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Binding Energy in and Equilibrium Constant of Formation for the Dodecahedrane Compounds He@$C_{20}H_{20}$ and Ne@$C_{20}H_{20}$

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Using high-level ab initio methods, the binding energies were calculated for helium and neon inside the cage-like dodecahedrane molecule $C_{20}H_{20}$. The binding energy of He@$C_{20}H_{20}$ is 33.8 kcal/mol, including the change in zero-point energy. The corresponding energy for Ne@$C_{20}H_{20}$ is 98.3 kcal/mol. The ^{3}He nuclear magnetic resonance chemical shift is 1.51 ppm, relative to ^{3}He outside the molecule. The equilibrium constant for He@$C_{20}H_{20}$ was calculated, and the pressure corresponding to the experimentally synthesized compound is 4×10^{26} atm.

Introduction

Dodecahedrane, $C_{20}H_{20}$, has its carbon atoms at the vertexes of a regular dodecahedron. Because of the strain energy of the carbon skeleton and because all the hydrogens are eclipsed, dodecahedrane has been of interest to theoretical chemists for more than 25 years. Force-field[1] as well as molecular orbital methods[2−5] have been used to study the structure and stability of this molecule. Early in this period, Schulman and Disch[3] considered the formation of inclusion compounds of dodecahedrane with several atoms. They calculated the corresponding binding energies with the INDO (intermediate neglect of differential overlap) molecular orbital method.[3] Later, two additional reports on the interaction energies in the same complexes using the PRDDO (partial retention of diatomic differential overlap) molecular orbital method[4] and ab initio restricted Hartree−Fock (RHF) calculations with the STO-3G (Slater-type orbital, three Gaussian) basis set[5] were published. The binding energy in the helium compound He@$C_{20}H_{20}$ is of particular interest to us.

For several years, we have been able to introduce noble gas atoms (He, Ne, Ar, Kr, and Xe) into C_{60} and higher fullerenes.[6] The incorporation of these atoms takes place through a process involving high pressure and high temperature.[7] Several force-field[8−10] and molecular orbital methods[11−13] have been used to estimate the binding energies of the noble gas atoms in these compounds, along with the equilibrium constant for the incorporation process.[10,12] For the specific case of He and Ne, these calculations suggest that both atoms are slightly bound inside C_{60} through simultaneous van der Waals interactions with all 60 carbons. The cavity in dodecahedrane is much smaller than that in C_{60}; the distance between opposite carbons in the former is 4.3 Å, whereas in the latter it is 7.1 Å. It is then expected that the introduction of helium and neon into dodecahedrane creates molecules with a high energy content. The early molecular orbital calculations suggest that the interaction energy between dodecahedrane and helium is on the order of 20−40 kcal/mol.[3−5] The equilibrium constant for the incorporation process in this case would be extremely small, and a negligible amount of product would be formed.

It has been shown that it is possible to produce He@C_{60} and Ne@C_{60} by shooting beams of He^+ and Ne^+ ions onto a surface covered by C_{60}.[14] After exposure to the ion beam, the fullerene is recovered and then pyrolized under vacuum to measure the amount of noble gas released. This methodology has now been applied successfully to the incorporation of helium into dodecahedrane.[15] The results show that at ion energies >100 eV, the He^+ ions can penetrate the five-membered rings of dodecahedrane and that the resulting He@$C_{20}H_{20}$ is stable for weeks. It was also observed that by bombarding dodecahedrane with fast, neutral helium atoms, He@$C_{20}H_{20}$ is formed. As expected, the yield of the incorporation process is low; ∼1 in 10 000 molecules of dodecahedrane contains a helium atom.[15]

In view of these results, we decided to carry out high-level ab initio calculations to have a better idea of the value of the interaction energy in He@$C_{20}H_{20}$. In addition, from the results of these calculations we estimate a value for the equilibrium constant for the incorporation process using statistical mechanics. For C_{60}, it has been shown that neither Hartree−Fock (HF) nor density functional calculations are able to find a binding interaction between the fullerene cage and the noble gas atoms.[11−13] It is only when electron correlation is taken into consideration that reasonable values are obtained for the binding energies because the binding is due to van der Waals forces. We have calculated the interaction energy in He@$C_{20}H_{20}$ using HF, density functional, and MP2 theories. Our best values were obtained at the MP2(FC)/6-311G(d,p) level of theory. We have also included corrections for basis set superposition errors.

