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Molecular Structures of Alumina Nanoballs and Nanotubes: A Theoretical Study

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Molecular structures of alumina nanoballs and nanotubes have been determined. Tetrahedral, octahedral, and icosahedral alumina nanostructures were derived from Platonic solids and Archimedean polyhedra and were optimized by quantum chemical methods. I_h-symmetric balls, resembling their isovalence electronic analogues, fullerenes, are preferred. The nanoballs consist of adjacent Al_5O_5 and Al_6O_6 rings, similar to C_5- and C_6-rings of fullerenes. The structural characteristics of alumina nanoballs are dominated by π-electron donation from oxygen to aluminum. Alumina nanotubes can be derived from icosahedral nanoballs. The tubes alternate between D_{5d}- and D_{5h}-symmetries and are capped by halves of the icosahedral balls.

Introduction

The discovery of fullerenes[1] and carbon nanotubes[2] has been followed by a rapid development in the field of nanoscale materials. Tubular or spherical nanoparticles of several inorganic compounds with various stoichiometries have already been synthesized. These include, among many others, nanotubes of boron nitride[3] (1:1 stoichiometry), silica[4] (1:2), and alumina[5] (2:3). Chemical and physical properties of the novel materials, being dependent also on the size and shape of the nanostructures, differ significantly from fullerenes and carbon nanotubes. Owing to the versatility, inorganic nanostructures are on their way into various future applications.

While several inorganic nanostructures have been synthesized, structure determinations have focused on fullerenes and carbon nanotubes[6] and on their boron nitride analogues.[7] The molecular structures of the recently synthesized alumina (Al_2O_3) nanotubes, for example, are not available. In this theoretical study, we demonstrate how the alumina nanoballs and nanotubes can be built. We derive the nanoballs from regular polyhedra, Platonic solids and Archimedean polyhedra,[8] of which the nanotubes can be formed. As a result, we illustrate the variety of molecular structures applicable for inorganic nanostructures consisting of 2:3 stoichiometry, as well as determine the stability rules for Al_2O_3 nanoballs and -tubes.

Computational Details

Since the objective of the paper was to compare the structures and stabilites of significantly large nanostructures, highly sophisticated quantum chemical approaches were out of question. The main emphasis being on qualitative trends, the HF/3-21G* method was a practical choice. The reliability of Hartree−Fock calculations was verified by repeating the geometry optimizations by the B3LYP/6-31G* method for the analogues of regular polyhedra, as well as by the MP2/6-311G* method for two smallest nanostructures, the analogues of tetrahedron and cube. The nanostructures were constrained to the symmetry in question and were fully optimized. Frequency calculations were performed to confirm the nature of the minima. Throughout the study, Gaussian 98 quantum chemical software[9] was applied.

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Results and Discussion

From Regular Polyhedra to Alumina Nanostructures. Platonic solids are constructed from regular convex polygon and are identified with a notation $\{p,q\}$, where p is the number of sides in each face and q is the number of faces that meet at each vertex.[10] Five Platonic solids exist: tetrahedron {3,3}; cube {4,3}; octahedron {3,4}; dodecahedron {5,3}; icosahedron {3,5}. Considering the derivation of nanostructures with different stoichiometries, q is of major relevance. Alumina nanostructures, in which the stoichiometry is 2:3, can only be formed from those Platonic solids where $q = 3$, i.e., tetrahedron, cube, and dodecahedron.

The methodology for the derivation of alumina nanostructures is illustrated in Figure 1. The aluminum atoms are placed into the vertexes of each polyhedra, and the vertexes are connected via oxygen bridges. Consequently, the planes formed by the adjacent aluminums, which are not bound to each other, represent the faces of Platonic solids. Interestingly, each structure contains a framework also for another polyhedron, which can be observed by imagining a plane between the bridging oxygen atoms and by placing the oxygens into the vertexes. For Al_4O_6 the second polyhedron is another Platonic solid, octahedron {3,4}. For Al_8O_{12} and $Al_{20}O_{30}$ they are cuboctahedron and icosidodecahedron, respectively, both representing Archimedean polyhedra. Hence, the alumina nanoballs derived from Platonic solids can be considered as compounds of two polyhedra. Symmetry from the original Platonic solid is always preserved, giving T_d-symmetry to Al_4O_6, O_h-symmetry to Al_8O_{12}, and I_h-symmetry to $Al_{20}O_{30}$.

