geometry optimizations [41]. Kleinman–Bylander form of non-local norm conserving pseudo potentials are used to describe core electrons [42] while numerical pseudoatomic orbitals of the Sankey–Niklewski type [43] are used to represent the valence electrons. The energy shift parameter is taken as 150 meV to describe the size of pseudoatomic orbitals. The fineness of a finite grid is defined by Mesh cut-off, whose value lie within the range 250 Ry. In order to obtain ground state properties, minimization of total energy of the system has been executed. The residual forces of the system are relaxed up to 0.004 eV/Ang. The energy eigen values have been plotted in order to give density of states (DOSs) spectra.

Test calculations were performed on small fullerenes (Cₙₜ, n < 60) to check the accuracy of our results. The geometrical parameters for small fullerenes are calculated and shown in table 1 and the results are in agreement with known experimental and theoretical results [3, 44]. We found that our calculated values follow the same pattern and are in agreement with a recent study which employs tight binding method [45]. Since our group has already study the carbon based systems so the parameters have been checked [17, 46, 47].

3. Results and discussion

3.1. Structural properties

We have optimized the ground state structures of symmetrical and asymmetrical sized small fullerene dimers using method described in computational details. The ground state geometries of small fullerene cages are considered to form the dimer structures. In dimeric pattern, the small carbon cages can connect through four
possible modes, i.e. (a) point–point mode forming a [1 + 1] dimer with C–C bond between two cages, (b) side–side mode forming a [2 + 2] dimer with a 2-fold bond, (c) face–face mode forming a [5 + 5] dimer with a 5-fold bond between two pentagonal rings, and (d) face–face mode forming a [6 + 6] dimer with a 6-fold bond between two hexagonal rings as shown in figure 1. Each dimer structure with these four configurations is optimized and the structure which has minimum total energy is the most stable isomer.

Table 1. Average diameter, average bond distance and HOMO-LUMO gaps of small fullerene cages.

| Fullerene Cage | Average bond distance (Å) | HOMO-LUMO gap (eV) |
|----------------|---------------------------|-------------------|
| C_{20}         | 4.14                      | 1.48              | 0.75              |
| C_{24}         | 4.83                      | 1.49              | 0.33              |
| C_{32}         | 5.25                      | 1.46              | 1.41              |
| C_{36}         | 5.60                      | 1.46              | 0.43              |

Figure 1. Four possible configurations through which fullerene cages connect (a) [1 + 1] point–point mode, (b) [2 + 2] side–side mode, (c) [5 + 5] face–face mode between two pentagons and (d) [6 + 6] face–face mode between two hexagons.

Table 2. Average diameter ($D_{av}$) and connecting bond length for symmetrical sized dimers.

| Dimer (C_n-C_m) | Connecting bond length (Å) | $D_{av}$ (Å) |
|----------------|-----------------------------|--------------|
|                | [1 + 1]                     | [2 + 2]      | [5 + 5] | [6 + 6] |
| C_{20}-C_{20}  | 1.51                        | 1.55         | 1.61 | —      |
| C_{24}-C_{24}  | 1.53                        | 1.56         | 1.58–1.75 | 1.59  |
| C_{28}-C_{28}  | 1.56                        | 1.58         | 1.58–1.60 | 1.62  |
| C_{32}-C_{32}  | 1.54                        | 1.56         | 1.58–1.62 | 1.59  |
| C_{36}-C_{36}  | 1.54                        | 1.58         | 1.58–1.60 | 1.59  |
| C_{40}-C_{40}  | 1.57                        | 1.56         | 1.58–1.65 | 1.58–1.62 |
| C_{44}-C_{44}  | 1.51                        | 1.58         | 1.55–1.59 | 1.55–1.58 |
| C_{50}-C_{50}  | 1.59                        | 1.57         | 1.56–1.61 | 1.57–1.60 |

3.1.1. Symmetrical sized dimers

Symmetrical sized dimers C_{20}-C_{20}, C_{24}-C_{24}, C_{28}-C_{28}, C_{32}-C_{32}, C_{36}-C_{36}, C_{40}-C_{40}, C_{44}-C_{44} and C_{50}-C_{50} have been investigated in detail.

C_{20} with $h_0$ symmetry forms C_{20}-C_{20} dimer structure in [2 + 2] side–side mode as the most stable geometry. We have also calculated the relative energy differences ($E_r$) of all the configurations to check for any isomeric structures. In C_{20}-C_{20} dimer, [3 + 5] and [1 + 1] modes have $E_r$ w.r.t. [2 + 2] configuration of the order of 0.382 eV and 1.27 eV respectively, which clearly shows that [2 + 2] mode has the highest stability. The average diameter ($D_{av} = 4.14$ Å) of cages remains almost same as that of single C_{20} cage. The bond lengths lie in the range 1.38–1.40 Å and the connecting bond length between the cages is 1.55 Å as shown in table 2.

We have calculated the interaction energies of all the possible structures using the following expression

$$\Delta E = E_{total}(C_n + C_m) - 2E(C_n),$$

where $E_{total}(C_n + C_m)$ and $E(C_n)$ are the total energies of the dimer and individual cages respectively. In order to obtain more realistic values of $E_{int}$, the necessary corrections in the Basis set due to inconsistent treatment of the basis set for each monomer [48, 49], the basis set superposition error term (BSSE) has been added to the
interaction energies and is given by equation

\[ E_{\text{int}} = E_{\text{total}}(C_n - C_m) - 2E(C_m) - E_C. \] (2)

The negative values of \( E_{\text{int}} \) indicate the greater stabilities of the dimer while the positive values show that the dimer is less stable, so the dimers with negative \( E_{\text{int}} \) have a possibility to be formed experimentally. \( C_{20}-C_{20} \) dimer with \([2 + 2]\) side–side mode require more energy \((-4.35\, \text{eV})\) to dissociate into two cages of dimer structure as compared to other configurations (figures 1(a) and (c)), which indicates that this configuration is the most favorable one.

