

## Computational Study on Cesium Azide Trapped in a Cyclopeptidic Tubular Structure

Nerina Armata,<sup>†</sup> John M. Dyke,<sup>‡</sup> Francesco Ferrante,<sup>†</sup> and Gianfranco La Manna<sup>\*,†</sup>

*Dipartimento di Chimica Fisica “F. Accascina”, Università degli Studi di Palermo, Viale delle Scienze, Parco d’Orleans II - 90128 Palermo, Italy, and School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom*

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**Abstract:** The structures and the electronic properties of host–guest complexes formed by a cyclopeptidic tubular aggregate and the species  $\text{CsN}_3$ ,  $\text{Cs}_2(\text{N}_3)_2$ , and  $\text{Cs}_2\text{N}_6$  have been investigated by means of density functional theory. Taking advantage of the azide property to act as a bridge ligand between two or more metal cations, it may be possible to trap  $\text{N}_3^-$  ions inside a confined space. This could be important for the preparation of polynitrogen molecules  $\text{N}_n$ . Results show that there are significant attractive interactions between the azide ion and the cavity walls, which make the ion stay inside the inner empty space of the cyclopeptidic aggregate. The confinement of the species  $\text{Cs}_2(\text{N}_3)_2$  forces the azide moieties to get closer together. Further, the  $\text{Cs}_2\text{N}_6$  molecule shows a remarkable interaction with the tubular host, which may indicate a stabilization of  $\text{N}_6$ .

### 1. Introduction

Azide ions are versatile ligands, which can coordinate with metal cations, either via their ends or on their sides, like, e.g., copper(II), in  $[\text{Cu}_2(\text{tetramethylethylenediamine})(\text{N}_3)(\text{OH})](\text{ClO}_4)_2$ ,<sup>1</sup> and nickel(II), in  $[\text{Ni}(\text{N}_3)_2(2,2\text{-dimethylpropane-1,3-diamine})_2]$ ,<sup>2</sup> as well as Cs and Zn in  $\text{Cs}_2\text{Zn}(\text{N}_3)_4$ .<sup>3</sup> The property of the  $\text{N}_3^-$  ion to act as a bridging ligand has been recently discovered to occur in crystals of crown ether complexes such as those formed by  $[\text{Cs}([18\text{-crown-6})(\text{N}_3)]_2]$ , where two azide ions form a bridge between two cesium cations each coordinated by crown ethers.<sup>4</sup> It would be useful to take advantage of this property in order to trap azide ions inside a confined space, which would prevent the crystallization of the metal azide, giving rise to possible high-energy releasing molecules.<sup>5</sup> We could speculate that this confined space would force two or more  $\text{N}_3^-$  ions close one to each other, promoting the formation of polynitrogen  $\text{N}_n$  clusters.

Our research group is interested in the computational study of the structural and electronic properties of open-ended organic tubular aggregates,<sup>6</sup> which can act as hosts by

encapsulating small molecules or ions. In this paper we report a computational investigation of the structures and electronic properties of the host–guest complexes formed by a cyclopeptidic tubular structure and the following guest species: one cesium azide, two cesium azides, and the  $\text{Cs}_2\text{N}_6$  molecule. There is an analogy between the system built up by two cesium azide molecules capped at each end by two crown ethers, and the system that would be formed by two cesium azide molecules inside the cavity of a tubular aggregate. In both cases the cesium ions can be coordinated by a number of oxygen atoms (ether-like in the first system, carbonylic in the second). However, inside the tubular aggregate the  $\text{N}_3^-$  ions would be in a confined region, and here could be activated with respect to the formation of a polynitrogen compound like  $\text{N}_6$ .<sup>7,8</sup>

The host species considered here is a covalent captured dimeric aggregate of the octacyclopeptide from D,L-alternated  $\alpha$ -aminoacids, *cyclo*[(L-Ala-D-MeN-Ala-L-Hag-D-MeN-Ala)<sub>2</sub>], where D-MeN-Ala is a N-methylated D-alanine residue and L-Hag indicates a residue of L-homoallylglycine. Two molecules of such a macrocycle are able to stack one on top of the other giving rise to an open-ended hollow tubular structure by the formation of eight interunit hydrogen bonds, which involve the carbonyl oxygens of one macrocycle and

\* Corresponding author e-mail: lamanna@unipa.it.

<sup>†</sup> Università degli Studi di Palermo.

