Endofullerenes: size effects on structure and energy

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The geometric and energy characteristics of endohedrals $X@C_n$ (X = He, Ne, Ar; n = 20, 24, 30, 32, 40, 50, 60) were calculated by the density functional theory. The insertion of the helium atom leads to only a slight change in the geometry of the fullerene cage of the endohedrals. As the size of the trapped atom increases, the average C—C bond length increases in proportion to the radii of these atoms (by 0.05 Å for $Ne@C_{20}$ and 0.12 Å for $Ar@C_{20}$). The inclusion energies of endofullerenes and the pressure of the cage exerted on the endo atom were calculated for all the above-mentioned endohedrals.

Key words: fullerenes, endofullerenes, dodecahedrane, density functional theory.

The synthesis and investigation of endo derivatives of fullerenes have recently attracted increasing attention.[1] However, most of studies in this field were devoted to endohedrals of higher fullerenes C_n ($n \geq 60$). Various derivatives of these compounds with inert gases,[1] metals,[1] nitrogen, and phosphorus[2,3] were synthesized and theoretically studied. However, endo derivatives of small fullerenes with $n < 60$ (only fullerenes C_{20} [4] and C_{36} [5] were synthesized) are presently unknown. Scarce theoretical studies were carried out primarily by the density functional theory for endohedrals of C_{28} (see the studies[6,7] and references cited therein), C_{32},[8] and a series of endohedrals with composition $He@C_n$ (n = 20, 24, 28, 32, 36, 40, or 50).[9]

The aim of the present study was to predict the possibility of synthesizing endo derivatives $X@C_n$ of small fullerenes containing atoms of inert gases. For this purpose, we carried out systematic calculations of various isomers of carbon clusters C_n and endohedrals $X@C_n$ containing helium, neon, or argon by the density functional theory. The relative stabilities of the endohedrals were analyzed. Their energy characteristics and the charges on the endo atoms were investigated depending on the nature of the endohedrals as part of the general problem of compressed atoms.[10]

Calculation method

Calculations were carried out by the density functional theory (DFT) with the three-parameter exchange-correlation potential B3LYP [11] using the GAUSSIAN-98 program.[12] The standard valence-split 6-31G* and 6-311G* basis sets[11] were used. For endohedrals $X@C_n$ (X = He, Ne, or Ar), the inclusion energies ΔE_e of the products of the reaction $X + C_n \rightarrow X@C_n$ were calculated using the basis set superposition error (BSSE) correction and taking into account the difference between the zero point energies (ZPE) of the endohedral $X@C_n$ and the C_n cage (for n = 20, 24, 30, and 32); BSSE were estimated by the standard compensation method.[13] In all calculations of $X@C_n$, the endo atom was placed in the center of the C_n cage, where it remained after full geometry optimization of the endohedrals (in all cases). In the minimum thus determined, the symmetry of the initial system persists, and all vibrational frequencies have real values.

Results and Discussion

Geometry. With the aim of analyzing the geometry of the endohedrals in the ground state, which was assumed to be singlet (according to the published data on the fullerenes under consideration and their endohedrals containing inert gases; see Ref. 14 and references cited therein), we first calculated the isomers of fullerenes C_n with n = 20, 24, 30, 32, 40, 50, and 60. Their symmetry and the numbering of fullerene isomers (according to the accepted nomenclature[15]) are presented in Fig. 1 and Table 1. Table 1 also gives the data on the shapes and sizes of the isomers of fullerenes calculated at the B3LYP/6-31G* level of theory. For the fullerenes having a nearly spherical shape, the average diameters D are tabulated. For the fullerenes having an elongated shape, the diameter ranges are given (all diameters were calculated as the distances between the opposite atoms).

