Stabilization of the C_{20} cage by encapsulation of H^+ and He^{2+} ions

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It is shown by *ab initio* calculations using second-order Møller–Plesset perturbation theory and 6-31g*, aug-cc-pVDZ and aug-cc-pVTZ basis sets and coupled cluster singles, doubles and perturbative triples method with the 6-31g* basis set, that it is possible to stabilize the cage structure of the smallest fullerene C_{20} by encapsulating small cations like H^+ and He^{2+}. While the latter stabilizes the cage structure by charge transfer, the former prefers to form a covalent linkage with the carbon atoms.

Keywords: Atoms-in-molecules, encapsulation of protons, fullerene, natural bond orbital, perturbation theory.

Introduction

There has been a lot of interest in the cage structures of carbon since the discovery of C_{60}, buckminsterfullerene[1]. The C_{20} cluster is the smallest size cage that can be formed by fused pentagons. Small fullerenes have been proposed as possible intermediates to the formation of C_{60} or larger fullerenes and hence their stability has been the subject of investigation for some time[2–4]. Experiments conducted by Bowers and co-workers[5,6] and Hunter *et al.*[7] suggested that a monocyclic ring structure is dominant for carbon clusters containing 11–30 atoms. Several high-quality *ab initio* calculations have been carried out over the years to examine the relative stability of the different isomers of C_{20}. The results of the theoretical studies, unfortunately, are very much dependent on the level of theory and the choice of basis set. Recent studies at coupled cluster singles, doubles and perturbative triples (CCSD(T)) and Møller–Plesset fourth-order perturbation (MP4) theory levels suggest that the bowl structure is perhaps the most stable conformer of C_{20} followed by the cage and the ring[8].

Cross *et al.*[9] succeeded in capturing a helium atom inside the dodecahedrane ($C_{20}H_{20}$) cage by shooting a beam of helium ions at a continuously deposited surface of dodecahedrane. Chen *et al.*[10] investigated theoretically the geometries and energetics of several endo- and exohedral complexes of dodecahedrane with neutral atoms as well as their isoelectronic charged analogs. Prinzbach *et al.*[11] studied the gas-phase production and photoelectron spectroscopy of the smallest fullerene C_{20}. There are a few theoretical studies reported on endohedral C_{20} fullerene complexes in the literature[12,13]. Therefore, it was considered worthwhile to study the conditions under which the cage structure of C_{20} could be stabilized. Preliminary studies revealed that $He@C_{20}$ may not be stable. Hence, the stability of $H^+@C_{20}$ (complex A), $2H^+@C_{20}$ (complex B), $3H^+@C_{20}$ (complex C) and $He^{2+}@C_{20}$ (complex D) was examined.

Methodology

All the calculations were performed using the Gaussian 03 suite of programs[14]. Geometry optimization calculations for all the complexes were carried out at the Møller–Plesset second-order perturbation theory (MP2) level, using the 6-31g* basis set without imposing any symmetry constraint. Vibrational frequency calculations were carried out at the same level of theory to ensure that the geometries obtained correspond to true minima. Subsequently, single-point energy calculations were performed using aug-cc-pVDZ and aug-cc-pVTZ basis sets at the MP2 level of theory. Since the CCSD(T) computations with large basis sets (aug-cc-pVDZ/TZ) are formidable for the given system size, it is a standard practice to estimate the energy at the CCSD(T)/aug-cc-pVTZ level using the energy value at the MP2/aug-cc-pVTZ level and by computing the difference between the energy values at CCSD(T)/'small-basis-set' and MP2/'small-basis-set' levels. The 6-31g* basis set has been chosen as the 'small basis set' in the present study.

A potential energy surface scan was performed for the approach of He^{2+} and H^+ along the axis defined by the geometrical centre of the C_{20} cage and the centre of one of the pentagonal faces of the cage. Wave functions were generated from the Gaussian output files for a topological analysis of the electron density according to

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'atoms-in-molecules' (AIM)[15] quantum theory using the AIM2000 program[16]. The natural bond orbital (NBO) analysis was carried out to examine the charge transfer process[17,18]. The nucleus independent chemical shift (NICS) was calculated at the geometrical centre, i.e. the origin of the reference, of each of the complexes to ascertain the aromatic character of the complex[19]. Stabilization energy (ΔE_s) values for each of the complexes were computed as the difference between the energy of the complex ($E_{complex}$) and that of the cage (E_{cage}): $\Delta E_s = E_{complex} - E_{cage}$. The basis set superposition error (BSSE) was estimated using the counterpoise correction method of Boys and Bernardi[20]. The error was calculated considering the cage as one fragment and the protons (one or two or three) or the doubly charged helium ion as the second fragment. The cage deformation energy (E_{def}) was obtained as the difference between the energy of the cage in the complex and that of the empty cage.