Repeating this methodology for different values of q would produce structures with a stoichiometry of 2:q. Hence, octahedron ($q = 4$) would lead to 1:2, and dodecahedron ($q = 5$) to 2:5 stoichiometry. Such structures are not applicable for alumina but may be relevant for other inorganic nanostructures having the stoichiometries in question.

Archimedean polyhedra are constructed from two or more different regular convex polygons so that every vertex is equivalent. While the definition also includes two infinite groups, prisms and antiprisms, they are not considered in this context. Archimedean polyhedra are identified by a notation (a,b,c,d), in which the characters identify the polygons (3 = triangle, 4 = square, and so on) meeting at each vertex. There are a total of 13 Archimedean solids: truncated tetrahedron (3,6,6); cuboctahedron (3,4,3,4); truncated octahedron (4,6,6); truncated cube (3,8,8); rhombicuboctahedron (3,4,4,4); truncated cuboctahedron (4,6,8); snub cuboctahedron (3,3,3,3,4); icosidodecahedron (3,5,3,5); truncated icosahedron (5,6,6); truncated dodecahedron (3,10,10); rhombicosidodecahedron (3,4,5,4); truncated icosidodecahedron (4,6,10); snub icosidodecahedron (3,3,3,3,5). Alumina nanostructures can only be formed from those Archimedean polyhedra, in which three faces meet at each vertex, i.e., which are denoted by three characters. Hence, the number of characters is equivalent to the definition of q in the case of Platonic solids.

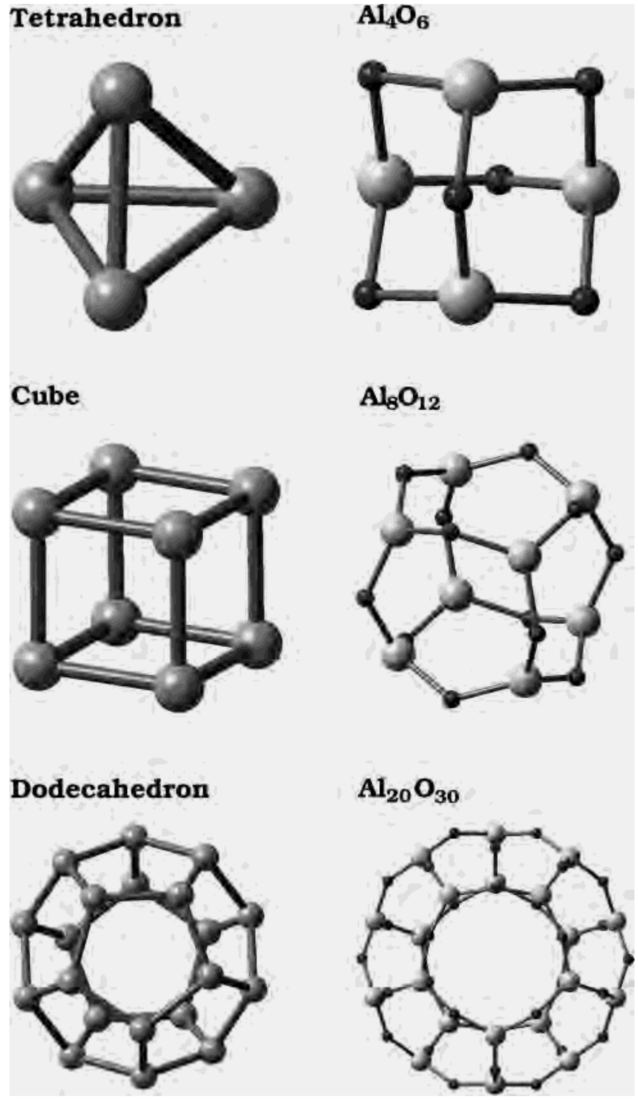

Figure 1. From Platonic solids to alumina nanostructures.