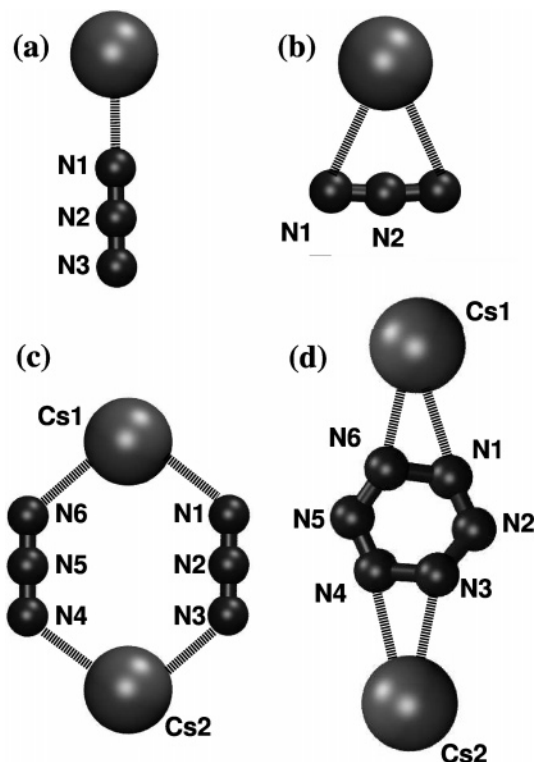
<sup>‡</sup> University of Southampton.

the complementary amidic hydrogens of the other macrocycle. The selective N-methylation of the cyclopeptide rules out the formation of aggregates larger than the dimer. In this system the homoallylglycine residues of the stacked units can react to give a covalent bridge, thus stabilizing the aggregate. The diameter of the tubular cavity is 9 Å ca., and one can estimate a cavity volume of 350 Å<sup>3</sup> if an height of 5.5 Å is considered. The space enclosed by the cavity is thus enough to host two cesium azide molecules. This system, which is very similar to that synthesized and characterized experimentally by Ghadiri et al.,<sup>9</sup> starting from the cyclopeptidic structural unit *cyclo*[(L-Phe-D-MeN-Ala-L-Hag-D-MeN-Ala)<sub>2</sub>], was chosen as a model of octacyclopeptidic tubular aggregates.

## 2. Computational Methods

The geometry optimization of all species discussed in this paper was performed by using the DFT generalized gradient functional BP86<sup>10</sup> along with the Resolution of Identity approximation (RI)<sup>11</sup> in its multipole accelerated variant.<sup>12</sup> In the RI-DFT approximation the electron density is expanded in a set of auxiliary basis functions centered on the nuclei. This procedure results in a reduction of the number of Coulomb integrals and remarkably smaller computational timing. The split valence plus polarization SV(P) basis set<sup>13</sup> was used for light atoms; a *p* function with an exponent of 0.8 has been added to the hydrogen centers, with a resultant contraction scheme of (7s4p1d/4s1p)/[3s2p1d/2s1p]. With regards to the cesium, a pseudopotential containing a polarization d function in the valence basis set was shown to give very satisfactory results on some organocesium compounds.<sup>14</sup> Since we are interested in a qualitative description of the structures of the considered systems, the Stuttgart '97 relativistic small core pseudopotential<sup>15</sup> with no polarization d function was used for cesium atoms: it describes 46 core electrons, while a basis set with the contraction scheme (7s6p)/[5s3p] is associated with the 9 valence electrons.<sup>16</sup> The harmonic approximation was used to obtain the vibrational frequencies. The calculations were performed by using the TURBOMOLE v5.7 package.<sup>17</sup>

Single point calculations on the optimized geometries were performed by using two different functionals. For comparison with our previous studies on cyclopeptides, the B3LYP hybrid functional<sup>18</sup> was used to calculate the relative energies of different conformers of the structural cyclopeptidic unit and those of the host molecule. On the other hand, in order to obtain a better description of noncovalent contributions, which can play an important role in the host–guest interactions, the interaction energies between the guests and the host molecule were calculated by using the hybrid meta functional MPWB1K.<sup>19</sup> This functional allowed estimates of the van der Waals interactions in biologically relevant systems which were much better than those obtained with the B3LYP functional,<sup>20</sup> including a better description of the dependence on the reduced density gradient in molecular regions that are important for weak interactions. In both series of calculations, the cc-pvdz basis set<sup>21</sup> was used for light atoms and the 3-21G basis set<sup>22</sup> was used for cesium. The basis set superposition error (BSSE) in the host–guest



**Figure 1.** Optimized geometries of the isolated guest molecules: (a,b) linear and side-on CsN<sub>3</sub>, (c) Cs<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>, and (d) Cs<sub>2</sub>N<sub>6</sub>. The adopted atoms labeling is reported.