The geometry of the fullerenes was studied in more detail by calculating the bond lengths and radii for the

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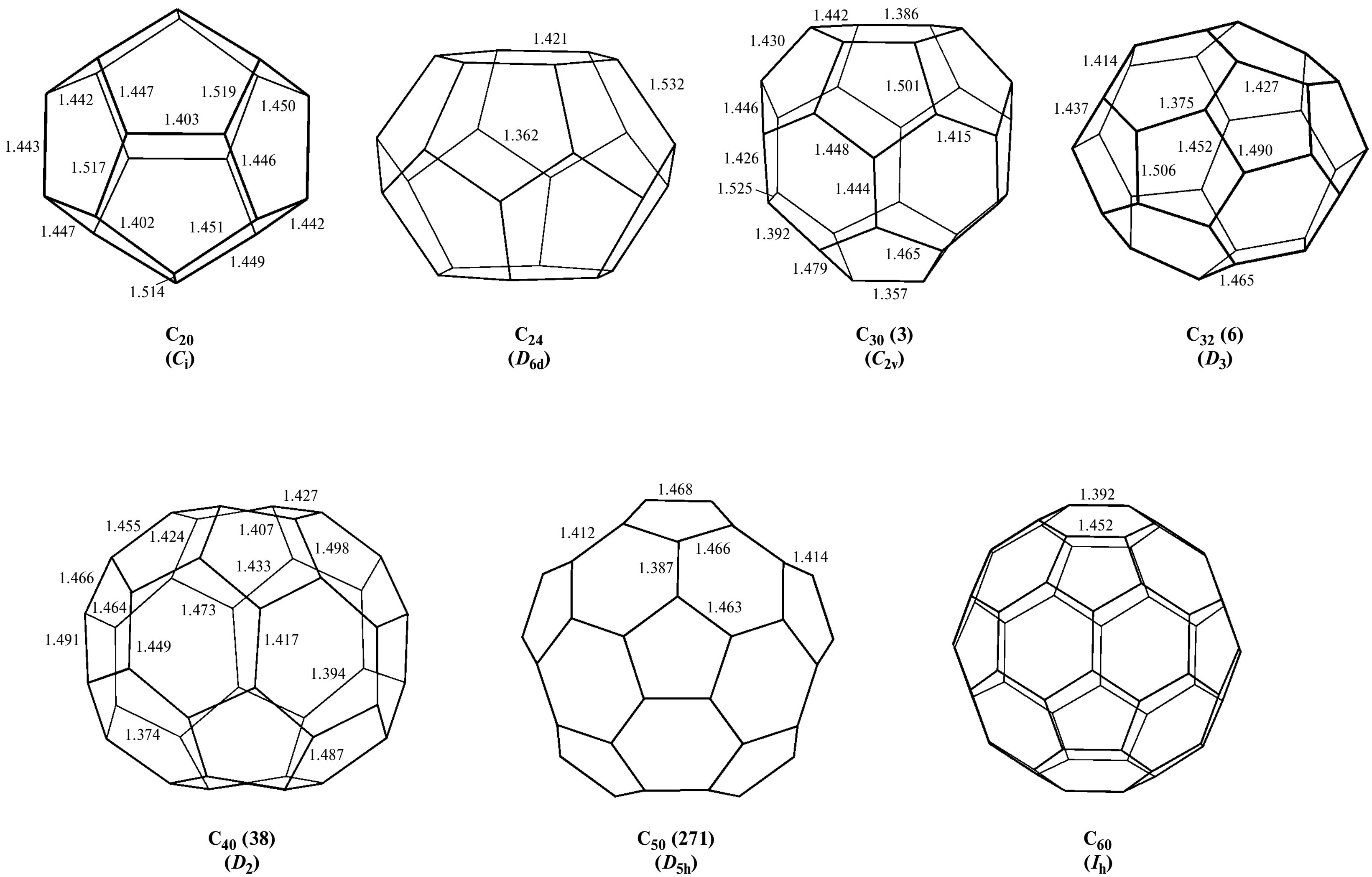

Fig. 1. Geometry of the most stable fullerenes C_n calculated at the B3LYP/6-31G* level of theory. Only the lengths of nonequivalent bonds are given.