Results and discussion

Earlier *ab initio* calculations showed that a proton could form a π-complex with the benzene ring and could go through the centre of the molecule without facing any barrier[21]. It was found to be valid for the motion of a proton through a pentagonal or a hexagonal face of C_{60} as well[22].

A potential energy scan for the motion of a proton through any one of the pentagonal faces of C_{20} showed that it faced no barrier as the maximum energy that it experienced at the centre of the pentagonal face was below the energy corresponding to the proton separated asymptotically from C_{20}, as shown in Figure 1. The covalently bonded exohedral complex is not predicted by the scan, but it is obtained as an off-centre minimum at 1.19 Å away from the nearest carbon atom. It is clear from Figure 1 that H^+ experiences a maximum at the centre of the cage and a minimum at an off-centre endohedral geometry. A similar scan for He^{2+} approaching C_{20} also does not produce any minimum for the exohedral complex, but a minimum corresponding to the endohedral complex could be found exactly at the centre of the cage (Figure 1).

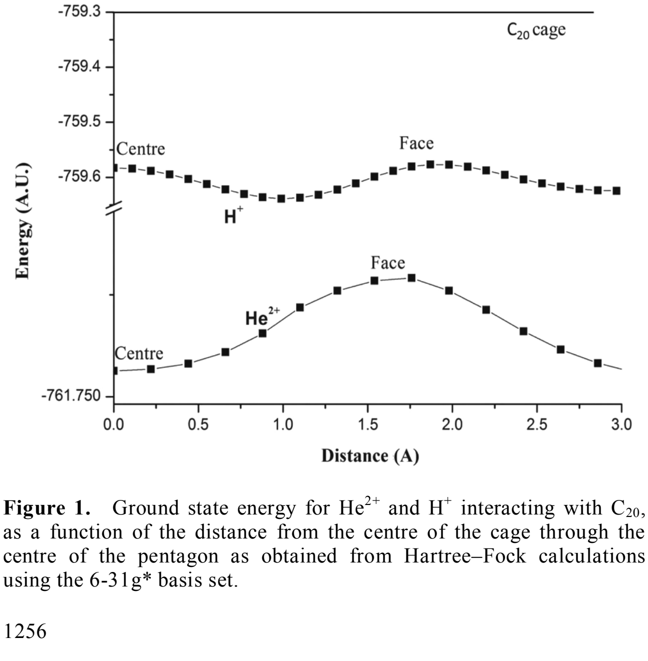

Figure 1. Ground state energy for He^{2+} and H^+ interacting with C_{20}, as a function of the distance from the centre of the cage through the centre of the pentagon as obtained from Hartree–Fock calculations using the 6-31g* basis set.

From the potential energy scan it was anticipated that more than one proton could be accommodated inside the C_{20} cage. Hence, the geometries of H^+ (complex A), $2(H^+)$ (complex B), $3(H^+)$ (complex C) and He^{2+} (complex D) encapsulated C_{20} cages were computed. Placing more than 3 (H^+) inside the cage turned out to be highly endothermic in nature. All the ionic species formed stable endohedral complexes with C_{20}, as shown in Figure 2 *a*. All of them were found to be true minima in the potential energy surface. The stabilization energy values are listed in Table 1. It must be pointed out that He^{2+} stabilizes the cage ten times more than H^+, $2(H^+)$ or $3(H^+)$. Naively, one could have expected the interaction energy to increase linearly with an increase in the number of H^+ getting encapsulated inside the cage. The protons would naturally repel each other. In addition, there is some indication of a weak H_2^+ and a strong H_3^+ formation inside the cage (see below). As a result, complex B is marginally more stable than complexes A and C.

All the endohedral complexes of C_{20} retain the cage structure, though all of them result in deformation. The deformation energy (ΔD) varies from 0.38 eV for A to 0.73 eV for B, 1.09 eV for C and 0.73 eV for D. He^{2+} occupies the centre of the cage, whereas H^+ prefers an off-centre position. The latter was found closer to two carbon atoms than the rest of the carbon atoms and is 1.19 Å away from the nearest carbon atom. When two protons were encapsulated, they were found to occupy opposite sides of the cage. They were also close to two carbon atoms with a C–H distance of 1.19 Å. When $3H^+$ ions were encapsulated, they came closer and formed a molecular cluster at the centre of the cage. The protons were 0.76–1.80 Å away from the carbon atoms.