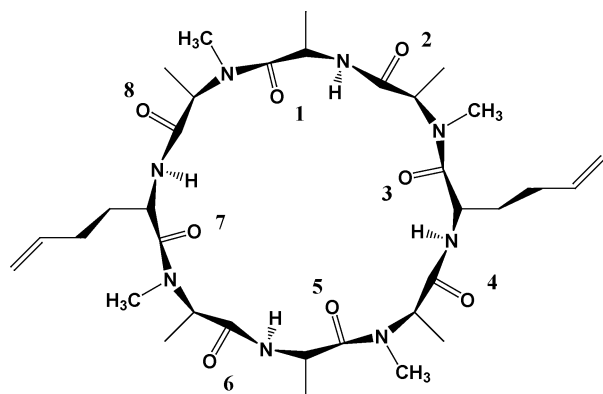
interaction energies was estimated by means of the counterpoise procedure,<sup>23</sup> taking into account also the fragments' relaxation energies. These calculations were performed by using the Gaussian 03 package.<sup>24</sup>

## 3. Results and Discussion

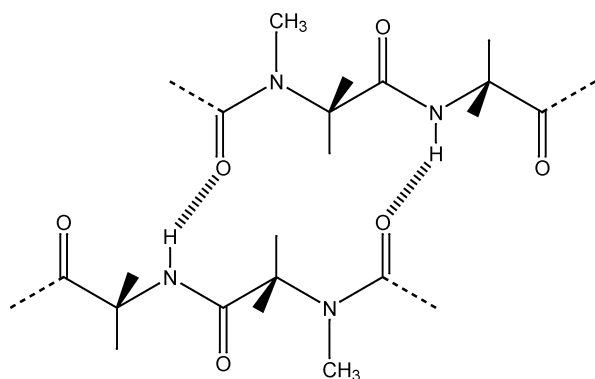
**3.1. The Guest Species.** The optimized geometries of the guest molecules are depicted in Figure 1. Experimental characterizations and computational studies have shown<sup>25</sup> that the geometry of an alkaline metal azide in the gas phase or in a nitrogen matrix depends on the size of the alkaline cation. Smaller cations (Li, Na) give rise to linear molecules, while in the case of larger cations (Rb, Cs) a side-on geometry is the most stable, because both the N terminal atoms of N<sub>3</sub><sup>−</sup> show a strong interaction with the central atom. However, the energy differences between the linear and side-on geometries, shown in Figure 1a,b, are not large enough to ultimately discriminate one form with respect to the other.

In the CsN<sub>3</sub> case the side-on geometry is 4 kJ mol<sup>−1</sup> more stable than the linear one according to the computational approaches used in the present study, a value that is intermediate between the B3LYP (1 kJ mol<sup>−1</sup>) and MP2 (11 kJ mol<sup>−1</sup>) values reported by Dyke et al.<sup>25</sup> Therefore both the linear and side-on geometries of CsN<sub>3</sub> have been considered as possible guests for the tubular system.

The molecule Cs<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> (Figure 1c) is built up with two azide ions connected by two cesium ions; it has *D*<sub>2h</sub> symmetry. To our knowledge, this species has never been characterized as an isolated system, but a similar structure



**Figure 2.** The octacyclopeptide *cyclo*[(L-Ala-D-MeN-Ala-L-Hag-D-MeN-Ala)<sub>2</sub>], the structural unit of the host molecule.



**Figure 3.** Linearized picture of the hydrogen bonds between two cyclopeptidic structural units stacked in an antiparallel fashion.

is adopted when two CsN<sub>3</sub> moieties are coordinated in the crown ether complex [Cs([18]-crown-6)(N<sub>3</sub>)<sub>2</sub>].<sup>4</sup>