\( C_{24} \) with \( D_{6h} \) symmetry forms a most stable dimer with \([6 + 6]\) face–face mode between two hexagons. In \( C_{24}-C_{24} \) dimer, \( E_i \) for \([2 + 2]\) mode w.r.t. \([6 + 6]\) mode is 1.29 eV which point towards the stability of \([2 + 2]\) mode as well. The relative energy difference for other modes w.r.t. \([6 + 6]\) mode is comparatively larger. The average diameter of \( C_{24} \) cage in isolated form is 4.69 Å, which decreases to 4.48 Å when connected in \([6 + 6]\) mode of dimer leading to distortion in the structure. The bond lengths vary between 1.40 and 1.55 Å and the connecting bond length between the cages is 1.59 Å. From the values of interaction energy, \([6 + 6]\) configuration has maximum chances to be formed as compared to other counterparts.

\( C_{28} \) cage having \( T_d \) symmetry forms a most stable structure with \([5 + 5]\) face–face mode between two pentagons after their dimerization. \([1 + 1]\) and \([6 + 6]\) configurations have \( E_i \) w.r.t. \([5 + 5]\) of the order of 0.56 eV and 1.31 eV respectively. \([2 + 2]\) configuration has \( E_i \) 0.07 eV which indicates that after \([5 + 5]\) mode, it has the highest probability to be formed. The average diameter (4.83 Å) of \( C_{28}-C_{28} \) dimer remains identical as compared to the individual cage. The C–C bond lengths vary from 1.40 to 1.58 Å in \( C_{28}-C_{28} \) dimer and the connecting bond lengths lay from 1.58 to 1.60 Å. \( E_{\text{int}} \) values indicate that the dimer structure with \([5 + 5]\) mode has largest stability amongst all the other modes.

\( C_{32} \) \((D_3)\), \( C_{36} \) \((D_{6h})\), \( C_{40} \) \((D_2)\) and \( C_{44} \) \((D_2)\) cages form most stable dimers when connected through \([2 + 2]\) side–side mode. For \( C_{32}-C_{32} \), the relative energy difference of \([1 + 1]\) mode is quite high w.r.t. \([2 + 2]\) mode, which further establishes \([2 + 2]\) as the most stable configuration. \( E_{\text{int}} \) values show that \([5 + 5]\) and \([6 + 6]\) modes of \( C_{32} \) dimer are unstable. For \( C_{40}-C_{40} \) dimer, \( E_i \) value for \([1 + 1]\) mode is of the order of 0.23 eV, whereas \([5 + 5]\) and \([6 + 6]\) modes are unstable. In \( C_{44}-C_{44} \) dimer, only \([2 + 2]\) mode is energetically favorable as shown in table 3. The \( D_{av} \) of individual cages do not show much change after dimerization except \( C_{44}-C_{44} \) dimer, where \( D_{av} \) decreases from 6.15 to 6.0 Å. The average bond lengths for \( C_{32}-C_{32} \) and \( C_{44}-C_{44} \) dimers lie in the range 1.37 Å–1.53 Å, whereas for \( C_{40}-C_{40} \) dimer the bond lengths vary from 1.38 to 1.60 Å. The cages are held together through the connecting bonds of the order of 1.56 Å–1.58 Å. For \( C_{30}-C_{50} \) dimer, all the possible configurations show positive \( E_{\text{int}} \) and are energetically unstable.

\( C_{36} \) with \( D_{6h} \) symmetry has a most stable dimer structure in \([2 + 2]\) side mode. The \([1 + 1]\) and \([5 + 5]\) modes have relative energy difference of 0.18 and 0.30 eV, whereas for \([6 + 6]\) mode relative energy difference is comparatively large. The connecting bond lengths for both configurations are shown in table 2 and the \( D_{av} \) of dimer structure decreases to 5.5 Å w.r.t. single cage (5.6 Å). Interaction energy shows that the dimer with \([2 + 2]\) mode is most favorable dimer structure between other isomers of \( C_{36}-C_{36} \) dimer.

The interaction energies for all symmetrical sized dimers show that these dimer structures are energetically favorable and therefore, are likely to be formed. \( E_{\text{int}} \) value decreases from \( C_{20}-C_{20} \) to \( C_{36}-C_{36} \) dimer, which shows that the small sized dimers are more likely to be formed as compared to large sized fullerene dimers. The observed structural behavior of symmetrical sized fullerene dimers can be seen from variation in average diameters and connecting bond lengths. In all the dimers except \( C_{24}-C_{24} \) and \( C_{28}-C_{28} \), the most stable configuration with which the fullerene prefers to attach is \([2 + 2]\). \( C_{24}-C_{24} \) and \( C_{28}-C_{28} \) dimer shows maximum preference to be formed in \([6 + 6]\) and \([5 + 5]\) mode. The average connecting bond length at which the dimers get stable is 1.58 Å. The fullerene have a tendency to settle away from each other as the single C–C bond length is