The results of Mulliken population analysis and natural population analysis carried out for all the endohedral complexes are presented in Table 2. It is clear from the results that the charge transfer from He^{2+} to the cage is nearly complete. There seems to be a neutral He atom with +2 charge distributed over the entire C_{20} cage. The $H^+@C_{20}$ complex retains some positive charge on H.

A great deal of information about the nature of bonding in a molecule or a complex can be obtained from a topological analysis of the electron density. In the complex D, there are 20 bond critical points (BCPs) connecting the ion to the cage, while there are only two and four BCPs connecting the H^+ to one and two pairs of carbon atoms in complexes A and B respectively, as shown in

Table 1. Stabilization energy (ΔE_s) values (eV) obtained for the endohedral complexes A–D using MP2 level of theory and different basis sets and CCSD(T) level of theory with the 6-31g* basis set

Complex	ΔE_s (MP2) 6-31g*	ΔE_s (MP2) aug-cc-pVDZ	ΔE_s (MP2) aug-cc-pVTZ	ΔE_s (CCSD(T)) 6-31g*	ΔE_s (est. CCSD(T)) aug-cc-pVTZ
A	–4.93	–5.24	–5.35	–5.15	–5.57
B	–5.12	–6.02	–6.19	–5.31	–6.38
C	–3.96	–6.13	–6.23	–3.01	–5.28
D	–57.58	–58.31	–58.46	–57.00	–57.88

Table 2. Mulliken and natural population analysis (NPA) of the endohedral complexes

Structure	Mulliken charge on X	Mulliken charge on C	NPA charge on X	NPA charge on C
A	0.346	–0.040, –0.040	0.514	–0.073 and –0.074
B	0.297	0.028 on all four carbons	0.471	0.004 for all four carbons
C	–0.051	0.14 to 0.16	0.12	0.12 for near-C atoms
D	0.010	0.100	0.000	0.100

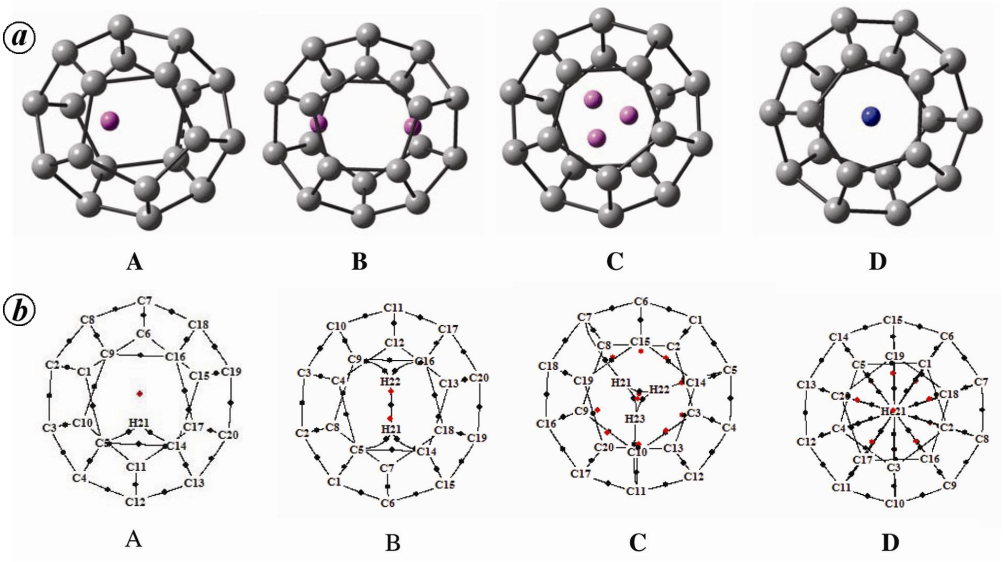

Figure 2. ***a***, Optimized geometries of H^+ (A), $2H^+$ (B), $3H^+$ (C) and He^{2+} (D) inside the C_{20} cage. ***b***, Bond critical points are shown in black and the cage critical points are shown in red.