These seven polyhedra are illustrated in Figure 2, together with their alumina analogues, which were derived by the methodology described for Platonic solids. The symmetries are preserved, giving T_d for $Al_{12}O_{18}$, O_h for $Al_{24}O_{36}-Al_{48}O_{72}$ and I_h for $Al_{60}O_{90}-Al_{120}O_{180}$. Repeating the process for the other six Archimedean polyhedra would produce nanostructures with 1:2 (cuboctahedron, rhombicuboctahedron, icosidodecahedron, and rhombicosidodecahedron) or 2:5 (snub cuboctahedron and snub icosidodecahedron) stoichiometries.

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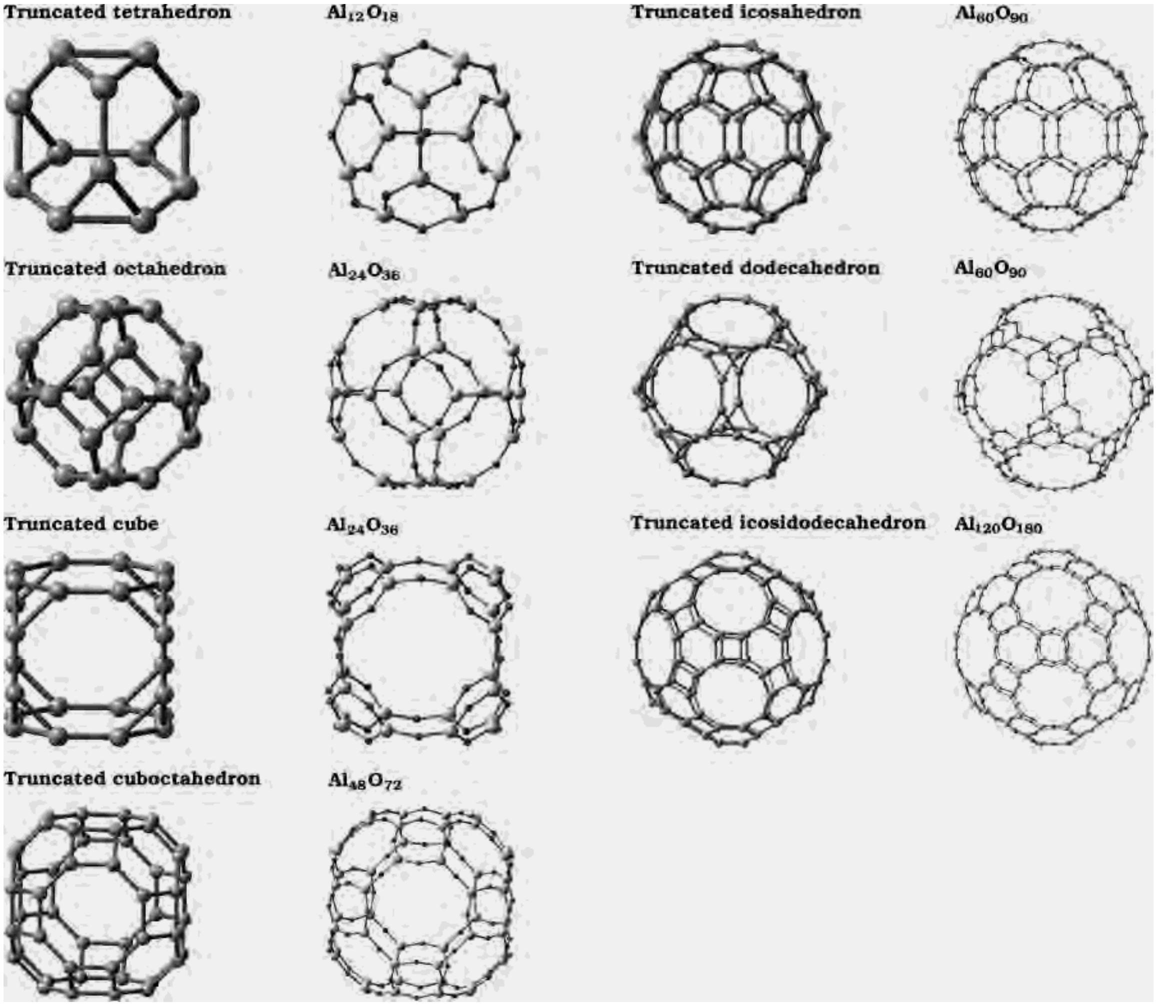