Finally, we also calculated the nuclear magnetic resonance (NMR) chemical shift of the helium atom in He@$C_{20}H_{20}$ using the GIAO (gauge-invariant atomic orbital) approach.[16] We have previously studied the effect of fullerene structure on the helium-3 NMR chemical shift of helium complexes.[17] It is

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interesting to see the effect of the pure σ cage of dodecahedrane on the magnetic environment of the helium atom.

Theoretical Models

The main goal of this work is to obtain the best possible value of the binding energy of He and Ne inside dodecahedrane with ab initio MO calculations. The binding energy can be used to estimate the equilibrium constant for the process shown in eq 1, where X = He or Ne:

$$X + C_{20}H_{20} \rightleftarrows X@C_{20}H_{20} \tag{1}$$

To a first approximation, the binding energy (ΔE_e) can be obtained by simply calculating the electronic energies (E) of the three species involved,

$$\Delta E_e = E_{X@C20H20} - E_{C20H20} - E_X \tag{2}$$

In a second level of approximation, the differences in zero-point energies (ZPE) between reactants and product must also be included. Because X is an atom, there is no ZPE associated with it. The binding energy, including the effects of ZPE (ΔE_0), becomes:

$$\Delta E_0 = \Delta E_e + ZPE_{X@C20H20} - ZPE_{C20H20} \tag{3}$$

Because of the size of the basis sets used in the calculations just described, we also considered it necessary to include a correction for basis set superposition errors (BSSE). These errors appear when an ab initio calculation is carried out with a small basis set. Consider two different chemical species A and B that form a complex $A-B$. In the calculation of $A-B$, A and B are better described within the complex because each has the opportunity to use the orbitals of the other species. In the calculation of A and B as separate entities, however, each one has only the orbitals assigned to it by the current basis set. As a result, the energy calculated for the complex is lower than it should have been if more orbitals had been included in the calculation of A and B. The numerical value of this error should decrease as the basis set used in the calculations becomes larger.

One way to estimate the magnitude of the BSSE is by the counterpoise correction (CC).[18] In this correction, each of the monomeric species in the complex is calculated with the addition of the empty orbitals of the other species (no nuclei or electrons). These additional empty orbitals are placed at the positions occupied by the nuclei of the other species in the equilibrium geometry of the complex. Thus, the counterpoise-corrected electronic energy (ΔE_{eCC}) becomes:

$$\Delta E_{eCC} = E_{X@C20H20} - E_{C20H20}(G,X) - E_X(G,C_{20}H_{20}) \tag{4}$$

where the second and third terms on the right-hand side of eq 4 correspond to the electronic energies of $C_{20}H_{20}$ and X, respectively, calculated at the equilibrium geometry of the complex and including the empty orbitals of the other monomeric species. Keeping in mind the considerations just presented, the counterpoise-corrected binding energy, including ZPEs (ΔE_{0CC}), is then:

$$\Delta E_{0CC} = \Delta E_{eCC} + ZPE_{X@C20H20} - ZPE_{C20H20} \tag{5}$$

The ZPEs are the same as those in eq 3; that is, derived from the vibrational analysis of each of the monomeric species at their equilibrium geometries and using only the orbitals assigned to them by the current basis set.