Table 1. Diameters of small fullerenes and C_{60} calculated at the B3LYP/6-31G* level of theory

Fullerene	Symmetry	Isomers[15]	D/Å
C_{20}	C_i		3.7—3.9
C_{24}	D_{6d}		3.4—4.6
C_{30}	D_{5h}	$C_{30}(1)$	4.0—5.3
	C_{2v}	$C_{30}(2)$	4.6—5.2
	C_{2v}	$C_{30}(3)$	4.7—4.9
C_{32}	C_2	$C_{32}(1)$	4.7—5.8
	D_2	$C_{32}(2)$	4.4—6.1
	D_{3d}	$C_{32}(3)$	4.4—6.6
	C_2	$C_{32}(4)$	4.5—5.5
	D_{3h}	$C_{32}(5)$	4.2—5.5
	D_3	$C_{32}(6)$	4.8—5.6
C_{40}	D_2	$C_{40}(38)$	5.3—5.9
C_{50}	D_{5h}	$C_{50}(271)$	5.4—6.9
C_{60}	I_h		7.1

Table 2. Geometric parameters and effective pressures of the C_n cage refined at the B3LYP/6-311G* level

Compound[a]	d(C—C)/Å	l/Å	R/Å	P/atm
C_{20} (C_i)	1.402—1.519	1.452	2.033	—
He@C_{20}	1.410—1.527	1.463	2.049	150000
Ne@C_{20}	1.423—1.553	1.486	2.082	470000
Ar@C_{20}	1.439—1.587	1.535	2.149	1100000
C_{24} (D_{6d})	1.362—1.532	1.455	2.248	—
He@C_{24}	1.363—1.542	1.461	2.257	90
Ne@C_{24}	1.367—1.558	1.473	2.275	230000
Ar@C_{24}	1.379—1.608	1.506	2.326	630000
$C_{30}(3)$	1.357—1.525	1.444	2.516	—
He@C_{30}	1.356—1.530	1.447	2.520	44000
Ne@C_{30}	1.355—1.538	1.451	2.528	80000
Ar@C_{30}	1.358—1.560	1.467	2.553	280000
$C_{32}(6)$	1.375—1.506	1.442	2.591	—
He@C_{32}	1.376—1.508	1.444	2.594	24000
Ne@C_{32}	1.376—1.513	1.447	2.601	58000
Ar@C_{32}	1.383—1.530	1.460	2.623	200000
$C_{40}(38)$	1.366—1.498	1.440	2.899	—
He@C_{40}	1.366—1.500	1.440	2.900	5000
Ne@C_{40}	1.366—1.503	1.441	2.902	17000
Ar@C_{40}	1.368—1.516	1.447	2.913	65000
$C_{50}(271)$	1.387—1.468	1.434	3.238	—
He@C_{50}	1.388—1.468	1.435	3.239	20000
Ne@C_{50}	1.388—1.468	1.435	3.240	10000
Ar@C_{50}	1.393—1.471	1.437	3.245	26000
C_{60} (I_h)	1.392, 1.452	1.432	3.544	—
He@C_{60}[b]	1.392, 1.452	1.432	3.544	—
Ne@C_{60}	1.392, 1.452	1.431	3.543	—
Ar@C_{60}	1.393, 1.453	1.432	3.545	—

[a] Either the symmetry or the numbering of the fullerene isomer (see Ref. 15) is given in parentheses.
[b] The estimates of the effective pressure P for endohedrals of C_{60} are not given, because the calculated values of Δl and ΔR are too small to believe that the calculations gave reasonable values.

fullerene cages of the most stable isomers, which were chosen based on the criterion of the total energy (E_{total}) minimum (see below). The results of refined calculations at the B3LYP/6-311G* level for the most stable fullerenes and their endohedrals are presented in Table 2, in which the ranges of the C—C bond lengths (d) after optimization and the average C—C bond lengths (l) are given for all systems. The calculated data are sufficiently reliable, as evident from a comparison of these data for C_{60} with the results of calculations by the B3LYP/6-31G** method[16] and X-ray diffraction data for the [6,6] and [6,5] bonds.[17] (The bond lengths calculated in the present study are 1.392 and 1.452 Å, whereas the bond lengths calculated earlier[16] are 1.395 and 1.453 Å, respectively, and the corresponding experimental values[17] are 1.388(9) and 1.432(5) Å.)