Figure 2. From Archimedean polyhedra to alumina nanostructures.

Table 1. Bond Distances (Å) and Bond Angles (deg) of Alumina Nanostructures $(Al_2O_3)_n$ Derived from Platonic Solids

parent polyhedra	symm	formula	param	HF/3-21G*	B3LYP/6-31G*	MP2/6-311G*
tetrahedron	T_d	Al_4O_6	Al−O	1.715	1.743	1.742
			Al−O−Al	104.1	101.1	101.2
			O−Al−O	112.0	113.3	113.3
cube	O_h	Al_8O_{12}	Al−O	1.692	1.715	1.716
			Al−O−Al	127.5	123.3	123.9
			O−Al−O	117.6	118.6	118.4
dodecahedron	I_h	$Al_{20}O_{30}$	Al−O	1.681	1.700	
			Al−O−Al	148.4	144.2	
			O−Al−O	119.2	119.7	

Alternative, aluminum oxide clusters can be built from tetrahedral AlO_4 and octahedral AlO_6 sites. While these clusters grow by addition of Al_2O_3 units, they possess molecular formula of $AlO{\cdot}nAl_2O_3$ instead of $(Al_2O_3)_n$.[11] Consequently, comparison between these two types of structures is not straightforward and is beyond the scope of this paper.

Structures and Relative Stabilitities of Alumina Nanostructures. The geometries of alumina nanostructures derived from Platonic solids and Archimedean polyhedra were optimized to evaluate the performance of the methods as well as to determine the preferred structural characteristics. HF/3-21G* and B3LYP/6-31G* methods were applied up to truncated icosahedron and truncated dodecahedron ($Al_{60}O_{90}$), whereas two smallest nanostructures, the analogues of tetrahedron and cube, were also optimized by MP2/6-311G*. Bond distances and bond angles of Platonic solids are listed in Table 1. The geometries produced by B3LYP/6-31G* and MP2/6-311G* are in a very good agreement with each other. The HF/3-21G* method shows systematic deviations from the higher level methods, underestimating Al−O bond lengths by 0.02−0.03 Å, overestimating Al−O−Al bond angles by 3−4°, and underestimating O−Al−O bond angles by approximately 1°.

Relative stabilities were estimated by considering the structures in the form $(Al_2O_3)_n$ and dividing the total energy

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Table 2. Relative Stabilities (kJ/mol) of Alumina Nanostructures $(Al_2O_3)_n$ Derived from Platonic Solids and Archimedean Polyhedra

