Cage-size effects on the encapsulation of P₂ by fullerenes

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Abstract
The classic pnictogen dichotomy stands for the great contrast between triply bonding very stable N₂ molecules and its heavier congeners, which appear as dimers or oligomers. A banner example involves phosphorus as it occurs in nature as P₄ instead of P₂, given its weak π-bonds or strong σ-bonds. The P₂ synthetic value has brought Lewis bases and metal coordination stabilization strategies. Herein, we discuss the unrealized encapsulation alternative using the well-known fullerenes’ capability to form endohedral and stabilize otherwise unstable molecules. We chose the most stable fullerene structures from Cₙ (n = 50, 60, 70, 80) and experimentally relevant from Cₙ (n = 90 and 100) to computationally study the thermodynamics and the geometrical consequences of encapsulating P₂ inside the fullerene cages. Given the size differences between P₂ and P₄, we show that the fullerenes C₇₀–C₁₀₀ are suitable cages to side exclude P₄ and host only one molecule of P₂ with an intact triple bond. The thermodynamic analysis indicates that the process is favorable, overcoming the dimerization energy. Additionally, we have evaluated the host-guest interaction to explain the origins of their stability using energy decomposition analysis.

KEYWORDS
bonding analysis, encapsulation, endohedral, energy decomposition analysis, multiple bond

1 | INTRODUCTION

Stable compounds featuring multiple bonds between heavy main group elements have long been thought unrealizable. Consequently, the so-called “double-bond rule” emerged, formalizing the impossibility of achieving them due to the relative weakness of π-bonds of those p-block elements beyond the second period, providing fundamental instability of compounds. Eventually, this rule was disproven by synthetic strategies based on sterically crowded substituents and coordination to Lewis bases/acid pairs to provide kinetic and thermodynamic stability. Thus, experimental achievement recounts compounds containing double and triple bonds between Groups 13, 14, and 15 tricoordinate and dicoordinate atoms. The unsaturated Group 15 compounds belong to a captivating chapter of this topic with the classic pnictogen dichotomy. Although triply bonded diatomic N₂ species is a ubiquitous inert gas, its heavier homologues are highly reactive and prone to form oligomers. For instance, the most stable phosphorus species is tetra-atomic P₄ (Tₐ) white phosphorus, whereas P₂ is only found as free molecules at high temperatures in the gas phase or in isolation matrices at 17 K. The dimerization process from P₂ to form P₄ has been experimentally estimated to be thermodynamically favorable by 53.6 kcal/mol. This observation has been traditionally explained according to the double...
In contrast, Kutzelnigg discussed that taking into account thus a total cyclic(alkyl)amino carbene (CAAC), the moiety.

Since then, a plethora of endohedral fullerenes (EF) with encapsulated noble gases were synthesized by collision of helium, neon or argon atoms with C60− or of noble gas cations with neutral C60. Six years later, endohedral fullerenes (EF) with encapsulated noble gases were synthesized by collision of helium, neon or argon atoms with C60− or of noble gas cations with neutral C60. Since then, a plethora of endohedral fullerenes—as well as several synthetic derivatives—have been reported. Classical EFs are those of the type M@Cn, M2@Cn, and M3@Cn (M = Li, Ca, Pr, Y, Ba, Ce, Nd, and Gd, among others or noble gases and 60 < n < 88). On the other hand, EFs that involve metal clusters are called endohedral metallofullerenes (EMFs). Among them, we can distinguish between the following types: (i) metallic nitride EFs (M3N@Cn, M = metal and 68 < n < 96); (ii) metallic carbide EFs (M2C@Cn, M = metal and 68 < n < 92); (iii) metallic oxide EFs (M4O2@Cn and M4O3@Cn); and (iv) dimetallic EFs (M2@Cn). The most well-known EMF is Sc3N@C60 that is the third most abundant fullerene after C60 and C70. Finally, another group of EFs contain small molecules such as H2, CO, HF, CH4, NH3, N2 and CO2, and O2 and H2O2, which are introduced in many cases with a procedure called molecular surgery. With this procedure, Murata et al. have also introduced H2 into C70, observing a relative population of 97:3 of H2@C70 and 2H2@C70.