| Dimer | Before BSSE correction \((\Delta E)\) | After BSSE correction \((E_{\text{int}})\) |
|-------|-----------------------------------|-----------------------------------|
|       | 1 + 1  | 2 + 2  | 5 + 5  | 6 + 6  | 1 + 1  | 2 + 2  | 5 + 5  | 6 + 6  |
| \(C_{20}-C_{20}\) | –4.16  | –5.43  | –5.04  | —      | –3.26  | –4.35  | –3.36  | —      |
| \(C_{24}-C_{24}\) | –3.27  | –4.95  | –4.87  | –5.13  | –2.33  | –3.89  | –2.85  | –3.18  |
| \(C_{28}-C_{28}\) | –2.47  | –3.42  | –3.67  | –2.66  | –1.45  | –1.94  | –2.01  | –0.70  |
| \(C_{32}-C_{32}\) | –1.59  | –2.54  | –0.76  | –0.97  | –0.69  | –1.35  | 0.97   | 0.95   |
| \(C_{36}-C_{36}\) | –2.93  | –2.72  | –3.00  | –2.22  | –1.39  | –1.57  | –1.27  | –0.34  |
| \(C_{40}-C_{40}\) | –1.97  | –2.21  | –0.87  | –1.96  | –0.49  | –0.72  | 0.85   | 0.05   |
| \(C_{44}-C_{44}\) | –1.76  | –2.59  | –2.42  | –1.33  | 1.04   | –0.34  | 0.20   | 3.45   |
| \(C_{50}-C_{50}\) | 0.02   | –1.46  | 0.64   | 0.86   | 1.00   | 0.92   | 0.81   | 2.02   |
1.54 Å. In all the dimers formed, the \( D_{av} \) decreases w.r.t. the individual cages. However, when the type of intercage bonding changes, there is variation in C–C bonds leading to change in the \( D_{av} \), which leads to redistribution of charges at localized sites.

### 3.1.2. Asymmetrical sized dimers

We have extended our investigation to study of asymmetrical sized dimers \( C_{20}–C_{24} \), \( C_{24}–C_{28} \), \( C_{28}–C_{32} \), \( C_{32}–C_{36} \), \( C_{36}–C_{40} \), \( C_{40}–C_{44} \) and \( C_{44}–C_{50} \) using the method described in computational details. \( C_{20}–C_{24} \), \( C_{24}–C_{28} \) and \( C_{28}–C_{32} \) form the most stable dimer with \( [2 + 2] \) side–side mode. The relative energy differences are high for other configurations as compared to \( [2 + 2] \) side–side mode. The average C–C bond lengths vary from 1.37 to 1.57 Å for these three dimer structures. There is variation of the order of 0.10–0.15 Å in the \( D_{av} \) of \( C_{20}–C_{24} \) and \( C_{28}–C_{32} \) in comparison to their individual counterparts, whereas for \( C_{44}–C_{50} \) \( D_{av} \) remains almost same as compared to single cages. The connecting bond lengths, average diameters and interaction energies are tabulated in tables 4 and 5 for all the asymmetrical sized dimers. The interaction energy for these dimers is calculated using the following expression

\[
\Delta E = E_{total}(C_n - C_m) - E(C_n) - E(C_m),
\]

where \( E_{total}(C_n - C_m) \), \( E(C_n) \) and \( E(C_m) \) are the total energies of the dimer and individual cages respectively. The BSSE correction \( E_C \) is added to \( \Delta E \) and final interaction energy is calculated using expression

\[
E_{int} = E_{total}(C_n - C_m) - E(C_n) - E(C_m) - E_C.
\]

The calculated interaction energies before and after BSSE correction are shown in table 5. Table 5 shows extra stability of \( [2 + 2] \) mode for \( C_{20}–C_{24} \), \( C_{24}–C_{28} \) and \( C_{28}–C_{32} \) due to higher interaction energy. The connecting bond lengths lie in the range 1.56–1.59 Å for these three dimers.

In case of \( C_{24}–C_{28} \) dimer, the most stable dimer forms, when \( C_{24} \) cage is combined to \( C_{28} \) cage through \( [2 + 2] \) side mode. \( E_i \) shows that \( [1 + 1] \), \( [2 + 2] \) and \( [6 + 6] \) modes are less stable as compared to \( [5 + 5] \) mode. The average diameter remains almost same for both the individual cages after their dimerization, while the average C–C bond lengths vary between 1.39 and 1.60 eV. The connecting bond lengths vary from 1.59 to 1.64 Å. \( \Delta E \) value for \( [5 + 5] \) configuration is highest for \( C_{24}–C_{28} \) among all other possible modes.

For \( C_{32}–C_{36} \), \( C_{36}–C_{40} \) and \( C_{44}–C_{50} \) dimers, the most stable dimer structure has \( [1 + 1] \) point–point mode, whereas for \( C_{40}–C_{44} \) \( [6 + 6] \) mode has highest stability. \( [6 + 6] \) mode of all the asymmetrical dimers except \( C_{40}–C_{44} \) and \( C_{24}–C_{28} \) is energetically unfavorable. In \( C_{32}–C_{36} \) dimer, the relative energy differences are large for \( [2 + 2] \) and \( [5 + 5] \) modes w.r.t. \( [1 + 1] \) configuration. For \( C_{36}–C_{40} \) dimer, \( [5 + 5] \) mode has relative energy

### Table 4. Interaction energy (\( \Delta E \)), average diameter (\( D_{av} \)) and connecting bond length for asymmetrical sized dimers.