Figure 2 *b*. In complex C, there are only three BCPs connecting the ions to the cage. There are only one and two symmetrically displaced cage critical points (CCPs) in complexes A and B, respectively. In contrast, 12 cage critical points are found in the complexes C and D. The He^{2+} ion forms a pentagonal cone with each of the 12 pentagonal faces. Clearly, the protons interact locally with the two (and four) carbon atoms. Even $3H^+$ ions interact with the cage locally, but He^{2+} interacts with the entire cage. The electron density (ρ) and the Laplacian of the electron density ($\nabla^2\rho(r)$) values at the bond critical points give us information about the nature of bonding. In complexes A and B, negative values of $\nabla^2\rho(r)$ at the BCPs connecting the proton(s) and the carbon atoms of the cage indicate a covalent interaction (Table 3). The complex C shows a closed shell interaction with the cage, as is evident from the positive values of $\nabla^2\rho(r)$ at the BCPs. The complex D is characterized by a small ρ and a positive $\nabla^2\rho(r)$, indicating a non-covalent interaction. In complex B, a BCP is found to exist between the two H atoms. The interaction between them is weak and non-covalent. In complex C, three BCPs exist between the three H atoms. The ellipticity value, defined as $\varepsilon = ((\lambda_1/\lambda_2) - 1)$, suggests the cylindrical nature of the electron density in the bond path. It is close to zero for $He^{2+}@C_{20}$, but it deviates largely for the protonated C_{20} complexes, indicating the participation of π electrons in bonding in complexes A and B.

The concept of aromaticity, first introduced for planar conjugated systems like benzene, is associated with high chemical stability. It is extended to three-dimensional delocalized systems with nearly spherical symmetry like fullerenes. The NICS value at the geometrical centre of a molecule provides a simple and efficient magnetic criterion of aromaticity. According to the NICS values listed in Table 3, the cage encapsulating protons shows aromaticity comparable to that of benzene[23], but He^{2+} encapsulation increases its aromaticity by an order of magnitude.

The natural bond orbital (NBO) analysis reveals the role of intermolecular orbital interaction in the endohedral complex, particularly the charge transfer. This is carried out by considering all possible interactions between the filled donor and the empty acceptor NBOs and estimating their importance by the second-order perturbation theory. For each donor NBO (*i*) and acceptor NBO (*j*), the stabilization energy (E_2) value associated with electron delocalization between the donor and the acceptor is estimated as

$$E_2 = -q_i \frac{(F_{ij})^2}{\varepsilon_j - \varepsilon_i}, \tag{1}$$

where q_i is the orbital occupancy, ε_j and ε_i are the diagonal elements and F_{ij} is the off-diagonal NBO Fock matrix element. The amount of charge transfer (Q_{CT}) is estimated using the following approximation

$$Q_{\text{CT}} = q_i \left(\frac{F_{ij}}{\varepsilon_j - \varepsilon_i} \right)^2. \tag{2}$$

Table 3. AIM parameters and NICS values for the endohedral complexes A–D

Species	Nature of critical point	$\rho(r)$	$\nabla^2\rho(r)$	Ellipticity (ε)	NICS (ppm)
A	b_1^a	0.217	–0.14	5.458	–14.16
	b_2^a	0.217	–0.14	5.216	
	c_1^b	0.008	0.028	–0.250	
B	b_3^c	0.221	–0.144	7.598	–18.88
	b_4^c	0.221	–0.148	6.612	
	b_5^d	0.221	–0.144	6.848	
	b_6^d	0.221	–0.144	7.327	
	b_7^e	0.013	0.036	6.449	
	c_2^f	0.012	0.044	–0.544	
	c_3^f	0.012	0.044	–0.544	
C	b_8^g	0.076	0.192	1.66	–82.62
	b_9^g	0.080	0.188	0.108	
	b_{10}^g	0.078	0.188	0.483	
	b_{11}^h	0.234	–0.384	2.53	
	b_{12}^h	0.234	–0.38	2.68	
	b_{13}^h	0.234	–0.388	2.44	
	c_4^i	0.039	0.208	–0.422	
D	b_{14}^j	0.034	0.216	0.006	–116.64
	c_5^k	0.028	0.184	–0.002	

[a]BCPs connect H^+ to C atoms labelled 5 and 14 respectively. [b]Only CCP in complex A. [c]BCPs connect H^+ to C atoms labelled 5 and 14 respectively. [d]BCPs connect H^+ to C atoms labelled 9 and 16 respectively. [e]BCP that connects the two H^+ ions. [f]Two CCPs in complex B. [g]BCPs connect H^+ to C atoms labelled 7, 5 and 11. [h]BCPs that exist among three H^+ ions in complex C. [i]One of the 12 CCPs found in the complex. All other CCPs have similar properties. [j]BCP connects He^{2+} with the C atom labelled 20. All the other BCPs are similar to this BCP in properties. [k]CCP in the cage formed by He^{2+} with one of the pentagonal faces containing the C atom labelled 20. All the other CCPs have similar properties.