Effective pressure. The calculated data on the geometry of the fullerenes and their endohedrals make it possible to estimate the pressure exerted by the C_n cage on the atom located inside the endohedral. This estimate can be obtained as follows. If fullerene C_n has N C—C bonds, each of which is elongated by Δl in the presence of the endo atom, an increase in the potential energy ΔU of the C_n cage is

$$\Delta U = (1/2)Nk(\Delta l)^2,$$

where k is the force constant of the C—C bond. The approximation of the C_n cage by a continuous elastic spherical shell of radius R shows that the surface tension of this shell is

$$\sigma = \Delta U/\Delta S, \qquad \Delta S = 8\pi R(\Delta R),$$

where ΔS and ΔR are increments of the surface area of the sphere and its radius, respectively. Then, the "surface pressure" P exerted by the shell is determined by the equation

$$P = 2\sigma/R,$$
$$P = 2\sigma/R = (1/8\pi)\cdot[Nk(\Delta l)^2]/(R^2\Delta R).$$

To obtain an approximate estimate of P by the above-given equation, k was taken as $7\cdot10^5$ dyn cm^{-1}, which is intermediate between the constants for the C—C single bond ($5.2\cdot10^5$) and the C=C double bond ($9.6\cdot10^5$ dyn cm^{-1}).[18] The average values of R, ΔR, and Δl, which were calculated by geometry optimization of the systems under consideration at the B3LYP/6-311G* level, were used. The calculated pressures P are listed in Table 2. It can be seen that, in spite of a somewhat tentative character of this value, it correlates with the general tendency for an increase in stability of the endohedral with increasing size of the carbon cage.

Energetics. The following energy characteristics were calculated: the total energy E_{total}, the energy gap ΔE between the higher occupied and lower unoccupied

Table 3. Total energies (E_{total}), the inclusion energies of He@C_n without (ΔE_e) and with the BSSE correction (ΔE_e + BSSE), and the energy gaps (ΔE) between HOMO and LUMO in fullerenes C_n (I) and their endohedrals He@C_n (II) (at the B3LYP/6-31G* level)

Compound	Symmetry	$-E_{total}$/a.u.		ΔE/eV		ΔE_e	ΔE_e + BSSE
		I	II	I	II	kcal mol^{-1}	
C_{20}	C_i	761.44446	764.23415	1.95	1.82	73.65	73.62
C_{24}	D_{6d}	913.84001	916.68369	1.83	1.95	39.77	40.58
C_{30}(1)	D_{5h}	1142.46790	1145.32626	1.46	1.37	30.56	31.11
C_{30}(2)	C_{2v}	1142.55021	1145.42379	2.31	2.32	21.00	21.97
C_{30}(3)	C_{2v}	1142.55659	1145.43432	1.36	1.36	18.40	19.60
C_{32}(1)	C_2	1218.74595	1221.62485	1.52	1.56	17.66	18.76
C_{32}(2)	D_2	1218.71502	1221.58748	1.34	1.33	21.71	22.67
C_{32}(3)	D_{3d}	1218.71512	1221.58409	1.60	1.58	23.90	24.50
C_{32}(4)	C_2	1218.79149	1221.67484	2.02	2.07	14.87	16.10
C_{32}(5)	D_{3h}	1218.70847	1221.58098	2.64	2.73	21.67	21.83
C_{32}(6)	D_3	1218.83283	1221.71878	2.60	2.62	13.24	14.72
C_{40}(38)	D_2	1523.72830	1526.62862	2.00	2.01	4.22	5.77
C_{50}(271)	D_{5h}	1904.92839	1907.83343	1.38	1.36	1.26	2.57
C_{60}	I_h	2286.17423	2289.07988	2.76	2.76	0.88	1.58

Table 4. Total energies E_{total}, the inclusion energies of X@C_n, the energy gaps ΔE for fullerenes and their endohedrals refined at the B3LYP/6-311G* level, and the charges Q_X on the endo atoms (in terms of the Mulliken population analysis)