It is known that there must be enough space inside the fullerene cage to encapsulate an atom, a cluster, or a molecule. Otherwise, the interaction between the encapsulated atom (molecule) and the fullerene cage becomes energetically unfavorable. Nonetheless, in some cases, the guest can also modify and define the shape of the host. The reported van der Waals radii of P and sp2 C atoms are both approximately 1.80 Å and the P2 and P4 bond lengths are 1.893 Å and 2.223 Å, respectively. Thus a total (C⋯P⋯C⋯C) distance of ca. 9.1 Å would be required for encapsulation of P2, while for P4 the distance would increase up to ca. 9.4 Å. By simple geometrical considerations, a size exclusion effect could be feasible by fullerenes between C70 (cage diameter 8.33 Å) and C90 (cage diameter 10.74 Å). However, whether the encapsulation stabilization would be sufficient to overcome the thermodynamic challenge of P2 dimerization needs to be evaluated. This systematic

![Scheme 1](image1)

**Scheme 1** Stabilization approaches of P2 triple bond unit: (A) transition metal coordination; (B) Lewis base stabilization; (C) encapsulation approach. Dip = 2,6-disopropyl-phenyl; tBu = tert-butyl.

bond rule, suggesting a weak π-bond between the phosphorus atoms. In contrast, Kutzelnigg discussed that taking into account only the overlap populations, it is expected that the triple bond in N2 and P2 are approximately equal in strength. However, he pointed out that the bond strength also depends on how strongly the valence electrons are attached to the elements, and hence, in qualitative terms, the bond energy on N2 is significantly stronger than P2. Many years later, Jerabek and Frenking brought a quantitative assessment using energy decomposition analysis (EDA). Notably, they found that the contribution of the π-bonding in P2 (40.5%) is higher than in N2 (34.4%). Thus, the tendency of P2 to dimerize is related to the enhanced stability due to the σ-bonds formed rather than π-bonding lost.

The constant quest for environmentally friendly processes which are of preparative value has triggered many investigations on the introduction of phosphorus atoms under mild conditions. In this vein, P2 is an interesting reagent for producing heterocycles through M2P2 coordination mode, yielding a significant decrease in the shape of the host.

The outcome of these reactions is a side-on bridging P2 and P4 bond lengths are 1.893 Å and 2.223 Å, respectively. Thus a total (C⋯P⋯C⋯C) distance of ca. 9.1 Å would be required for encapsulation of P2, while for P4 the distance would increase up to ca. 9.4 Å. By simple geometrical considerations, a size exclusion effect could be feasible by fullerenes between C70 (cage diameter 8.33 Å) and C90 (cage diameter 10.74 Å). However, whether the encapsulation stabilization would be sufficient to overcome the thermodynamic challenge of P2 dimerization needs to be evaluated. This systematic

![Scheme 1](image2)
study aims to give a comprehensive overview of the structural and electronic features of endo-
hedral fullerenes \( C_n \) \((n = 50, 60, 70, 80, 90, \text{ and } 100) \) upon encapsulation of \( P_2 \), and also the evaluation of
the dominating physicochemical factors.

## 2 | METHODS

All structures were optimized with a combination of Turbomole 7.3.1 software\(^6\) and Gaussian 16 C.01 software.\(^7\) Initial fullerene geomet-
tries of a given isomer were extracted from the fullerene software.\(^8\)
This program uses the face-spiral algorithm of Manolopoulos and Fowler with a force field optimization to generate the fullerene co-
dinates.\(^9\) Geometry optimizations were performed at the BP86-D3 (BJ)/def2-SVP level of theory without symmetry constraints. Analyti-
cal harmonic frequencies were computed to determine the nature of stationary points and to calculate unscaled zero-point energies (ZPEs)
as well as thermal corrections and entropic effects using the standard statistical-mechanics relationships for ideal gas.\(^10\) Single-point BP86-
D3(BJ)/def2-TZVP calculations were also performed at the stationary points to improve the electronic energies. The basis set superposition
error (BSSE) has been assessed through single-point calculations with the counterpoise method.\(^11\)