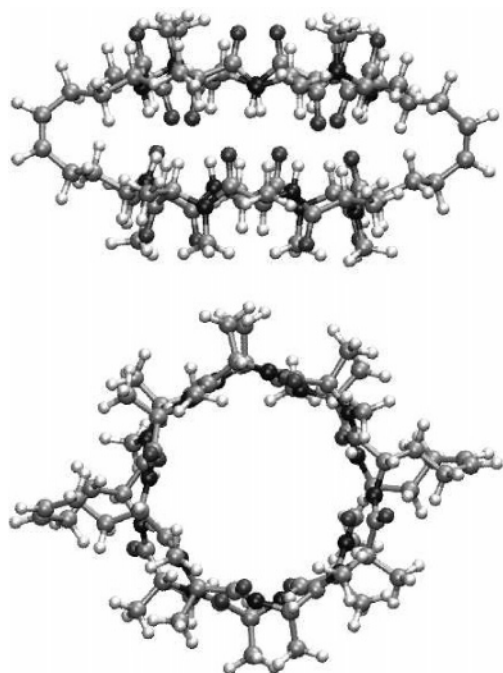
In this work, the Cs<sub>2</sub>N<sub>6</sub> molecule, containing the hexanitrogen cluster (Figure 1d), has been subjected to a number of optimizations starting from initial geometries where the conformation of the cyclic N<sub>6</sub> and/or the relative positions of the two cesium ions were different. The results showed that a minimum where the two Cs atoms are perpendicular to the N<sub>6</sub> ring does not exist, at least at this level of calculation. On the other hand, when the cesium ions lie in the plane crossing the N<sub>6</sub> ring, different conformations (planar, boat, chair) of the ring converge to the same boatlike structure, which was checked to be a minimum by the absence of imaginary frequencies. This structure has a C<sub>2</sub> symmetry axis passing through the center of the N<sub>6</sub> ring. The geometry of the N<sub>6</sub> ring in Cs<sub>2</sub>N<sub>6</sub> corresponds to that of the isolated N<sub>6</sub> with D<sub>2</sub> symmetry, which is a minimum according to refs 7 and 8 and to the optimization performed at the level of theory used here.

**3.2. The Cyclopeptide.** As a preliminary step, the geometry of the structural unit of the host molecule, *cyclo*[(L-Ala-D-MeN-Ala-L-Hag-D-MeN-Ala)<sub>2</sub>], (Figure 2) was optimized. Previous investigations<sup>26</sup> revealed that in the case of octacyclopeptides derived from D,L-alternated  $\alpha$ -aminoacids only one conformation is able to stack through hydrogen bond formation (Figure 3). The structure of this conformation has been used to build the initial guess of the cyclopeptidic backbone. The side chains of homoallylglycine (Hag),

however, can adopt different conformations. Since the stacking of the present cyclopeptide can occur only on the side without N-methylation, the only relevant conformations of the Hag side chain are those involving the dihedral angle C $\beta$ –C $\gamma$ –C $\delta$ –C $\omega$ , that is those corresponding to the rotation around the C $\gamma$ –C $\delta$  bond. The energy of the molecule has been calculated (B3LYP) by performing a scan of the above dihedral angle for only one of the Hag side chains (step=24°). An absolute minimum has been obtained at the value of –120°, with two relative minima at 0° and 120°, respectively. The value 0° for the dihedral angle has been discarded, because the Hag side chain is directed toward the N-methylated region so that this conformation could not give rise to covalent capture. The –120° and 120° values for the dihedral angle have been assigned to both the Hag residues, and the three conformers so obtained (–120,–120; –120,–120; 120,120) were fully optimized. The values –120° and 120° correspond to different conformers, because of the C<sub>4</sub> symmetry of the cyclopeptide backbone. The most stable conformation is that having the dihedral angle C $\beta$ –C $\gamma$ –C $\delta$ –C $\omega$  of –120° on both Hag side chains.

**3.3. The Host Molecule.** Under appropriate conditions, the cyclopeptide described above gives rise to a dimeric aggregate, and the presence of the homoallylglycine residues allows a covalent capture of the two structural units. In such an aggregate eight hydrogen bonds are formed, but the covalent capture reaction can occur only if the two Hag residues belonging to the different structural units are spatially superimposed one on top of the other. So, in order to arrange the initial geometry of the aggregate, two cyclopeptidic units were stacked in their most stable conformation with regards to the allylic moiety, at the correct distance for the formation of the hydrogen bonds. According to the results of the optimization of this system, the most relevant geometric distortions caused by assembling with only hydrogen-bond formation are those which allow the atoms responsible for these bonds to lie at about 90° with respect to the backbone plane. These distortions cause small variations of the values of bond angles and dihedral angles, whereas the bond lengths of the backbone are almost unaffected.

The cyclopeptidic aggregate with covalent capture (Figure 4) was built starting from the optimized geometry of the same aggregate without covalent capture and considering the product of the reaction between the side chains of the Hag residues. Ghadiri et al.<sup>9</sup> characterized three different conformations for this kind of system. Therefore, the geometry optimization has been performed for the cis–cis, trans–cis, and trans–trans stereoisomers around the double bonds in both sides of the aggregate. The most important difference that can be seen from the structural analysis of these isomers is the difference in lengths of the eight hydrogen bonds, whose values are reported in Table 1. In particular, taking the hydrogen bond lengths in the aggregate with no covalent capture as reference values, a reasonable shortening (0.1 Å) of the four hydrogen bonds close to the covalent capture region is observed in the cis–cis isomer. In the trans–cis form there is a similar shortening for the hydrogen bonds close to the region where the capture is of cis-type, while