parent polyhedra[a]	symm	formula	n	rings	E_{HF}/n (au)	E_{B3LYP}/n (au)	$\Delta E_{HF}/n$	$\Delta E_{B3LYP}/n$
tetrahedron (P)	T_d	Al_4O_6	2	$4 \times Al_3O_3$	−705.0029	−710.7882	361.3	281.0
cube (P)	O_h	Al_8O_{12}	4	$6 \times Al_4O_4$	−705.0952	−710.8638	118.7	82.6
dodecahedron (P)	I_h	$Al_{20}O_{30}$	10	$12 \times Al_5O_5$	−705.1303	−710.8887	26.6	17.0
truncated tetrahedron (A)	T_d	$Al_{12}O_{18}$	6	$4 \times Al_3O_3$ $4 \times Al_6O_6$	−705.1058	−710.8752	91.0	52.6
truncated octahedron (A)	O_h	$Al_{24}O_{36}$	12	$6 \times Al_4O_4$ $8 \times Al_6O_6$	−705.1299	−710.8899	27.6	13.9
truncated cube (A)	O_h	$Al_{24}O_{36}$	12	$8 \times Al_3O_3$ $6 \times Al_8O_8$	−705.1160	−710.8838	64.1	29.8
truncated cuboctahedron (A)	O_h	$Al_{48}O_{72}$	24	$12 \times Al_4O_4$ $8 \times Al_6O_6$ $6 \times Al_8O_8$	−705.1346	−710.8937	15.3	4.0
truncated icosahedron (A)	I_h	$Al_{60}O_{90}$	30	$12 \times Al_5O_5$ $20 \times Al_6O_6$	−705.1404	−710.8952	0.0	0.0
truncated dodecahedron (A)	I_h	$Al_{60}O_{90}$	30	$20 \times Al_3O_3$ $12 \times Al_{10}O_{10}$	−705.1200	−710.8870	53.7	21.6

[a] P = Platonic solid; A = Archimedean polyhedra.

of the system by n. Such procedure allows the comparison between structures of various size by providing the energy/Al_2O_3 unit (Table 2). Calculations were performed by HF/3-21G* and B3LYP/6-31G* methods. While the HF/3-21G* method overestimates the differences in stabilities, the qualitative trends in relative stabilities are in a very good agreement with B3LYP/6-31G* calculations, the correlation coefficient being as high as 0.996.

The tetrahedron has clearly the lowest stability, which originates from the electron deficiency of aluminum. The vacant p-orbital of aluminum should be fulfilled by π-electron donation from the lone pairs of oxygen.[12] Consisting only of Al_3O_3 rings, such electron donation cannot occur properly, since the Al−O−Al angle is forced to bend to 101°. This is far from the optimal Al−O−Al angle of 180°, which would give the best overlap between the oxygen and aluminum p-orbitals. Switching to a cube, being made of Al_4O_4 rings and having the next lowest stability albeit much better than that of the tetrahedron, increases the Al−O−Al angle to 123°. A dodecahedron, which contains Al_5O_5 rings, already has an Al−O−Al angle of 144° and is therefore much more stable than the smaller Platonic solids. In addition to the apparent influence on stability, the magnitude of π-electron donation can be observed in Al−O bond lengths, i.e., in bond order. The Al−O bond of the tetrahedron is 1.743 Å, which decreases to 1.715 Å for a cube and to 1.700 Å for a dodecahedron. It should be noted that typical Al−O bonds are much longer, 1.8−2.0 Å,[13] demonstrating the relevance of π-electron donation from oxygen to aluminum, which shortens the bonds.

The π-coordination from oxygen to aluminum dominates the stabilities of Archimedean polyhedra as well. The lowest relative stabilities are obtained for a truncated tetrahedron, truncated cube, and truncated dodecahedron, all of which contain unfavorable Al_3O_3 rings. Slight destabilization by Al_4O_4 rings is not so apparent, owing to the simultaneous presence of larger rings, more capable of O−Al electron donation (truncated octahedron and truncated cuboctahedron). Still, the truncated icosahedron, consisting of Al_5O_5 and Al_6O_6 rings, is clearly favored, since each oxygen can participate in the electron donation reasonably well.