TABLE 1: Summary of the Levels of *Ab Initio* Theory Employed in Our Calculations[a]

name	model	ZPE[a]
3-21G	HF/3-21G	Y
6-31G(d)	HF/6-31G(d)	Y
6-31G(d)′	HF/[6-31G(d) C,H; 6-311G(d,p) He]	Y
6-311G(d,p)	HF/6-311G(d,p)	Y
B3LYP	B3LYP/6-31G(d)	Y
B3LYP′	B3LYP/[6-31G(d) C,H; 6-311G(d,p) He]	Y
B3LYP″	B3LYP/6-311G(d,p)	Y
MP2	MP2(FC)/6-31G(d)	N
MP2′	MP2(FC)/[6-31G(d) C,H; 6-311G(d,p) He]	N
MP2″	MP2(FC)/6-311G(d,p)	N

[a] The last column describes whether zero-point energies were obtained in each particular case.

Methodology

The ab initio calculations were carried out using the *Gaussian 94*[19] program package running on either a Digital Personal Workstation 500 au (Digital Unix) or on a homemade IBM-compatible PC (Pentium II, 412 MHz) under the Linux operating system.

Several ab initio models were used: HF, density functional (Becke3LYP[20]), and MP2, as well as different basis sets. Tight geometry optimizations were carried out at each of the levels of theory employed, assuming the I_h point group in all cases. The frequency analyses were carried out only on a subset of the methods used for obtaining electronic energies because this kind of calculation requires substantial computational resources. In particular, it was not possible to obtain vibrational frequencies at any of the MP2 levels employed; hence, no ZPEs were obtained in these cases. The CCs were carried out at all levels of theory used for obtaining electronic energies.

Table 1 contains a summary of the methods employed along with the labels associated with each one. As seen in Table 1, in several of the calculations, a mixture of basis sets was used. A larger basis set was assigned to He in these cases, to improve its description within the calculation. As will be seen later, the addition of more orbitals to He does make a difference in terms of the binding energy, in particular when using the MP2 method. For those calculations carried out mainly with the 6-31G(d) basis set, 6 d orbitals were used, whereas 5 d orbitals were employed for the 6-311G(d,p) basis set.

Using the B3LYP method, a previous study of the interaction energies of He in C_{60} showed that the default integration grid used in density functional calculations is not appropriate to obtain energy values of the appropriate numerical accuracy.[12] As our computational resources were not sufficient to handle the requirements imposed by the grid used by Patchkovskii and Thiel,[12] we used an integration grid of intermediate size (40 radial shells and 434 angular points giving a total of 9212 points per carbon atom). This grid was used in all B3LYP calculations described in this work.

All the MP2 calculations were run using the frozen-core (FC) approximation, that is, only the electrons in the valence shell were considered.

The vibrational frequencies obtained in the frequency calculations were scaled down by known factors. The scaling factors used are shown in Table 2.[21-23] The masses of the atoms were taken as those of the most common isotopes (C = 12.0000, H = 1.0078, He = 4.0026, Ne = 19.9924).

TABLE 2: Scaling Factors Used in Those Models in Which Vibrational Frequencies Were Obtained

model	scaling factor
3-21G	0.9085[a]
6-31G(d)	0.8929[b]
6-31G(d)′	0.8929[c]
6-311G(d,p)	0.9051[d]
B3LYP	0.9613[e]
B3LYP′	0.9613[c]
B3LYP″	0.9613[c]

[a] Reference 21. [b] Reference 22. [c] There are no reported scaling values for these model chemistries. We used those that we assumed were the most appropriate in each case. [d] Reference 21. [e] References 23 and 21.

TABLE 3: Geometric Parameters for the Molecules under Study (in Å) Extracted from the MP2″ Results

compound	C−H distance	C−C distance	cage diameter
$C_{20}H_{20}$	1.095	1.551	4.348
$He@C_{20}H_{20}$	1.095	1.558	4.368
$Ne@C_{20}H_{20}$	1.094	1.575	4.412

The symmetries of the vibrations are reported as given by *Gaussian 94*. However, for some particular vibrations in the B3LYP″ model, the symmetry was not assigned. The assignment was then made by comparison with the symmetries and numerical values of the vibrational frequencies obtained at lower levels of theory.