| Dimer   | \( D_{av} \) (Å) | Connecting bond length (Å) |
|---------|------------------|-----------------------------|
|         | \( C_n \)  | \( C_m \)  | \([1 + 1]\) | \([2 + 2]\) | \([5 + 5]\) | \([6 + 6]\) |
| \( C_{20}–C_{24} \) | 4.22 | 4.70 | 1.52 | 1.56 | 1.57–1.65 | — |
| \( C_{24}–C_{28} \) | 4.74 | 4.87 | 1.54 | 1.57 | 1.59–1.64 | 1.58–1.62 |
| \( C_{28}–C_{32} \) | 4.73 | 5.39 | 1.55 | 1.57 | 1.58–1.61 | 1.58–1.62 |
| \( C_{32}–C_{36} \) | 5.34 | 5.50 | 1.54 | 1.57 | 1.57–1.62 | 1.55–1.62 |
| \( C_{36}–C_{40} \) | 5.37 | 5.89 | 1.55 | 1.58 | 1.57–1.63 | 1.53–1.69 |
| \( C_{40}–C_{44} \) | 5.89 | 6.34 | 1.56 | 1.59 | 1.57–1.62 | 1.58–1.61 |
| \( C_{44}–C_{50} \) | 6.13 | 6.61 | 1.57 | 1.57 | 1.58–1.60 | 1.55–1.65 |

### Table 5. Interaction energy before and after BSSE correction for asymmetrical sized dimers.

| Dimer   | Before BSSE correction (\( \Delta E \)) | After BSSE correction (\( E_{int} \)) |
|---------|----------------------------------------|--------------------------------------|
|         | \( 1 + 1 \) | \( 2 + 2 \) | \( 5 + 5 \) | \( 6 + 6 \) | \( 1 + 1 \) | \( 2 + 2 \) | \( 5 + 5 \) | \( 6 + 6 \) |
| \( C_{20}–C_{24} \) | –3.45 | –5.18 | –4.93 | — | –2.65 | –4.13 | –2.81 | — |
| \( C_{24}–C_{28} \) | –2.36 | –3.91 | –4.29 | –3.86 | –1.75 | –2.69 | –2.54 | –1.89 |
| \( C_{28}–C_{32} \) | –2.19 | –2.59 | –2.23 | –1.84 | –1.24 | –1.46 | –0.55 | 0.09 |
| \( C_{32}–C_{36} \) | 2.33 | –2.20 | –2.00 | –0.27 | –1.16 | –1.02 | –0.02 | 1.72 |
| \( C_{36}–C_{40} \) | –2.04 | –1.99 | –1.79 | –0.67 | –0.77 | 2.52 | –0.06 | 1.42 |
| \( C_{40}–C_{44} \) | –1.18 | –1.37 | –1.13 | –1.38 | –0.25 | 0.50 | –0.69 | –1.18 |
| \( C_{44}–C_{50} \) | –0.67 | –1.46 | –0.78 | –0.06 | –0.89 | 3.56 | 1.43 | 1.78 |
difference of 0.71 eV. The other modes i.e. [1 + 1] and [6 + 6] are unstable and are not likely to be formed. For C_{44}–C_{20}, only [1 + 1] is possible while all other modes are not stable. The D_{av} in C_{32}–C_{32} dimer shows variation of 0.1 Å w.r.t. single cages. In C_{36}–C_{40} dimer, the D_{av} for C_{36} cage decreases from 5.60 to 5.37 Å, whereas for C_{40} cage it increases from 5.75 to 5.89 Å w.r.t. the individual cages. The D_{av} increases after dimerization for C_{40}–C_{44} dimer as compared to their individual counterparts. The connecting bond lengths are of the order of ~1.5 Å and the average C–C bond lengths vary from 1.38 to 1.60 Å.

The interaction energies for asymmetrical sized dimers show similar behavior as that of symmetrical sized dimers. There is an increase in E_{int} from C_{20}–C_{24} to C_{44}–C_{50} dimer, which suggest that the dimers of small size have more chances to form as compared to larger ones. For all asymmetrical sized dimers except C_{24}–C_{28}, the average connecting bond length is 1.56 Å, which is comparable to single C–C bond length. In comparison to symmetrical sized dimers, the fullerene cages in asymmetrical sized dimers are more closely bound. There is significant variation in the average diameters of asymmetrical sized dimers, which point towards their valuable magnetic properties.

### 3.2. Magnetic properties

To study the magnetic properties of small fullerene dimers, spin polarized calculations have been performed on all possible dimer combinations [1 + 1], [2 + 2], [5 + 5] and [6 + 6]. The HOMO–LUMO gaps for spin up and down electron states, DOSs, total magnetic moments (MMs) and localized MMs (figure 2) have been calculated for both symmetrical and asymmetrical sized dimers as summarized below.

#### 3.2.1. Symmetrical sized dimers

The symmetrical sized dimers with similar size were taken into consideration to analyze their magnetic properties. The HOMO–LUMO energy gaps for electrons with spin up and spin down and total MMs for C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, C_{44}, C_{50} with [1 + 1], [2 + 2], [5 + 5] and [6 + 6] modes are shown in table 6.