Compound	Symmetry	$-E_{total}$ /a.u.	ΔE_e	ΔE_e + BSSE	ΔE_e + BSSE + ZPE*	ΔE /eV	Q_X
			kcal моль$^{-1}$				
C_{20}	C_i	761.59305				1.94	
He@C_{20}	C_i	764.38451	76.29	75.20	78.63	1.82	0.02
Ne@C_{20}	C_i	890.20135	214.99	206.78	207.29	1.75	−0.01
Ar@C_{20}	C_i	1288.18039	606.09	504.61	497.87	1.99	0.26
C_{24}	D_{6d}	914.01628				1.83	
He@C_{24}	D_{6d}	916.86252	41.91	41.91	45.11	1.94	0.02
Ne@C_{24}	D_{6d}	1042.78461	114.57	116.20	117.85	2.01	0.0
Ar@C_{24}	D_{6d}	1440.95344	386.57	345.21	340.79	2.07	−0.13
C_{30}(3)	C_{2v}	1142.77330				1.34	
He@C_{30}	C_{2v}	1145.65513	19.58	19.99	22.23	1.35	0.02
Ne@C_{30}	C_{2v}	1271.64507	49.66	55.60	56.74	1.32	0.04
Ar@C_{30}	C_{2v}	1670.00197	203.64	189.80	188.04	1.24	−0.08
C_{32}(6)	D_3	1219.06382				2.61	
He@C_{32}	D_3	1221.95431	14.14	14.84	16.81	2.62	0.02
Ne@C_{32}	D_3	1347.95798	35.61	42.72	43.95	2.71	0.04
Ar@C_{32}	D_3	1746.35732	162.96	154.15	153.36	2.85	−0.07
C_{40}(38)	D_2	1524.01232				1.99	
He@C_{40}	D_2	1526.91806	4.57	5.28	—	2.00	0.02
Ne@C_{40}	D_2	1652.95058	7.94	15.38	—	2.02	0.06
Ar@C_{40}	D_2	2051.46148	65.28	65.48	—	2.08	0.01
C_{50}(271)	D_{5h}	1905.27856				1.33	
He@C_{50}	D_{5h}	1908.18924	1.47	2.12	—	1.33	0.01
Ne@C_{50}	D_{5h}	2034.23024	−0.48	5.77	—	1.32	0.05
Ar@C_{50}	D_{5h}	2432.79139	25.33	26.41	—	1.24	0.05
C_{60}	I_h	2286.59069				2.74	
He@C_{60}	I_h	2289.50190	1.14	1.51	—	2.74	0.01
Ne@C_{60}	I_h	2415.54564	−2.54	1.45	—	2.74	0.02
Ar@C_{60}	I_h	2814.13409	6.14	7.39	—	2.74	0.04

* For endofullerenes X@C_n ($n \geq 40$), ZPE was ignored.

molecular orbitals (HOMO—LUMO), and the inclusion energy of endohedrals $\Delta E_e = E_{total}(X@C_n) - E_{total}(C_n) - E_{total}(X)$. The results are given in Table 3 (at the B3LYP/6-31G* level) and Table 4 (at the B3LYP/6-311G* level).

As expected, the total energies E_{total} fall down as the number of atoms n in fullerene C_n and the atomic number of the trapped atom increase. The changes in the values of E_{total} for different isomers of the same fullerene are of interest. Two isomers $C_{30}(2)$ and $C_{30}(3)$ with the same symmetry C_{2v} are characterized by nearly equal values of E_{total}, whereas E_{total} for $C_{30}(1)$ differs from the above energies by approximately 0.1 a.u. (see Table 3). This is consistent with the fact that the isomers $C_{30}(2)$ and $C_{30}(3)$ have the same symmetry C_{2v}, whereas the symmetry of the isomer $C_{30}(1)$ is D_{5h}. For six isomers of C_{32}, E_{total} varies within 0.13 a.u., which is nearly equal to the value observed for C_{30}, but the correlation between the total energy and the symmetry is not obvious because of five different symmetry groups. This is also true for E_{total} of the endohedrals $He@C_{30}$ and $He@C_{32}$. It should be noted that, in terms of the E_{total} minimum criterion, our conclusions about the highest stability of the isomers $C_{30}(3)$ and $C_{32}(6)$ are in agreement with the conclusions[19] based on the DFT and semiempirical calculations.