Electronic structure analyses have been performed on the BP86-
D3(BJ)/def2-TZVP wavefunction. Natural Population Analysis (NPA)\(^2\) and the associated Wiberg bond orders have been carried out
using GENNBO 7.0 program.\(^13\) The formal partial charges were obtained using the topological fuzzy Voronoi cells (TFVC) atomic def-
nition\(^4\) as implemented in APOST3D code.\(^5\)

The nature of the host-guest interaction was investigated by means of the EDA, developed by Morokuma\(^5\) and by Ziegler and Rauk,\(^7\) at the
BP86-D3(BJ)/TZ2P\(^8\) level of theory using ADF2019.101. Core electrons were treated by the frozen-core approximation and scalar relativistic effects have been incorporated by the zeroth-order regular approximation (ZORA).\(^9\)

The bonding analysis focuses on the instantaneous interaction energy \( \Delta E_{\text{int}} \) of a bond A–B between two fragments A and B in the
particular electronic reference state and in the frozen geometry AB. This energy is divided into four main components (Equation 1).

\[
\Delta E_{\text{int}} = \Delta E_{\text{inst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}
\]

The term \( \Delta E_{\text{inst}} \) corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the pre-
pared atoms (or fragments) and it is usually attractive. The Pauli repul-
sion \( \Delta E_{\text{Pauli}} \) is the energy change associated with the transformation from the superposition of the unperturbed densities of the isolated
fragments to the wave function \( \Psi_0 = N\bar{A}\ell[\Psi_{\text{A}}\Psi_{\text{B}}] \), which properly obeys the Pauli principle through explicit antisymmetrization (\( \bar{A} \) oper-
ator) and renormalization (\( N = \text{constant} \)) of the product wave function. It comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction \( \Delta E_{\text{orb}} \) accounts for bond pair formation, charge transfer, and polarization effects from the intermediate state to the final AB wavefunction.\(^10\) In the case
dispersion corrections\(^51\)\(^6\) are introduced, the term \( \Delta E_{\text{disp}} \) is com-
puted and added to Equation 1. Further details on the EDA method can be found in the literature.\(^62\) In the case of the dimers, relaxation
of the fragments to their equilibrium geometries at the electronic gro-
und state is termed \( \Delta E_{\text{prep}} \), because it may be considered as prepara-
tion energy for chemical bonding. The addition of \( \Delta E_{\text{prep}} \) to the
intrinsic interaction energy \( \Delta E_{\text{int}} \) gives the total energy \( \Delta E \), which is, by
definition, the opposite sign of the bond dissociation energy \( D_e \), in this case associated to the encapsulation energy:

\[
\Delta E(-D_e) = \Delta E_{\text{int}} + \Delta E_{\text{prep}}
\]

## 3 | RESULTS AND DISCUSSION

### 3.1 | Geometries and energetics

The most stable isomer of \( C_{60} \) is the well-known \( C_{60}/C_{0}D_{5h}(\#1812) \), the only \( C_{60} \) isomer obeying the isolated pentagon rule (IPR).\(^6\) Similarly, for \( C_{70} \), the experimentally characterized isomer is the \( C_{70}/C_{0}D_{5h}(\#8149) \) one.\(^6\) There is no IPR structure for \( C_{50} \) and previous computa-
tional studies point to the \( C_{50}/C_{0}D_{5h}(\#271) \) and \( C_{50}/C_{0}D_{5d}(\#270) \) iso-
mers as the most stable ones,\(^5\) depending on the particular level of
theory applied. For \( C_{80} \), the experimentally characterized isomer is the
\( C_{80}/C_{0}D_{5d}(\#31919) \).\(^6\) Sure et al. computational studied all 31,924 iso-
mers of \( C_{80} \) and found several additional isomers close in energy.\(^6\) In particular, isomer \( C_{80}/C_{0}D_{5d}(\#31918) \) was found the most stable one at
PBE-D3/def2-TZVP level of theory, while \( C_{80}/C_{0}D_{7d}(\#31919) \) found the lowest energy isomer for DLPNO-CCSD(T)/CBS energies.
Finally, Koenig et al. have recently experimentally characterized tubu-
lar \( C_{90}/C_{0}D_{5h} \) and \( C_{100}/C_{0}D_{5d} \) isomers.\(^68\)