C_{20} fullerene cage with I_h symmetry has zero magnetic moment in isolated form. However, the symmetry and magnetic state of C_{20} has been a point of disagreement in the reported results, which may be due to the accuracy of the electron correlation effects in small fullerenes [50]. C_{20} has shown magnetic to non-magnetic transition and vice versa for I_h and D_{3d} symmetries respectively [51]. After dimerization, C_{20}–C_{20} dimer in [1 + 1] and [5 + 5] modes shows magnetic behavior with total MM of 2.0 μ_B, whereas the most stable configuration with [2 + 2] mode shows non-magnetic behavior. The local MMs on all individual C atoms for [5 + 5] mode in C_{20}–C_{20} dimer are shown in figure 2. The major contribution to total MM is contributed by second nearest neighbors (NNs) from the connecting bond atoms, which contributes about 65% of total MM. Atoms at first NN positions and atoms at connecting bridges contribute about 42% and 10% respectively to total MM. In order to visualize the magnetic ordering, the electron spin distribution of stable dimer structures C_{20}–C_{20} [2 + 2] and C_{20}–C_{20} [5 + 5] have been plotted in figure 3. Figure clearly shows distinct spin density for spin up and down on different C atoms. Figure 3(a) shows symmetrical spin charge density on both monomers w.r.t. 2 + 2 connecting bond which results in non-magnetic C_{20}–C_{20} [2 + 2] dimer. However, when two C_{20} monomers are connected in [5 + 5] mode, the spin up density on different Catoms dominates w.r.t. spin down density resulting in the magnetic structure (see figure 3(b)).

The HOMO–LUMO gap of spin up and spin down electrons show distinct pattern in dimer configurations w.r.t. gap in individual building block. The non-magnetic dimer configurations show equal magnitude of HOMO–LUMO gaps for spin up and spin down electron states, whereas magnetic dimers show unequal HOMO–LUMO gaps.

C_{24}–C_{24} dimer exhibits high magnetism with total MM of 4.0 μ_B in [6 + 6] mode in comparison to isolated C_{24} fullerene which shows 0.0 μ_B magnetic moment. When connected with [1 + 1] and [5 + 5] modes the dimer shows MM of 2.0 μ_B, whereas in [2 + 2] mode the total MM is 0.0 μ_B. To understand the origin of magnetism, local MMs on all C atoms were calculated. The local MM in [6 + 6] mode indicates that first and second NNs of both cages contribute ~51% and 49% respectively towards total MM, whereas there is no contribution from connecting bond atoms to total MM. However, in [5 + 5] mode, 80% of contribution comes from second NNs. The HOMO–LUMO gaps for spin up and spin down states are unequal in [1 + 1], [5 + 5] and [6 + 6] modes showing the magnetic behavior of dimer.

C_{28} fullerene cage has total magnetic moment of 4.0 μ_B in isolated form. When it forms a most stable dimer in [5 + 5] mode, total MM increases to 6.0 μ_B. The magnetic moment for [2 + 2] and [6 + 6] configurations is 4.0 μ_B, while for [1 + 1] point–point mode total MM is 6.0 μ_B. The local MM in [5 + 5] mode show that there is a contribution of 23.5%, 25.8% and 40% for first, second and third NNs respectively towards total MM, whereas in [2 + 2] mode major contribution comes from the second, third and forth NNs. The connecting bond atoms for both modes show a small contribution of only 1%–2% to total MM. Figure 3(c) shows that there is a difference in spin up and spin down densities on various Catoms. The spin up density dominates w.r.t. spin...
down density which results in the magnetic behavior of C_{28}–C_{28} dimer in [1+1] mode. All the possible configurations have significant magnetic order in HOMO-LUMO gaps of spin up and spin down states showing their magnetic behavior.

In isolated form C_{36} cage is magnetic with magnetic moment of 2.0 μB. The magnetic moment remains same after dimerization of the carbon cage in [5+5] mode. Total MM increases to 4.0 μB for [2+2] and [6+6] mode, while for [1+1] mode it has value 2.0 μB. The second, third and fifth NNs form connecting bond atoms make a contribution of 20%, 42% and 48.7% respectively to total MM in [5+5] mode. For [2+2] mode, the major contribution of local MM is 51% for third NN and the remaining local MM are distributed evenly on first,

Figure 2. Local magnetic moments of symmetrical sized small fullerene dimers in μB.
second, fifth and sixth neighbors. The HOMO-LUMO gaps for spin up and spin down states have finite energy difference, which show their magnetic behavior.

As the fullerenes C$_{32}$, C$_{40}$, C$_{44}$ and C$_{50}$ are non-magnetic in their isolated forms and after dimerization in [2 + 2] mode continuous to remain non-magnetic. However, [1 + 1] and [5 + 5] configurations acquire finite magnetic moment after the formation of dimer due to change in inter–cage bonding. In [1 + 1] and [5 + 5] modes, C$_{32}$–C$_{32}$ and C$_{40}$–C$_{40}$ dimers acquire finite magnetic moment of 2.0 $\mu_B$, whereas [6 + 6] mode in both the dimers have zero magnetic moment. The local MMs at C atoms of connecting bonds show no contribution as the magnetic moment is localized away from them. The HOMO-LUMO gaps of spin up and down states are equal for non-magnetic modes [2 + 2] and [6 + 6], while the magnetic dimer configurations [1 + 1] and [5 + 5] have finite energy difference in their HOMO-LUMO gaps. C$_{44}$–C$_{44}$ dimer is found to be non-magnetic in all the four modes with zero magnetic moment. The HOMO-LUMO gaps for spin up and spin down electronic state.