In contrast to E_{total},, the correlation between the energy gap ΔE and the symmetry of the fullerene isomer is violated already for C_{30} and the endohedrals $He@C_{30}$. For C_{32} and $He@C_{32}$ this correlation is also absent. For the series of fullerenes C_n and their endohedrals $X@C_n$, there is also no correlation between the change in ΔE and the increase in both n and the atomic number X. However, the data on the energy gaps ΔE are of interest for the qualitative interpretation of experimental results, because ΔE correlates with the reactivity, mass spectra, and photoelectron spectra. The energy gap ΔE for fullerene C_{20} is smaller than that for C_{60} (see Tables 3 and 4), which is in agreement with the higher reactivity of the former fullerene. The relative arrangement of the HOMO—LUMO energy gaps presented in Tables 3 and 4 is also consistent with the results of mass spectrometry and photoelectron spectroscopy.[20]

From the standpoint of predicting the possible endohedrals of small fullerenes, calculations of the inclusion energies ΔE_e of endohedrals formed by the endothermic reaction $X + C_n \rightarrow X@C_n$ (the energy capacity of the system) are of most interest (see Table 4 and Fig. 2). The radii of the endo atoms were taken from the literature.[21] As expected, ΔE_e rapidly increases with decreasing size of fullerene C_n in the presence of the same endo atom. An increase in the size of the endo atom (for the same size of fullerene) is also accompanied by an increase in the energy capacity.

It should be noted that ΔE_e for $Ne@C_n$ (n = 30, 32, 40, 50, or 60) and $Ar@C_n$ (n = 40, 50, or 60) are lower than

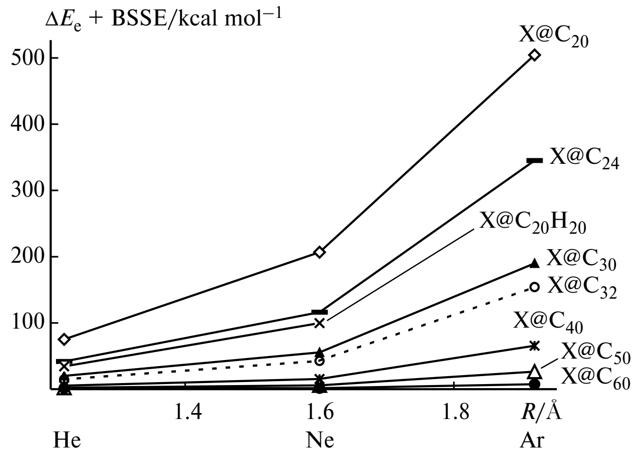

Fig. 2. Inclusion energies of endohedrals $X@C_n$ corrected for the basis set superposition error ΔE_e + BSSE (kcal mol^{-1}) depending on the radius of the endo atom X (X = He, Ne, or Ar) and the size of the fullerene cage n (calculation was carried out at the B3LYP/6-311G* level). The data for $X@C_{20}H_{20}$ were taken from the literature.[23]

that for $He@C_{20}$. These values correlate with the effective pressures P, which are smaller for the above-mentioned endohedrals containing neon or argon compared to that for $He@C_{20}$. The existence of the endohedral $He@C_{20}H_{20}$ was confirmed experimentally.[22] For the latter compound, the calculated inclusion energy[23,24] is close to that for $He@C_{20}$,[14] and the radius of the carbon cage is close to that of fullerene C_{20}. Based on comparison of these data and the above-mentioned data on the inclusion energies and effective pressures, one would expect that all endohedrals $He@C_n$ ($n \geq 20$) as well as endohedrals $Ne@C_n$ ($n \geq 30$) and $Ar@C_n$ ($n \geq 40$) could be synthesized.

Charges on endo atoms. The charges Q_X on the endo atoms (in terms of the Mulliken population analysis) are so small (except for Ar) that they are hardly indicative of any signs of chemical bonding (see Table 4). The unreasonably high value of Q_{Ar} in the endohedral $Ar@C_{20}$, whose existence seems to be impossible (see Tables 2 and 4), may reflect a substantial deformation of the valence electron shells in this hypothetical molecule. Presumably, the same is true for the endohedrals $Ar@C_n$ (n = 24, 30, or 32), although the calculated charges Q_x are insufficiently reliable because of an approximate character of the Mulliken population analysis. Nevertheless, it should be noted that the electron density redistribution between the C_{20} molecule and the endo atoms X of inert gases (X = He, Ne, or Ar) determined in the present study is similar to that found in calculations[24] for analogous endohedrals of dodecahedrane $X@C_{20}H_{20}$.

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