**Figure 4.** The optimized geometry of the host molecule with covalent bridge, from two different perspectives.

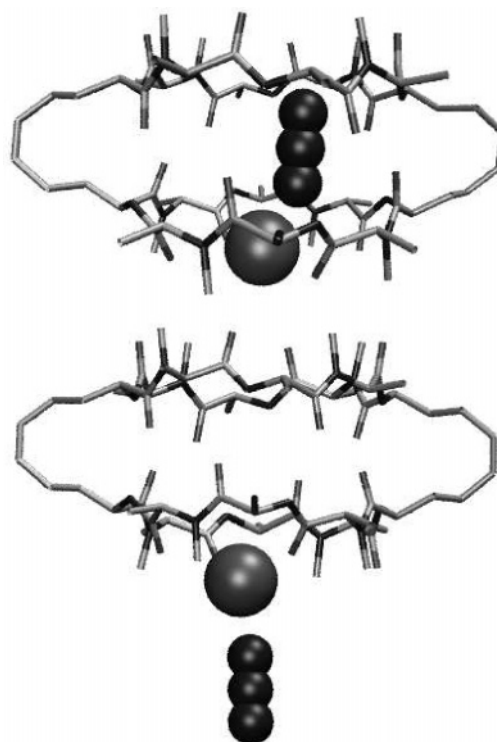
**Table 1.** Hydrogen Bond Lengths (Å) in the Host without Covalent Capture and in the Three Conformations of the Host with Covalent Capture (CC)

H bond	host	host CC cis–cis	host CC cis–trans	host CC trans–trans
1	1.913	1.824	1.832	2.001
2	1.912	1.918	1.930	1.868
3	1.913	1.921	1.859	1.884
4	1.913	1.815	1.972	1.987
5	1.910	1.821	2.003	1.963
6	1.911	1.909	1.862	1.854
7	1.912	1.932	1.918	1.858
8	1.914	1.821	1.831	1.992

the other two hydrogen bonds, in the trans capture zone, are longer by 0.1 Å. Finally, in the trans–trans isomer all four H-bonds in the covalent capture zone are longer than those placed where the capture is not present. Total energy values of trans–cis and trans–trans isomers are 9.5 and 14.5 kJ mol<sup>−1</sup>, respectively, larger than the total energy of the cis–cis form (B3LYP results). This can be explained by considering that a covalent bridge in the trans conformation gives rise to a ring strain which disfavors the formation of hydrogen bonds. As a result, the cis–cis isomer of the covalent-captured cyclopeptidic aggregate was used here as a host molecule.

**3.4. CsN<sub>3</sub>@host.** For this system it is possible to propose two starting geometries: one where the cesium atom is coordinated to the carbonyl oxygens not involved in H-bond formation and the azide ion is outside the cavity of the host, and another where the cesium is coordinated the same way but the azide is placed inside the cavity (Figure 5). Both systems were subjected to geometry optimization.

**3.4.1. Linear Form of CsN<sub>3</sub>.** A geometric distortion of the host which enables the approach of the oxygen atoms to



**Figure 5.** The optimized geometries of the CsN<sub>3</sub>@host (a) and CsN<sub>3</sub>\_out\_host (b) complexes. The CsN<sub>3</sub> guest is emphasized.

**Table 2.** Cesium–Oxygen Distances (Å) in the Host–Guest Complexes

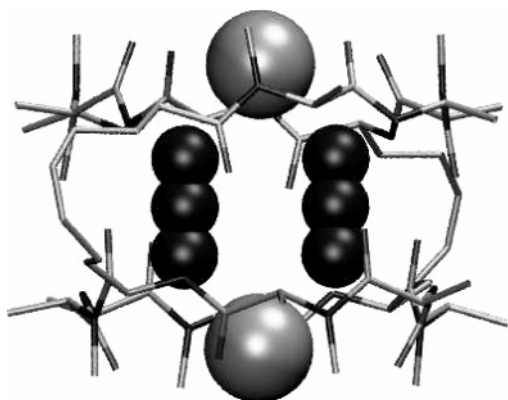
	CsN <sub>3</sub> @	CsN <sub>3</sub> out	Cs <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> @	Cs <sub>2</sub> N <sub>6</sub> @(I)	Cs <sub>2</sub> N <sub>6</sub> @(II)
Cs1...O2a <sup>a</sup>	4.589/ 4.213 <sup>c</sup>	5.504	4.058	4.592	4.605
Cs1...O4a	3.361/ 3.347	3.329	3.507	3.456	3.388
Cs1...O6a	3.524/ 3.443	3.501	3.713	3.413	3.477
Cs1...O8a	3.532/ 3.405	3.409	3.571	3.441	3.432
Cs2...O2b <sup>b</sup>			4.222	4.602	4.603
Cs2...O4b			3.687	3.476	3.502
Cs2...O6b			3.604	3.390	3.477
Cs2...O8b			3.541	3.432	3.441