To understand the change in the electron density of dimer configuration w.r.t. individual fullerene, the DOSs are calculated and shown in figure 4. Figure 4(a) validates that C$_{20}$ fullerene cage and C$_{20}$–C$_{20}$ dimer in

| Dimer    | Total magnetic moment ($\mu_B$) | Dimer    | HOMO-LUMO gaps (eV) |
|----------|--------------------------------|----------|---------------------|
|          | [1 + 1] | [2 + 2] | [5 + 5] | [6 + 6] | [1 + 1] | [2 + 2] | [5 + 5] | [6 + 6] |
| C$_{20}$–C$_{20}$ | 2.00     | 0.00   | 2.00  | —      | C$_{20}$–C$_{20}$ | 0.91  | 1.02  | 1.13  | 1.13  | 1.37  | 0.65  | —      | —      |
| C$_{24}$–C$_{24}$ | 2.00     | 0.00   | 2.00  | 4.00   | C$_{24}$–C$_{24}$ | 0.72  | 0.34  | 0.59  | 0.59  | 0.79  | 0.47  | 1.60   | 0.62   |
| C$_{28}$–C$_{28}$ | 6.00     | 4.00   | 6.00  | 4.00   | C$_{28}$–C$_{28}$ | 1.52  | 0.81  | 1.79  | 0.43  | 1.94  | 0.81  | 0.34   | 0.65   |
| C$_{32}$–C$_{32}$ | 2.00     | 0.00   | 2.00  | 0.00   | C$_{32}$–C$_{32}$ | 1.85  | 0.37  | 1.31  | 1.31  | 0.60  | 0.51  | 0.75   | 0.75   |
| C$_{36}$–C$_{36}$ | 2.00     | 4.00   | 2.00  | 3.96   | C$_{36}$–C$_{36}$ | 0.92  | 0.74  | 0.71  | 0.73  | 0.93  | 0.60  | 1.03   | 0.96   |
| C$_{40}$–C$_{40}$ | 2.00     | 0.00   | 2.00  | 0.00   | C$_{40}$–C$_{40}$ | 0.58  | 0.49  | 0.67  | 0.67  | 0.48  | 0.18  | 0.94   | 0.94   |
| C$_{44}$–C$_{44}$ | 0.00     | 0.00   | 0.00  | 0.00   | C$_{44}$–C$_{44}$ | 0.57  | 0.57  | 0.66  | 0.66  | 0.55  | 0.55  | 0.72   | 0.72   |
| C$_{50}$–C$_{50}$ | 1.67     | 0.00   | 1.95  | 0.00   | C$_{50}$–C$_{50}$ | 0.45  | 0.84  | 1.17  | 1.17  | 0.54  | 0.46  | 0.97   | 0.97   |

Figure 3. Spin density maps for non-magnetic and magnetic fullerene dimers.
[2 + 2] mode are non-magnetic and [5 + 5] mode has spin polarized states. The origin of magnetic moment in [5 + 5] mode comes from the 2p orbitals because of unequal spin up and down states near the Fermi level. For C24–C24 dimer, [6 + 6] mode shows a significant change in DOS w.r.t. single C24 cage which further points to its magnetic nature. [5 + 5] mode also show some decrease in the magnetization but there is a visible difference in up–down DOS (figure 4(b)). Both [6 + 6] and [5 + 5] modes show strong polarization around Fermi level in 2p orbitals while C24 fullerene cage is non-magnetic and has equal up and down states. Similarly, the DOS for other dimer cages also show significant changes near Fermi level, which is due to the redistribution of electrons in 2p orbitals (see figure 4).

The symmetrical sized dimers have shown significant variation in their magnetic moment w.r.t. the type of inter-cage bonding. Their MMs are mainly localized on first, second and third NNs from connecting bond atoms due to the redistribution of charges in spin up and spin down electron states. The contribution from connecting bond atoms towards total MM is very small which may be explained due to tetra-bonding of C atoms completing their valency by making four σ-bonds with neighboring C atoms. We have also plotted projected DOSs in figure 6 for few systems, which shows that 2p-orbitals in each case has maximum contribution towards total MM. The Muliken charge distribution analysis of the dimers suggest that the connecting bond C atoms loses charge in range 0.021–0.114 electrons, whereas the first NN gain charge of the order of 0.011–0.066 e’s. However, the gain in charge for second NN is ∼0.010–0.038 electrons. This redistribution of charges at different C sites is responsible for the variation in localized MMs. In symmetrical sized dimers, some of the C atoms show antiferromagnetic alignment w.r.t. their surrounding C atoms. However, the interaction between individual cages of the dimer is found to be ferromagnetic in nature.

3.2.2. Asymmetrical sized dimers

The magnetic properties calculated for symmetrical sized dimers as described in the previous section were calculated for asymmetrical sized dimers and are tabulated in table 7. Asymmetrical sized dimers with small difference in size were considered to understand their magnetic behavior. C20 and C24 in the isolated form are non-magnetic with zero magnetic moment, when they form C20–C24, the stable dimer structure with [2 + 2] mode remains non-magnetic. However, when C20–C24 connects with [1 + 1] and [5 + 5] bonding, the resultant structure becomes magnetic with magnetic moment of 1.9 μB and 2.0 μB respectively. The results suggest dependence of magnetic behavior on type of inter-connecting mode of dimer.