The CCs were calculated with the help of the MASSAGE keyword in *Gaussian 94* for each one of the model chemistries used. The basis set and geometries were read from the checkpoint file that contained the results of the calculations of the $X@C_{20}H_{20}$ complexes, and the nuclei and electrons of X or $C_{20}H_{20}$ were eliminated, leaving only the corresponding empty orbitals. In the calculation of the CCs, no symmetry was assumed in the wave function of the systems. The binding energies were calculated in accord with eqs 2−5. In the calculation of ΔE_{0CC}, the ZPEs obtained from the B3LYP″ vibrational analyses of $He@C_{20}H_{20}$ and $Ne@C_{20}H_{20}$ were used to correct the MP2 electronic energies.

The helium NMR shielding tensors of He and $He@C_{20}H_{20}$ were calculated using three different model chemistries [HF/6-311G(d,p), B3LYP″, and B3LYP/6-311+G(3df,2p)//MP2″] and the GIAO[24,25] method included in *Gaussian 94*. The chemical shift was then obtained by subtracting the value of the He isotropic magnetic tensor from that in $He@C_{20}H_{20}$.

Results

Table 3 contains C−H and C−C bond distances and the cage diameter of the three molecules under study obtained from optimization with the MP2″ model chemistry. The C−C bond distance for dodecahedrane, 1.551 Å, is slightly longer than the value obtained from X-ray diffraction studies of dodecahedrane derivatives,[26] which is approximately 1.544 Å.[27] The data also show that the geometry of the hydrocarbon cage is only slightly distorted with the introduction of a He or a Ne atom.

A summary of the energies calculated for $He@C_{20}H_{20}$ relative to $C_{20}H_{20}$ is given in Table 4. It is obvious that the cavity in dodecahedrane is so small that the He atom is well up on the repulsive part of the potential. For the HF and density functional methods, the value of the CC becomes smaller as the size of the basis set is increased. However, it becomes important again for the MP2 calculations. In the MP2″ model chemistry, the CC amounts to an increase of ∼10% (2.8 kcal/mol) in the binding energy of $He@C_{20}H_{20}$. The MP2 results show a substantial decrease in the overall binding energy over the HF results. The use of extended basis sets with the MP2′ and MP2″ models also gives an additional decrease because the added basis functions lower the energies of the excited configurations, which then get mixed with the ground configuration in the Møller−Plesset perturbation.

TABLE 4: Energies for $He@C_{20}H_{20}$ (in kcal/mol) Relative to He + $C_{20}H_{20}$

basis set	ΔE_e[a]	CC[b]	ΔE_{eCC}[c]	ΔZPE[d]	ΔE_{0CC}[e]
3-21G	31.40	3.98	35.38	2.69	38.07
6-31G(d)	37.38	0.25	37.62	2.79	40.42
6-31G(d)′	37.76	0.04	37.80	2.74	40.54
6-311G(d,p)	37.70	0.20	37.90	2.74	40.65
B3LYP	34.33	0.84	35.17	3.18	38.35
B3LYP′	34.22	0.03	34.25	3.09	37.34
B3LYP″	34.17	0.18	34.35	3.14	37.49
MP2	34.85	2.14	36.99	3.14[f]	40.13[f]
MP2′	28.97	3.02	31.98	3.14[f]	35.12[f]
MP2″	27.83	2.78	30.61	3.14[f]	33.75[f]

[a] Difference in electronic energies at the potential minima. [b] Magnitude of the counterpoise correction. [c] Difference in electronic energies after including the counterpoise correction. [d] Difference in zero-point energies. [e] Energy difference including zero-point energy and counterpoise correction. [f] In these cases, the B3LYP″ zero-point energy was used.