<sup>a</sup> Refers to the terminal carbonylic oxygens of the first structural unit. <sup>b</sup> Refers to the terminal carbonylic oxygens of the second structural unit. <sup>c</sup> CsN<sub>3</sub> with end-on geometry on the left, with side-on geometry on the right.

cesium was observed, as a result of the variations of the dihedral angles around the peptidic bonds in the two structural unit backbones. This distortion leads the cesium ion to be placed at 3.3–3.5 Å from three of the four oxygen atoms. Values for the Cs–O distances, shown in Table 2 along with the Cs–O distances in the other host–guest systems, are on average 0.4 Å longer than those evaluated by X-ray diffraction experiments in the [Cs([18]-crown-6)-(N<sub>3</sub>)<sub>2</sub>] complex and are in good agreement with those obtained by calculations at the same level of accuracy on that system.<sup>4</sup>

When the cesium azide is inside the cavity it loses its linear geometry, with the Cs–N–N angle equal to 150.7°. The distortion from linearity is attributable to the interaction between the azide ion and the internal walls of the cavity,





**Figure 6.** The optimized geometry of the  $\text{Cs}_2(\text{N}_3)_2$ @host complex. The  $\text{Cs}_2(\text{N}_3)_2$  guest is emphasized.

to which the azide group gets close. Further, when the azide is outside of the cavity there is only a negligible loss of linearity, with a  $\text{Cs}-\text{N}-\text{N}$  angle of  $172.5^\circ$ . In both systems, the  $\text{Cs}-\text{N}$  bond length is increased with respect to isolated  $\text{CsN}_3$  (by  $0.2 \text{ \AA}$  when  $\text{N}_3$  is inside the cavity, by  $0.1 \text{ \AA}$  when it is outside), whereas there are no significant variations of the  $\text{N}-\text{N}$  bond lengths. The interaction energy values (MPWB1K results), corrected for BSSE, are  $-77.5 \text{ kJ mol}^{-1}$  when the azide is inside the cavity,  $-69.2 \text{ kJ mol}^{-1}$  when it is outside.

**3.4.2. Side-On Geometry of  $\text{CsN}_3$ .** The geometry of the system formed by  $\text{CsN}_3$  having side-on geometry inside the tubular aggregate was also optimized. An inspection of Table 2 reveals a slightly larger distortion of the cyclopeptidic backbone, driven by the dragging of oxygen atoms toward the cesium, which is more positively charged than in the previous linear case. The  $\text{N}_3$  moves toward the cavity walls, placing its two N terminal atoms at  $3.02$  and  $3.28 \text{ \AA}$  from two carbonyl carbon atoms, respectively. The increase of the  $\text{Cs}-\text{N}$  bond length is about  $0.2 \text{ \AA}$  on either side, whereas the  $\text{N}-\text{N}$  bond lengths are essentially unchanged. The interaction energy is  $-72.8 \text{ kJ mol}^{-1}$ .

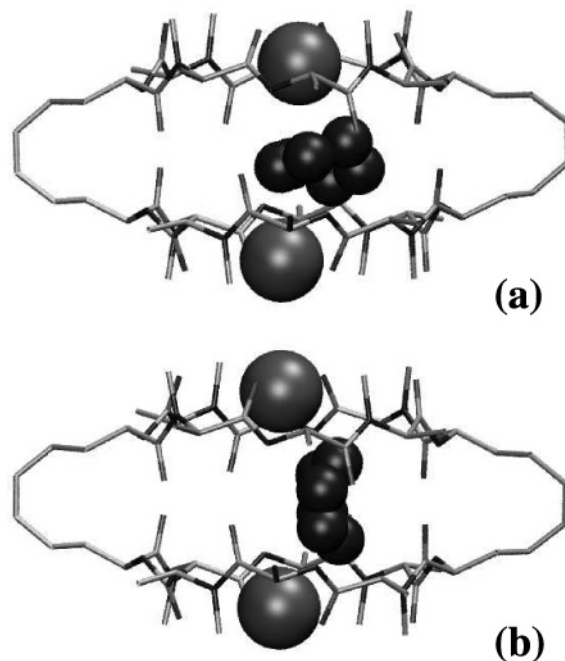
**3.5.  $\text{Cs}_2(\text{N}_3)_2$ @host.** The next step was to build the system formed by the cyclopeptidic structure as the host and two  $\text{CsN}_3$  molecules inside it. The initial geometry of the  $\text{Cs}_2(\text{N}_3)_2$  moiety was that obtained from the optimization of the isolated molecule. Two cesium ions were placed along the longitudinal axis of the aggregate, each one in the perpendicular plane passing through the terminal oxygen atoms. Once the full optimization was performed, the structure of the host molecule shows the same geometrical distortions found in  $\text{CsN}_3$ @host, namely the oxygen atoms get closer to the cesium ion, on both terminal sides (Figure 6). The two azide ions are placed almost exactly at the center of the cavity.