To understand the origin of magnetism in C20–C24, local MMs on each C atom was calculated and are shown in figure 5. The connecting bond atoms contribute very small magnetic moment towards total MM and the major contribution comes from second and third NNs from connecting bond which contribute 42% and 33% of total MM respectively. The HOMO-LUMO gap for spin up and spin down electron states show similar behavior as observed in symmetrical sized dimers.
Dimer are isoenergetic but they have different magnetic behavior. The cage contributes towards total MM as the cage is magnetic in isolated form and C32 is non-magnetic. The MMs respectively. The local MMs suggest that the maximum contribution of 70% comes from C28 cage, while C24 contribution comes from third and third NNs from connecting bond atoms. The HOMO-LUMO gaps for spin up and down states also show the dependence of inter-cage bonding on the magnetic behavior of dimer formed. The local MMs suggest that each cage contributes

### Table 7. Total Magnetic moments and HOMO-LUMO gaps for asymmetrical sized dimers.

| Dimer | Total magnetic moment (μ_B) | Dimer | HOMO-LUMO gaps (eV) |
|-------|-----------------------------|-------|---------------------|
|       | [1 + 1]                     |       | [1 + 1]             |
| C20–C24 | 1.90 0.00 2.00 —           | C20–C24 | 0.59 0.39 0.71     |
| C22–C24 | 2.00 2.00 4.00 3.95         | C22–C26 | 0.82 0.32 0.40 0.35 |
| C24–C26 | 4.00 2.00 4.00 2.00         | C24–C28 | 1.66 0.39 0.66 0.43 |
| C26–C30 | 1.95 2.00 2.00 4.00         | C26–C30 | 0.93 0.29 0.36 0.36 |
| C28–C34 | 2.00 3.96 2.00 4.00         | C28–C34 | 0.66 0.73 0.64 0.47 |
| C30–C38 | 2.00 4.00 2.00 4.00         | C30–C38 | 0.73 0.39 0.81 0.42 |
| C32–C40 | 1.98 2.00 1.92 0.00         | C32–C40 | 0.88 0.55 0.85 0.61 |

C28 fullerene is magnetic with magnetic moment of 4 μ_B in isolated form. When it forms a dimer with C24, the resultant most stable dimer structure with [5 + 5] mode becomes magnetic with total MM of 4.0 μ_B. The total MM decreases in [1 + 1], [2 + 2] and [6 + 6] configurations having total MM 2.0 μ_B, 2.0 μ_B and 3.95 μ_B respectively. The local MMs suggest that the maximum contribution of 70% comes from C28 cage, while C24 cage contributes only 30% of total MM, which indicates that C28 is inducing magnetism in C24. There is very small contribution of ~1.5% from connecting bond atoms towards total MM, whereas the maximum contribution comes from second and third NNs i.e. ~40% and 30% of total MM respectively. In [2 + 2] mode of C44–C50 dimer, only C28 cage contributes towards total MM where local MM is distributed away from connecting bond atoms. The HOMO-LUMO gap for spin up and spin down states for all the modes show finite energy difference for magnetic dimer.

In the combination of C28 and C32 cages, the most stable dimer structure [2 + 2] becomes magnetic after dimerization with total MM of 2.0 μ_B. The other modes [1 + 1], [5 + 5] and [6 + 6] of C28–C32 show magnetic behavior having total MM of 4.0 μ_B, 4.0 μ_B and 2.0 μ_B respectively. The local MMs on each C atom were calculated to comment on the magnetic behavior of dimer structure. For most stable [2 + 2] mode, only C28 cage contribute towards total MM as the cage is magnetic in isolated form and C32 is non-magnetic. The MMs are evenly distributed over first, third and fourth NNs from connecting bonds which contribute 23%, 32% and 36% respectively. The HOMO-LUMO gaps for spin up and down states have finite values.

In isolated form, C32 fullerene is non-magnetic whereas C36 has magnetic moment of 2.0 μ_B. After dimerization, the resultant dimer structure in most stable [1 + 1] mode has total MM of 1.9 μ_B. However, the total MM for [2 + 2], [5 + 5] and [6 + 6] increases to 2.0 μ_B, 2.0 μ_B and 4.0 μ_B respectively. In ground state [1 + 1] mode, both the cages contribute equally towards total MM of the dimer and the MMs are evenly distributed on third, fifth and seventh NNs from connecting bond atoms. The local MMs for [6 + 6] mode of C32–C36 dimer, contribution comes from C36 cage only and contribution of ~36% comes from first and third NNs from connecting bonds. The HOMO-LUMO gap values for spin up and spin down states also show the magnetic behavior of dimer in all the configurations.

The combination of magnetic C36 fullerene with non-magnetic C40 fullerene results in a magnetic dimer structure having total MM of 2.0 μ_B in most stable [1 + 1] mode. In other configurations [2 + 2], [5 + 5] and [6 + 6], the total MM is 3.96 μ_B, 2.0 μ_B and 4.0 μ_B respectively. The local MMs suggest that both the cages contribute equally towards total MM. The major contribution in total MM comes from first, third and fifth NNs from connecting bond atoms, whereas connecting bond atoms contribute ~1% towards total MM. The HOMO-LUMO gaps for spin up and spin down electron states show magnetic behavior of dimer and have finite values in all modes.

C40 and C44 cages are non magnetic in isolated form, but after dimerization the resultant dimer structure becomes magnetic in most stable [1 + 1] mode with total MM of 2.0 μ_B. [2 + 2] and [6 + 6] modes of C40–C44 dimer are isoenergetic but they have different magnetic behavior. [6 + 6] mode is non-magnetic with zero magnetic moment, while [2 + 2] has high magnitude of total MM of order of 4.0 μ_B. This explains the dependence of inter-cage bonding on the magnetic behavior of dimer formed. The local MMs suggest that each cage contributes ~50% towards total MM and the MMs are not localized on connecting bond atoms. The main contribution comes from first and third NNs from connecting bonds with ~24% and ~20% respectively. The HOMO-LUMO gaps for spin up and spin down states are equal for [6 + 6] mode indicating its non-magnetic behavior.