It is worth noting that for \( C_{80} \), the cage of \( h \) symmetry is the most
unstable among the seven isomers of \( C_{80} \) that satisfy the IPR.\(^6\) How-
ever, this cage leads to the most favored EMFs when two La atoms or a
Sc_{2}N unit are present inside \( C_{80}/C_{0}D_{7h} \). This result shows that the relative
stability of the different cages can change when atoms or metallic
clusters are encapsulated inside the cage. However, as we will show
later, interaction of \( P_2 \) with the cage is relatively weak, and, therefore
we do not expect major changes in the stability of the cages due to \( P_2 \) encapsulation. Moreover, the determination of the global minima of
all \( P_2@C_{n} \), \( n = 50, 60, 70, 80, 90, \text{ and } 100 \) is out of the scope of this work.
In addition to the particular \( C_{n} \) isomer, one has to take into
account that the \( P_2 \) moiety can exhibit different orientations inside
the cage. For this reason, we have performed an exploratory study of
the \( P_2@C_{60} \) species. Thus, we have considered first the \( C_{60}/C_{0}D_{7h} \) isomer
and up to four different well-defined orientations of the \( P_2 \) unit inside
the cage (see Table S3). Note that the encapsulation of \( P_2 \) lowers the
symmetry of the pristine cage, depending on its specific position
inside. In the \( D_{5d} \) geometry, the internuclear P–P bond axis is collinear
with the center of opposing pentagon poles. Similarly, a \( C_{2p} \) symmetry is
achieved by placing the P–P bond axis with the center of opposing six-membered rings (6-MRs). The third and the fourth struc-
tures were considered where the P–P bond axis is collinear with the
midpoints of two opposing 6,6- and 5,6-type C–C bonds, with
TABLE 1  Relative energies (in kcal/mol) of selected Cn isomers for pristine cages and upon P2 encapsulation. The numbering of the isomers stems from lexicographically ordered face-spiral pentagon indices. The column Symm. Refers to the change of symmetry due to encapsulation.

| Isomer | Cn | Symm. | ΔE | Symm. | ΔE |
|--------|----|-------|----|-------|----|
| C50    | 271 | D3h   | 3.6 | D3h   | 0.0 |
| C60    | 1812 | I      | 0.0 | I      | 0.0 |
| C80    | 31,919 | D2    | 0.6 | D2    | 0.0 |
| C90    | 31,918 | D2d   | 2.8 | D2d   | 1.2 |
| C100   | 31,920 | C2v   | 0.5 | C2v   | 0.5 |
|        | 31,912 | C2v   | 5.0 | C2v   | 6.9 |
|        | 31,923 | D3h   | 5.7 | D3h   | 9.8 |

*All calculations performed at the BP86-D3(BJ)/def2-TZVP//BP86-D3(BJ)/def2-SVP level of theory.

Symmetries D2h and C2h, respectively (see Figures S1-2). Both the D2d and C2h structures correspond to local minima, while D2h and C2v correspond to first- and second-order saddle points at the current level of theory. All stationary points are almost degenerated (i.e., within 0.3 kcal/mol), which would indicate that the host-guest interaction is not directional and essentially the P2 moiety exhibits free rotation inside the cage.

Next, we have considered the P2 encapsulation into two additional C60 cage isomers, namely the C60–C0(#1809) and C60–D3(#1804). As shown in Table 1, relative energies with respect to the lowest energy C60–Ih isomer are 36.5 and 54.4 kcal/mol for the pristine cages and 27.2 and 60.7 kcal/mol for the respective P2 endohedral species. The values for the pristine cages are in good agreement with those reported by Sure et al.67 For small fullerences, the effect of P2 encapsulation on the relative energies of the C60 isomers is not negligible. This effect can be seen in the case of C50, where the (#271) isomer is lower in energy than the (#270), which is found to be lower in energy for the pristine cage. However, when considering larger fullerences such as C60, the relative energies of the isomers are barely affected by the encapsulation of P2. Still, pristine C60–D3(#31919) and C60–D5d(#31918) isomers are found to be within <1 kcal/mol at the current level of theory, and upon P2 encapsulation the lowest energy structure is P2@C60–D3(#31919) by merely 0.5 kcal/mol (see Table 1).