TABLE 5: T_{1u} Vibrational Frequencies (in cm^{-1}) of the Helium and Neon Atoms and the Dodecahedrane Cage[a] (B3LYP″)

T_{1u} vibration	$C_{20}H_{20}$	$He@C_{20}H_{20}$	$Ne@C_{20}H_{20}$
atom	−	650.4	493.1
cage	702.1	790.6	721.1

[a] Only the two lowest T_{1u} vibrational modes are shown.

The change in ZPE (∼3 kcal/mol) comes mostly from the extra three vibrational degrees of freedom added when the He atom is put into the cage. This new vibration is triply degenerate with T_{1u} symmetry. Table 5 shows the average values (after scaling) of the lowest two sets of T_{1u} vibrations obtained from the B3LYP″ frequency analysis for $He@C_{20}H_{20}$. The frequency of the normal mode corresponding to the movement of the He atom inside dodecahedrane is 650.4 cm^{-1}. The second T_{1u} vibration in the table corresponds mostly to movement of the carbon cage, and its frequency increases by ∼88 cm^{-1} with the introduction of the He atom, relative to the frequency of the same vibration in dodecahedrane. The other vibrational frequencies change by several wavenumbers, some up and some down.

Our best estimate of the overall binding energy, ΔE_{0CC}, for $He@C_{20}H_{20}$ is 33.8 kcal/mol, obtained by using ΔE_{eCC} from MP2″ and the zero-point correction from B3LYP″. The corresponding energies for $Ne@C_{20}H_{20}$ are given in Table 6. As expected, it takes much more energy to put a Ne atom inside dodecahedrane than a He atom. The change in ZPE is smaller in this case (∼1 kcal/mol) because the extra vibration has a lower frequency because of the larger mass of the Ne atom (Table 5). The cage vibrational frequency increases only by 19 cm^{-1}. Our best estimate for ΔE_{0CC} for $Ne@C_{20}H_{20}$ is 98.3 kcal/mol, obtained by using ΔE_{eCC} from the MP2″ calculation and the ZPE correction from B3LYP″.

Table 7 shows the calculated He isotropic magnetic shifts calculated for He and $He@C_{20}H_{20}$ using the GIAO method under three different model chemistries. The results obtained at the highest level of theory employed (B3LYP/6-311+G(3df,2p)//MP2(FC)/6-311G(d,p)) show that the He atom is slightly deshielded (1.51 ppm) by the dodecahedrane cage. This is in sharp contrast with the calculated shielding obtained by Bühl et al. for $He@C_{60}H_{60}$ (−5.2 ppm).[28] Despite the identical

TABLE 6: Energies for $Ne@C_{20}H_{20}$ (in kcal/mol) Relative to $Ne + C_{20}H_{20}$

basis set	ΔE_e[a]	CC[b]	ΔE_{eCC}[c]	ΔZPE[d]	ΔE_{0CC}[e]
3-21G	79.26	31.33	110.59	1.18	111.77
6-31G(d)	101.91	3.02	104.93	1.34	106.27
6-311G(d,p)	105.19	−0.36	104.83	1.27	106.10
B3LYP	89.76	9.50	99.25	0.94	100.20
B3LYP″	97.46	2.31	99.77	0.97	100.74
MP2	82.81	13.00	95.81	0.97[f]	96.78[f]
MP2″	88.30	9.07	97.37	0.97[f]	98.34[f]

[a] Difference in electronic energies at the potential minima. [b] Magnitude of the counterpoise correction. [c] Difference in electronic energies after including the counterpoise correction. [d] Difference in zero-point energies. [e] Energy difference including zero-point energy and counterpoise correction. [f] In these cases, the B3LYP″ zero-point energy was used.