The non-magnetic C44 and C50 cages form a magnetic dimer structure with total MM of 2.0 μ_B in [1 + 1], [2 + 2] and [5 + 5] modes. However, the dimer in [6 + 6] mode remains non-magnetic. The local MMs for most stable [2 + 2] mode shows that only C44 cage contribute towards total MM and it comes from first and third NNs with 48.5% and 41% respectively. The HOMO-LUMO gaps for spin up and spin down states in
Figure 5. Local magnetic moments of asymmetrical sized small fullerene dimers in μB.
[1 + 1], [2 + 2] and [5 + 5] modes have finite energy difference which shows their magnetic behavior. The [6 + 6] configuration is non-magnetic having same spin up and down HOMO-LUMO gaps.

The DOS plots have also been plotted in figure 6 to understand the magnetic behavior of asymmetrical sized dimers. The plots show that there is significant variation in spin up and down states near the Fermi level after dimerization of cages. In C_{20}–C_{24} dimer, DOS plot give the magnetic behavior of [5 + 5] mode, as there are spin polarized states, while for [2 + 2] mode spin up and down states are identical (figure 6(a)). Similarly the DOS plots of other dimers show redistribution of electrons and presence of some unfilled states near the Fermi level and the contribution comes from 2p orbitals. The variation in spin up and down states of all these dimers points towards their magnetic nature.

Therefore, the results suggest that there is a large variation in magnetic behavior of individual cages when they form asymmetrical sized dimers. In some cases, both the cages contribute equally towards total MM, whereas in few of them only one cage contributes towards total MM. Further, the localized moments show that the connecting bond atoms are not the major contributors in total MM which may be due to the change in hybridization from sp^2 to sp^3. There is charge imbalance in spin up and spin down states of first, second and third NNs from connecting bonds which makes them contribute towards total MM. The local MMs show that some of the C atoms behave antiferromagnetically w.r.t. their neighboring C atoms. However, the individual cages in dimer structure interact ferromagnetically w.r.t. each other. Table 8 tabulates the local MM and contribution of 2s- and 2p-orbitals for five atoms of C_{24}–C_{28} dimer starting from maximum value of local MM. The table shows that 2p-orbitals of C atom has major contribution to local MM, which further contributes to total MM of dimer structure. The plots of projected DOSs also show the contribution of 2p-orbitals, which are plotted in figure 7. The redistribution of charges on C atoms has been studied using Muliken charge analysis which shows that both the fullerene cages lose charge in the range 0.014–0.128 e^- for connecting bond atoms. The first NNs gain charge of the order of 0.012–0.076 e^-s, whereas the gain in charge for second NNs is 0.002–0.029 e^- s. This charge redistribution at different sites leads to variation in MMs of individual C atoms.
4. Conclusions

We have investigated a feasibility of formation of symmetrical and asymmetrical sized small fullerene dimers and their magnetic properties using spin polarized density functional theory. All possible modes $([1+1],[2+2],[5+5]$ and $[6+6])$ through which the cages can connect were considered. The interaction energies of various symmetrical dimers shows that $[2+2]$ mode is most stable mode of formation except $\text{C}_{24}-\text{C}_{24}$ and $\text{C}_{28}-\text{C}_{28}$. Asymmetrical dimers $\text{C}_{20}-\text{C}_{24}, \text{C}_{24}-\text{C}_{28}, \text{C}_{28}-\text{C}_{32}$ connect through $[2+2]$ mode, $\text{C}_{32}-\text{C}_{36}, \text{C}_{36}-\text{C}_{40}, \text{C}_{44}-\text{C}_{50}$ connect through $[1+1]$ mode and $\text{C}_{40}-\text{C}_{44}$ connects through $[6+6]$ mode. All the dimer configurations are bonded weakly with connecting bonds ranging between 1.55 and 1.60 Å. The interaction energy suggests higher stability of symmetrical sized dimers than asymmetrical sized dimers.

Dimerization of the fullerenes result in significant change in electronic and magnetic properties w.r.t. isolated fullerene. All fullerenes in isolated form except $\text{C}_{28}$ and $\text{C}_{36}$ are non-magnetic and show interesting change in the magnetic behavior on dimerization. When two non-magnetic fullerenes are combined, the resultant dimer formed is magnetic. However, the combination of a magnetic and a non-magnetic fullerene leads to induced magnetism on non-magnetic fullerene in dimer configuration. When two magnetic fullerenes are combined, there is an enhancement or decrease in total magnetic moment of the resultant dimer. All magnetic dimers show different HOMO-LUMO gap for spin up and down electrons, whereas non-magnetic dimers have same HOMO-LUMO gap for spin up and spin down electrons. Magnitude of the magnetic moment is proportional to the difference in the HOMO-LUMO gap of spin up and spin down electron. The origin of magnetization may be understood in terms of structural distortion of fullerenes in dimer configuration.
distribution of charge from connecting C atoms and polarization of charge due to formation of connecting bonds. More is the structural distortion more is the magnetic moment of the dimer structure. Further, given suitable experimental conditions, these small fullerene dimer structures can be produced, which can facilitate them as good magnetic materials having potential applications in spintronics.

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ORCID iDs

Isha Mudahar @ https://orcid.org/0000-0001-7451-8839

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