Figure 1 depicts the final optimized geometries of all at P2@Cn and P4@Cn, n = 50–100, systems, obtained the BP86-D3(BJ)/def2-SVP level of theory together with their symmetry and the P–P bond length. On the one hand, in P2@Cn the P–P bond axis is collinear with the center of pentagon poles when possible by the geometry of the cage, as described for the C60 cage. This leads to P2@C70–D3h, P2@C80–C5v and P2@C100–C5v structures. In addition, only in the larger cages (C70 and C100) the center of mass of the P2 unit is slightly shifted from the geometrical center of the cage. When the cage is C50, the P2 unit is almost collinear with two opposing (5,6) C–C bonds, leading to a P2@C50–C5v structure. Finally, in P2@C80–D2, the P2 bond axis is collinear with the center of two opposing (6,6) C–C bonds of the cage. On the other hand, P4@Cn endohedrals achieve lower symmetries levels than P2@Cn. In this case, the P4 tetrahedron edges can point towards the center of the pentagon (P4@C50–C5v) or the hexagon (P4@C90–C3v). Alternatively, one of the P–P bonds matches opposing (6,6) C–C bonds furnishing P4@C70–C2v, P4@C80–D2, and P4@C90–C2v. In C100, the P4 molecule is shifted from the cage center, raising the P4@C100–Cv structure.

At the current level of theory, the bond length of free P2 and P4 are 1.917 and 2.233 Å, respectively, in rather good agreement with the experimentally measured for P2 (1.893 Å)15a and for P4 (2.223 Å).45b and also previous theoretical calculations (1.911, 2.221 Å).13

The encapsulation of P2 into the smaller size cages induces a shortening of P–P bond length, down to 1.823 Å in the case of C50. From C50 and larger cages the P2 distance remains essentially unaffected, already pointing to the absence of electronic effects (e.g., charge-transfer) from the cage.

Encapsulation energies, given by the following equation

\[ \Delta E = E_{P2@Cn} - (E_{Cn} + E_{P2}) \]  

(3)

\[ \Delta E = E_{P4@Cn} - (E_{Cn} + E_{P4}) \]  

(4)

provide a hint about the feasibility of the formation of the endohedral species.

Table 2 gathers the electronic and Gibbs energy values obtained for the species considered. A single-point counterpoise correction to estimate the BSSE is also reported. The ΔG values become monotonically more negative as the cage size grows up to C90, when it stabilizes. The encapsulation becomes exergonic only from C70 on, with ΔG values around ~30 kcal/mol.

As mentioned in the introduction, the most stable allotrope of phosphorous is the tetra atomic P4.7

The electronic and Gibbs energy values for the formation of P2 from P4 (Scheme 2) according to our calculations are +32.8 and +27.6 kcal/mol, respectively.

Thus, the encapsulation would be thermodynamically favored in the cases where the corresponding ΔG values are below ~27.6 kcal/mol. As seen in Table 2, P2@C70 already reaches this value. However, we estimate a BSSE on the encapsulation energy of around 2 kcal/mol, which would make the P2@C70 formation still endergonic. Nonetheless, in the case of the larger endohedrals the BSSE-corrected encapsulation Gibbs energies are negative enough to compensate for dissociation of P4, thus making these species feasible from a thermodynamically point of view.

We have also considered the encapsulation of P4 by the fullerences, to yield the corresponding P4@Cn species. The electronic and Gibbs energies can be also found in the Table 2. Our calculations...
suggest a highly endergonic process in all cases with values well over +50 kcal/mol, except for the case of C80 where the spherical shape helps a better fit of the P4 inside the cage. Still, the overall formation of P4@C80 is not favored with respect to that of P2@C80.

We explored the possible relationship between the energetics of the encapsulation and geometrical parameters of the cages for P2@Cn. Two parameters have been introduced to quantify the deformation of the Cn cages upon encapsulation. On the one hand, \( d_{\text{max}} \) is defined as the difference (in Å) between the maximum C–C distance of the endohedral species and that of the pristine cage. On the other hand, one can also consider, for each C atom of the cage, which is the furthest one. Averaging over all C atoms gives an average maximum distance (the corresponding standard deviation would measure its spread).