The most relevant issue is that, inside the cavity, the two azide ions are closer to each other (by  $1.1 \text{ \AA}$ ) than they are in the isolated  $\text{Cs}_2(\text{N}_3)_2$  species (see the comparison in Table 3). This phenomenon must be due to the increase of the  $\text{Cs}-\text{Cs}$  distance ( $> 1 \text{ \AA}$ ), caused by  $\text{Cs}-\text{O}$  interactions, along with the influence of the confined space in which the two  $\text{N}_3^-$  ions are trapped. Since changes are not observed in the  $\text{Cs}-\text{N}$  distances or in the  $\text{N}-\text{N}$  bond lengths, the increase of the  $\text{Cs}-\text{Cs}$  distance causes a decrease of the  $\text{N}-\text{Cs}-\text{N}$  angle,

**Table 3.** Optimized Geometric Parameters ( $\text{\AA}$ ) of Isolated  $\text{CsN}_3$  and  $\text{Cs}_2(\text{N}_3)_2$  and of Trapped  $\text{Cs}_2(\text{N}_3)_2$  and XRD Values of the  $\text{Cs}_2(\text{N}_3)_2$  Moiety in the  $[\text{Cs}(\text{[18]crown-6})(\text{N}_3)_2]$  Complex<sup>a c</sup>

	$\text{CsN}_3$	$\text{Cs}_2(\text{N}_3)_2$	$\text{Cs}_2(\text{N}_3)_2$ @	crown complex
$\text{Cs1}\cdots\text{Cs2}^a$	-	5.910	7.031	4.679 (4.982)
$\text{Cs1}-\text{N1}$	2.733/3.077 <sup>b</sup>	3.004	3.003	3.244 (3.197)
$\text{N1}-\text{N2}$	1.209/1.191	1.194	1.194	1.179 (1.201)
$\text{N2}-\text{N3}$	1.185/1.191	1.194	1.194	1.179 (1.189)
$\text{N3}-\text{Cs2}$	-	3.004	3.003	-
$\text{N1}\cdots\text{N6}$	-	4.801	3.726	-

<sup>a</sup> See Figure 1 for atom labeling. <sup>b</sup> Linear geometry on the left, side-on geometry on the right. <sup>c</sup> Calculated values in parentheses.



**Figure 7.** The optimized geometries of the  $\text{Cs}_2\text{N}_6$ @host complexes: I form (a) and II form (b). The  $\text{Cs}_2\text{N}_6$  guest is emphasized.

so that the two azides get closer. It is noteworthy that the species  $\text{Cs}_2(\text{N}_3)_2$  maintains its  $D_{2h}$  symmetry inside the cavity, probably because of the local  $C_4$  symmetry of the cavity itself. The interaction distances between the terminal N atoms of the azide groups and the carbonyl C atom of the cavity walls are between  $2.80$  and  $3.01 \text{ \AA}$ , a range that is slightly lower than the one calculated in the  $\text{CsN}_3$ @host case. The interaction energy, computed by using the MPWB1K functional on the optimized geometries and corrected for BSSE, is  $-40.3 \text{ kJ/mol}$ .

**3.6.  $\text{Cs}_2\text{N}_6$ @host.** The last system investigated is composed of the  $\text{N}_6$  cyclic boatlike polynitrogen species inside the host cavity, with two cesium atoms coordinated to the carbonylic oxygens. Starting from two slightly different geometries, two positions for the trapped  $\text{N}_6$  have been obtained. In the first of these, (I) (Figure 7a), the plane which crosses the  $\text{N}_6$  cycle is parallel to the stacking axis of the cyclopeptidic aggregate; in the second one, (II) (Figure 7b), that plane is perpendicular to this stacking axis. In both cases, the polynitrogen moves toward the cavity walls. By comparing the geometry of the isolated  $\text{N}_6$  with that adopted inside