TABLE 7: Isotropic Magnetic Shieldings of Helium (ppm) and the Corresponding Chemical Shift, Calculated with the GIAO Method at Three Different Levels of Theory

model	He	$He@C_{20}H_{20}$	δ
6-311G(d,p)	59.87	61.64	1.77
B3LYP″	59.93	59.31	−0.61
B3LYP‴[a]	58.41	59.93	1.51

[a] B3LYP‴ = B3LYP/6-311+G(3df,2p)//MP2(FC)/6−311G(d,p).

symmetry of these two molecules, the magnetic effect on the He nucleus is different, probably as a result of the different distances to the carbon cage.

Equilibrium Constant. Because we have calculated the vibration frequencies, it is a simple matter to get the equilibrium constant for the incorporation reaction shown in eq 1. From statistical mechanics we have,

$$\frac{\rho(\mathrm{He@C_{20}H_{20}})}{\rho(\mathrm{He})\rho(\mathrm{C_{20}H_{20}})} = K = \frac{q^{(\mathrm{int})}(\mathrm{He@C_{20}H_{20}})}{\lambda(\mathrm{He@C_{20}H_{20}})^3}\,\frac{\lambda(\mathrm{C_{20}H_{20}})^3}{q^{(\mathrm{int})}(\mathrm{C_{20}H_{20}})}\,\lambda(\mathrm{He})^3 \exp(-\Delta E/kT) \quad (6)$$

where ρ is the number density (molecules/cm^3), $q^{(\mathrm{int})}$ is the internal partition function (excluding translation), and λ is the thermal wavelength,

$$\lambda(i) = h(2\pi m_i kT)^{-1/2} \quad (7)$$

Converting from number density to pressure, $\rho(\mathrm{He}) = p(\mathrm{He})/kT$, gives,

$$\frac{\rho(\mathrm{He@C_{20}H_{20}})}{\rho(\mathrm{C_{20}H_{20}})} = Kp(\mathrm{He})/kT = K'p(\mathrm{He}) \quad (8)$$

The term K' can then be written as

$$K' = Cf(T)T^{-5/2}\exp(-\Delta E_0/kT) \quad (9)$$

$$C = 1.74 \times 10^{-5}\ \mathrm{Pa}^{-1}\ \mathrm{K}^{5/2} = 1.77\ \mathrm{atm}^{-1}\ \mathrm{K}^{5/2} \quad (10)$$

where *f(T)* is the ratio of internal partition functions. If we use the lowest vibrational state as the energy zero in calculating the partition function, then the ZPE must be included in the ΔE term (ΔE_e), as indicated. The term *f(T)* can then be calculated using the calculated vibration frequencies. Because the radius of dodecahedrane expands by only 0.5%, the rotational contribution to *f(T)* is negligible. The effect of putting the He atom inside dodecahedrane increases some frequencies by several wavenumbers and decreases others by similar amounts. The changes largely cancel out. However, the introduction of the He atom gives rise to an additional vibration of T_{1u} symmetry. This energy couples strongly with the lowest T_{1u} vibration of the empty dodecahedrane, so that there is no one vibration that is clearly the He motion. The term *f(T)* is close to one at low temperatures and then rises rapidly, reaching two at ∼700 K. Even a factor of 2 is negligible, given the uncertainty in ΔE_e.

The experiment produces dodecahedrane containing 0.01% He.[15] We can then calculate the pressure corresponding to equilibrium conditions. Using $\Delta E_e = 33.8$ kcal/mol, we have $p = 4 \times 10^{26}$ atm.

Conclusions

The dodecahedrane cage distorts very little after introduction of a He or even a Ne atom. Our best calculations predict an interaction energy of 33.8 kcal/mol for He and 98.3 kcal/mol for Ne, including ZPEs and corrections for BSSEs. Most of the differences in ZPE between $C_{20}H_{20}$ and $X@C_{20}H_{20}$ comes from the new T_{1u} vibration generated after the introduction of X into dodecahedrane. From statistical mechanics considerations and experimental results, the pressure of He inside dodecahedrane was calculated to be $p = 4 \times 10^{26}$ atm. In effect, we have made the world's smallest He balloons, and they have a very high pressure of He.

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