**Note:** The numbering of the isomers stems from lexicographically ordered face-spiral pentagon indices.

All values are in kcal/mol.

All calculations have been performed at the BP86-D3(BJ)/def2-TZVP//BP86-D3(BJ)/def2-SVP level of theory.

**TABLE 2** Change of symmetry after P2 or P4 encapsulation, electronic energy (\( \Delta E \)), Gibbs energy (\( \Delta G \)) for the encapsulation of P2 and P4 by Cn (n = 50, 60, 70, 80, 90, and 100), and basis set superposition error (BSSE) estimation.

| Isomer | P2 Symmetry | \( \Delta E \) | BSSE | \( \Delta G \) | P4 Symmetry | \( \Delta E \) | BSSE | \( \Delta G \) |
|--------|-------------|---------------|-------|---------------|-------------|---------------|-------|---------------|
| C50    | \( D_{5h} \rightarrow C_{2v} \) | 87.1          | 2.9   | 96.1          | \( D_{5h} \rightarrow C_{2v} \) | 418.9         | 7.1   | 421.8         |
| C60    | \( I_h \rightarrow D_{5h} \)   | 8.7           | 2.7   | 19.2          | \( I_h \rightarrow C_{3v} \)   | 215.1         | 4.1   | 217.1         |
| C70    | \( D_{5h} \rightarrow D_{3h} \) | –40.0         | 2.3   | –27.8         | \( D_{5h} \rightarrow C_{2} \) | 71.5          | 3.9   | 83.8          |
| C80    | \( D_2 \rightarrow D_{3h} \)   | –47.8         | 1.9   | –36.4         | \( D_2 \rightarrow D_2 \)     | –7.8          | 3.6   | 7.4           |
| C90    | \( D_{5h} \rightarrow C_{5v} \) | –46.3         | 1.8   | –35.0         | \( D_{5h} \rightarrow C_{2} \) | 40.3          | 3.2   | 52.8          |
| C100   | \( D_{5d} \rightarrow C_{5v} \) | –44.7         | 1.8   | –33.1         | \( D_{5d} \rightarrow C_{2} \) | 53.7          | 3.1   | 66.2          |

**FIGURE 1** Optimized geometries of endohedrals P2@Cn and P4@Cn (n = 50, 60, 70, 80, 90, and 100) at the BP86-D3(BJ)/def2-SVP level of theory. Symmetry of the endohedrals and average P–P bond length in Å.

**FIGURE 2** Encapsulation energy \( \Delta E \) (kcal/mol) for the reaction P2@Cn (n = 50, 60, 70, 80, 90, and 100) with respect to the total geometrical deformation of the host and guest (\( d_{\text{av}} + \Delta P_2 \)).
TABLE 3  P–P bond orders (BO, in a.u.) and partial charges (Q, in a.u.) of the P2 and P4 unit from Hilbert-space (NAO) and real-space (TFVC) analyses

| Endohedral | WBO (NAO) | FBO (TFVC) | Q (NAO) | Q (TFVC) |
|------------|-----------|------------|---------|----------|
| P2         | 3.00      | 3.08       | 0.00    | 0.00     |
| P2@C60     | 2.71      | 2.09       | 0.19    | 0.60     |
| P2@C80     | 2.92      | 2.43       | 0.20    | 0.29     |
| P2@C100    | 2.92      | 2.57       | 0.04    | 0.26     |
| P2@C20     | 2.92      | 2.62       | 0.02    | 0.26     |
| P2@C40     | 2.89      | 2.58       | 0.03    | 0.26     |
| P2@C60     | 2.88      | 2.57       | 0.03    | 0.27     |
| P3         | 1.01      | 1.18       | 0.00    | 0.00     |
| P4         | 0.83      | 0.78       | 0.52    | 2.46     |
| P4@C60     | 0.99      | 0.97       | 0.09    | 0.47     |
| P4@C100    | 0.99      | 1.00       | 0.06    | 0.46     |
| P4@C20     | 0.99      | 1.01       | 0.03    | 0.47     |
| P4@C60     | 0.98      | 1.00       | 0.02    | 0.50     |
| P4@C100    | 0.98      | 1.00       | 0.03    | 0.51     |

Note: All calculations have been performed at the BP86-D3(BJ)/def2-TZVP/BP86-D3(BJ)/def2-SVP level of theory.