**Table 4.** Optimized Geometric Parameters of Isolated and Trapped  $\text{Cs}_2\text{N}_6$ <sup>b</sup>

	$\text{N}_6$	$\text{Cs}_2\text{N}_6$	$\text{Cs}_2\text{N}_6@(\text{I})$	$\text{Cs}_2\text{N}_6@(\text{II})$
$\text{Cs1}\cdots\text{Cs2}^a$		7.880	6.361	7.063
N1–N2	1.308	1.280	1.412	1.396
N2–N3	1.308	1.347	1.432	1.277
N6–N1	1.370	1.460	1.279	1.418
Cs1–N6		2.911	3.395	3.185
Cs1–N1		3.005	3.457	2.958
Cs1–N5		4.057	3.112	4.345
Cs1–N2		4.270	3.326	3.554
N4–N5			1.404	1.394
N5–N6			1.426	1.277
N3–N4			1.271	1.418
Cs2–N3			3.123	3.170
Cs2–N4			3.123	2.957
Cs2–N5			3.123	3.682
Cs2–N2			3.168	4.372
N1–Cs1–N6		28.5	21.5	26.3
N6–N1–N2	111.3	116.2	117.9	117.2
N1–N2–N3	125.0	119.2	117.2	117.1
N2–N3–N4	111.3	110.3	107.3	108.3
N4–Cs2–N3			17.2	24.4
N3–N4–N5			117.5	117.1
N4–N5–N6			117.8	117.3
N5–N6–N1			116.8	108.4
Cs1–N6–N1–N2		172.7	62.0	–155.1
N6–N1–N2–N3	–22.1	9.3	42.2	44.2
N2–N3–N4–N5	42.9	34.2	2.0	–45.3
Cs2–N3–N4–N5			–88.5	109.9
N3–N4–N5–N6			44.2	44.0
N5–N6–N1–N2			3.6	–45.4

<sup>a</sup> See Figure 1 for atom labeling. <sup>b</sup> The geometric parameters of the isolated  $\text{N}_6$  cluster ( $D_2$  symmetry), optimized at the same level of theory used here, are reported for comparison. Lengths in Å, angles in deg.

the cavity (Table 4), a decrease of the Cs–Cs distance is observed, which is more marked in (I); further, in the three cases investigated here, isolated  $\text{Cs}_2\text{N}_6$  and trapped  $\text{Cs}_2\text{N}_6$  with I and II geometries, the cyclic polynitrogen has different positions with respect to the axis passing through the two cesium atoms, while maintaining the boatlike structure. In both I and II systems the Cs–O distances are very similar (Table 1), even if in I the cesium atoms lie much more inside the cavity. The interaction energies, corrected for BSSE, are  $-126.9 \text{ kJ mol}^{-1}$  and  $-84.6 \text{ kJ mol}^{-1}$  for I and II, respectively. The distances between the atoms involved in the interaction (N of the polynitrogen and carbonylic carbons) are in the range 3.0–3.2 Å in I and 3.2–3.5 Å in II. Although these distances from the cavity walls are greater than those existing in  $\text{Cs}_2(\text{N}_3)_2@ \text{host}$ , the interaction energies are 2–3 orders of magnitude higher. This seems to indicate an intrinsic stabilization of  $\text{Cs}_2\text{N}_6$  inside the cavity of the cyclopeptidic aggregate.

In order to evaluate the energy of the fragmentation of the  $\text{N}_6$  polynitrogen to three  $\text{N}_2$  molecules inside the cavity, the system  $\text{Cs}_2(\text{N}_2)_3@ \text{host}$ , where the Cs atoms are coordinated to the carbonylic oxygen atoms and the three  $\text{N}_2$  molecules are inside the cavity of the cyclopeptidic system, has been subjected to geometry optimization and single point energy calculation. The results obtained indicate that the

conversion from I to  $\text{Cs}_2(\text{N}_2)_3@ \text{host}$  should release  $296 \text{ kJ mol}^{-1}$  of energy.

## 4. Conclusion

The present study is intended to suggest a new strategy which gives rise to the confinement of azide ions with the aim of producing polynitrogen compounds, which could be interesting high-energy molecules. In the case investigated, involving the confinement of cesium azide units in a cyclopeptidic tubular structure, the azide ions lie inside the cavity of the host molecule, with the cesium ion coordinated to three carbonylic oxygen atoms of the host. When the  $\text{Cs}_2(\text{N}_3)_2$  species is enclosed in the cavity, the two azide ions are in close proximity, and they may, as a result, be activated to form the polynitrogen species  $\text{N}_6$ , which could be stabilized in the cyclopeptidic tubular aggregate. Further investigations are currently in progress concerning the interconversion from  $\text{Cs}_2(\text{N}_3)_2$  to  $\text{Cs}_2\text{N}_6$  inside the host cavity. A possible way to prepare these complexes might involve cocondensation of cesium azide and the cyclopeptide units and the characterization of the products with spectroscopic methods.

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