From the values listed in Table 4, it is clear that the species A and B attain large stabilization by charge transfer between carbon p and hydrogen n*. This can account for the covalent bond formation between the H^+ and the carbon atoms of the C_{20} cage. It is interesting to note that the stabilization energy value due to charge transfer between the C and the H atoms increases by almost 10 eV when two H^+ ions are incorporated instead of a single H^+. The charge transfer in B for the two protons is not independent of each other. It is cooperative in nature, as it becomes evident from the AIM analysis. In spite of this huge stabilization, A and B experience a repulsive interaction between the partially positive cage and the protons, keeping the overall stability of the endohedral complex to the order of 5 eV. When 3 H^+ ions are encapsulated in the C_{20} cage, they form a cluster by themselves and there is a weak closed shell interaction with the cage. Hence it shows comparatively low E_2 and Q_{CT} values. A similar complex has been observed for C_{60} fullerene[24]. The interaction between He^{2+} and the carbon atoms of the C_{20} cage in D is also electrostatic in nature, as can be inferred from the very low E_2 and Q_{CT} values.

The geometry, stability and bonding of corresponding exohedral complexes of A, B and D were also analysed. The protons have been found to form stable new species like $C_{20}H^+$ and $C_{20}H_2^{2+}$, as is evident from both NBO and AIM calculations. He^{2+} shows electrostatic attraction even at a large distance of 3.28 Å from the face, with a complete charge transfer to the cage. It is worth mentioning that the results obtained for the exohedral complexes are preliminary.

Summary and conclusion

The possibility of stabilizing the C_{20} cage by encapsulating H^+ and He^{2+} ions has been examined theoretically. It is found that He^{2+} stabilizes the cage by charge transfer, while the protons prefer to form a π-complex. Three encapsulated protons behave like an independent molecular cluster inside the cage. It is worth emphasizing that a He atom inside the cage does not stabilize it due to large repulsion ($\Delta E = 2.9$ eV). However, He^{2+} encapsulation is highly favourable. As a matter of fact, the charge transfer makes the cage aromatic in nature. Considering the first and second ionization potentials of C_{20} (6.59 and 11.56 eV respectively)[25] and He (24.59 and 54.42 eV respectively), it becomes clear that $He^{2+} + C_{20} \rightarrow He + C_{20}^{2+} + 60.86$ eV. Similarly, $H^+ + C_{20} \rightarrow H + C_{20}^{+} + 7.01$ eV.

Table 4. Results of second-order perturbation theory analysis of the Fock matrix within the NBO basis for the endohedral complexes. The label for the donor carbon is mentioned in parentheses

Structure	Donor orbital	Acceptor orbital	E_2 (eV)	$\varepsilon_j - \varepsilon_i$ (eV)	F_{ij} (eV)	Q_{CT} (eV)
A	p(C5)	n*(H^+)	29.240	5.170	10.232	104.957
	p(C14)	n*(H^+)	29.293	5.170	10.259	105.528
B	p*(C5)	n*(H^+)	39.84	4.082	10.722	171.027
	p(C14)	n*(H^+)	39.936	4.082	10.749	172.089
	p(C9)	n*(H^+)	39.909	4.082	10.749	172.089
	p*(C16)	n*(H^+)	39.867	4.082	10.722	171.027
C	σ(C7-C18)	n*(H^+)	0.310	20.953	2.286	0.544
	σ (C1-C5)	n*(H^+)	0.266	20.953	2.123	0.544
	σ (C11-C17)	n*(H^+)	0.294	20.953	2.231	0.544
D	p*(C20)	n*(He^{2+})	0.013	60.411	0.925	0.006

Hence, about nine times more energy is released when He^{2+} is encapsulated. This accounts for the extraordinary stability of the complex D over all other complexes considered. A bare proton will not only be trapped inside the cage, but is also expected to 'rattle' inside the cage, akin to H^+@C_{60} (ref. 22). Additionally, it has been found that several other ions like Li^+, Be^{2+}, C^{4+} and S^{4+} could be encapsulated inside the C_{20} cage. Smaller ions with a larger charge density stabilize the cage more.

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