4 | BONDING ANALYSIS

4.1 | Frontier molecular orbitals

It is not easy to trace the origin of the deformation of each cage. However, that of the P2 moiety should be related to the shape of the molecular orbitals in which the P2 unit is primarily involved and the corresponding P–P bond order. In the free P2 species, the σ and two π bonding orbitals are occupied, consistent with a formal triple bond. Charge transfer from the cage to the P2 host would populate its anti-bonding orbitals, leading to a decrease of the bond order and a concomitant P–P stretch. Nevertheless, similarly, any charge transfer from the P2 moiety to the cage would depopulate P–P bonding orbitals, causing the same effect. This means that the P–P bond order can only decrease upon encapsulation, disregarding the P–P distance. A similar analysis involves P4 unit, where the frontier orbitals consist of σ (e, t2) and σ* (t2) P–P orbitals. Thus, the observed compression of the P–P bond upon encapsulation on the smaller cages is due to the steric pressure of the cage (this will be more evident from the EDA analysis below).

Table 3 gathers the P2 and P4 bond orders and partial charges obtained with a Hilbert-space (NAO) and a real-space (TFVC) atomic definitions. The large disagreement between different atomic population analysis in endohedral fullerences has been pinpointed. For instance, in the endohedral borospherene complex Cl@B39, the charge on CI changes from −0.62 to 0.76 e depending on the method used. In that work, the authors found that real-space QTAIM charges are reliable. We use here real-space TFVC charges because they provide similar results to QTAIM charges at much lower cost.

The TFVC method predicts a charge transfer from the P2 moiety to the cage up to C70, and the opposite effect from C80. The charge transfer is very modest (ca. 0.3e) except for the smaller cage. On the other hand, NPA charges are usually negative for P2, and much smaller. Such a charge flow is equally distributed over the entire cage (see Figure S3 in the ESI). As mentioned above, any charge transfer (positive or negative) should induce a decrease of the P–P bond order. This is exactly what is observed with both schemes. The predicted effect on the bond order is much more pronounced for the TFVC method, going down to 2.09 for the P2@C60 species, where the charge transfer is maximal. However, for the most interesting larger cages the bond order of the P–P bond remains similar to that of the free P2 unit, indicating that upon encapsulation, the triple bond character of the P2 host is maintained. Similarly, P4 shows a significant charge transfer for the small cages, which is related to the reduction of the P–P bond order. With the size increase, charge transfer becomes smaller, and the bond order approaches the one observed for free P4 molecule.

Molecular orbital analysis has been carried out focusing on the σ and π orbitals of the P2 fragment at the BP86-D3(BJ)/def2-TZVP level of theory. As shown on Figure 3, the encapsulation induces an inversion of the relative energies of the σ and π orbital of P2. Thus, while for free P2 the σ is lower in energy, the contrary is found upon encapsulation for the smaller cages C50 and C60. This is likely to be due to the increased Pauli repulsion suffered by the σ electrons that are closer to the cage than the π ones. Also, in the smaller cages (C50, C60), the σ and π orbital of P2 orbitals are energetically destabilized for the same reason. In fact, in both cases the σ orbital becomes the HOMO−1. Then, the larger the cage, the more stabilized the σ and π orbitals become. The contrary occurs for the σ* and π* ones (not shown). It is also worth to note that the degeneracy of the σ and π orbitals is lost in the case of P2@C50 and P2@C80.

4.2 | Energy decomposition analysis

More detailed information about the nature of the interaction between P2 and Cn (n = 50, 60, 70, 80, 90, and 100) fullerene cages
EDA has proven to be a useful tool to assess the nature of the chemical bond in main group compounds and transition metal compounds, as well as the interaction in endohedrals. Nonetheless, a recent discussion has been placed about the path function nature of the energy components. Within EDA scheme, the interaction formation between two (or more) fragments is divided into Pauli repulsion, electrostatic interaction, and orbital interaction (for further details, see the computational section).

Table 4 shows the numerical results of the calculations where P₂ and Cₙ (n = 50, 60, 70, 80, 90, and 100) are both in singlet reference state in each fragment (see also Table S1). Thus, the P₂ species keeps...
the triple bond and the two lone pairs intact, according to the Frontier Molecular Orbitals displayed in Figure 3. The interaction energies $\Delta E_{\text{int}}$ follows the same trend as the dissociation energy ($D_n$) for the bigger fullerences (from $n = 70$ to 100). For those cases, the preparation of the fragments ($\Delta E_{\text{prep}}$) does not carry particular energy penalties as there is no significant deformation of the $P_2$ molecule or the fullerene cage upon complexation. This observation is in good agreement with the deformation analysis discussed above. Note, however, that this dissociation energy is negative for the $C_{50}$ and $C_{60}$ fullerences and the preparation energy is not negligible, that is, 25.4 and 9.0 kcal/mol, respectively.

$\Delta E_{\text{int}}$ is positive for $C_{70}$ (+65.6 kcal/mol) and decreases with the size of the cage until $C_{100}$ (−42.6 kcal/mol). The dissection of the $\Delta E_{\text{int}}$ reveals that the Pauli repulsion is a strongly destabilizing factor for smaller fullerences cages, as there is not enough space for hosting the $P_2$ molecule. As the size increases, the sum of the stabilizing interactions overcome the repulsive interaction. Interestingly, the dispersion interaction dominates the stabilization for $C_{70}$ (46.4%), $C_{60}$ (56.8%), $C_{50}$ (57.5%), and $C_{100}$ (55.5%). This observation is in good agreement with other reported systems. The second stabilizing contribution comes from the electrostatic interaction counting for 30%–40% for the stable encapsulations. The orbital interaction contributes with about ~10% for the attractive interaction and it becomes bigger for the smaller cages, namely 28.2% for $C_{50}$ and 20.7% for $C_{60}$. This small contribution of the orbital interaction term is in line with the partial charges computed in Table 4, revealing a small charge transfer from $P_2$ to the fullerences.

Table 4 also gathers the EDA results for the encapsulation of $P_4$ with $C_n$ (n = 50, 60, 70, 80, 90, and 100) in the singlet reference state. As discussed above, this process is thermodynamically unfavorable for all cases, resulting in negative dissociation energy values. The only exception is $C_{80}$ where the internal space is enough to host $P_4$ with a slightly positive $D_n$ value of 6.5 kcal/mol. Nonetheless, bigger cages $C_{90}$ and $C_{100}$ yield negative $D_n$ values as a consequence of the spheroidal shape. The preparation energy values ($\Delta E_{\text{prep}}$) suggest high energy penalties upon complexation, going from 114.5 kcal/mol ($C_{50}$) to 211 kcal/mol ($C_{80}$). In addition, the interaction energy values ($\Delta E_{\text{int}}$) reveal a destabilizing effect by the encapsulation caused by strong Pauli repulsion between the host and the guest.

5 | CONCLUSIONS

The feasibility of the encapsulation of $P_2$ in $C_n$ fullerences has been computationally assessed for cages from $n = 50$ to $n = 100$. We show fullerences $C_{70}$ to $C_{100}$ are suitable cages to incorporate $P_2$ instead of $P_4$, which is the most stable form of phosphorous. Upon inclusion of thermal and entropic effects, only the formation of endohedral $C_{40}$ to $C_{100}$ overcome the energetic penalty for the required $P_4$ dissociation into two $P_2$ dimers. Orbital analysis indicates that the triple bond in $P_2$ remains intact within the endohedral system, with very small host-guest charge-transfer. EDA shows that Pauli repulsion is roughly twice the amount of the (favorable) electrostatic interaction along the series. The dispersion energy contribution amounts to ca. −55 to −60 kcal/mol for all cages except the smallest one. From $n = 70$ on, the dispersion becomes dominant and accounts for the favorable encapsulation energies of $P_2$ in $C_{70}$ to $C_{100}$ cages.

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DATA AVAILABILITY STATEMENT

Data available in article supplementary material.

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