Alumina Nanoballs and -tubes. Due to the preference of a combination of Al_5O_5 and Al_6O_6 rings, the shapes of alumina nanostructures resemble balls, similar to icosahedral fullerenes. The relevance of this similarity becomes apparent from Figure 3, where fullerenes and alumina nanoballs are presented next to each other. It turns out that alumina nanoballs are isovalent with fullerenes. With 240 valence electrons, the $Al_{20}O_{30}$ dodecahedron is the isovalent electronic

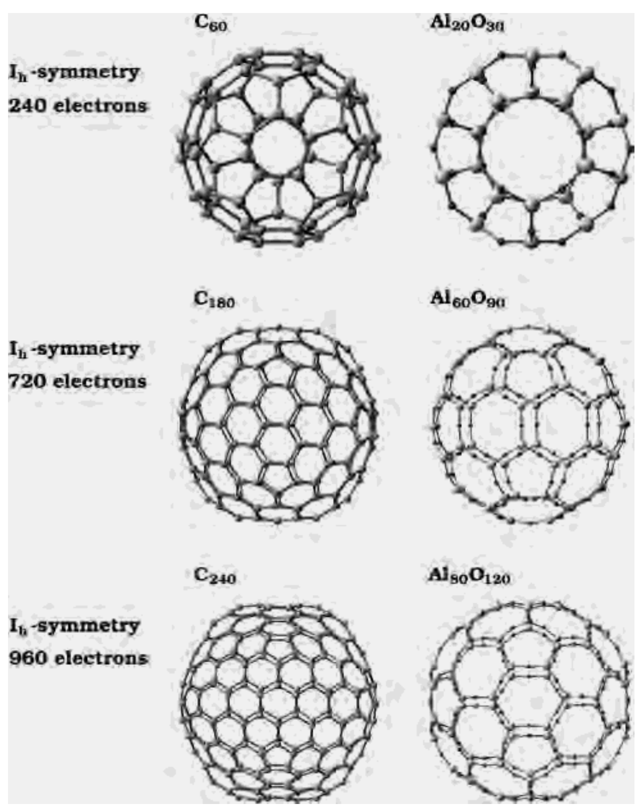

Figure 3. Isovalent isoelectronic pairs: icosahedral fullerenes vs icosahedral alumina nanoballs.

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Table 3. Diameters (nm) and Relative Stabilities (kJ/mol) of Three Smallest I_h-Symmetric Alumina Nanoballs $(Al_2O_3)_n$

formula	n	rings	diameter	E_{HF}/n (au)	$\Delta E_{HF}/n$
$Al_{20}O_{30}$	10	$12 \times Al_5O_5$	0.91	−705.1303	26.6
$Al_{60}O_{90}$	30	$12 \times Al_5O_5$ $20 \times Al_6O_6$	1.64	−705.1404	0.0
$Al_{80}O_{120}$	40	$12 \times Al_5O_5$ $30 \times Al_6O_6$	1.90	−705.1417	−3.3

analogue of C_{60} fullerene, which on the other hand, is the structural analogue of the $Al_{60}O_{90}$ nanoball, the truncated icosahedron. Having 720 valence electrons, $Al_{60}O_{90}$ nanoball is the isovalent electronic analogue of C_{180} fullerene. Correspondingly, the 960 valence electron $Al_{80}O_{120}$ zonohedra[14] is isovalent with C_{240} fullerene. Notwithstanding these apparent similarities, unlike fullerenes, alumina nanoballs cannot be aromatic owing to the significant difference between the electronegativities of Al and O.

The relative stabilities continue to improve for larger alumina nanoballs (Table 3). This is logical, since while the number of Al_5O_5 rings always remains constant (12), the number of more favorable Al_6O_6 rings increases as a function of the size of the ball. The difference in relative stability between $Al_{60}O_{90}$ and $Al_{80}O_{120}$, 3.3 kJ/mol per Al_2O_3 unit, may sound small, but when we consider that $Al_{80}O_{120}$ consists of 40 such units, the difference is as much as $3.3 \times 40 = 130$ kJ/mol. Apparently, the alumina nanoballs would be very large, much larger than $Al_{80}O_{120}$ with a diameter of 1.90 nm. So far no alumina nanoballs have been synthesized.

We shall show now how the alumina nanotubes can be derived from their parent nanoballs (Figure 4). For simplicity, we study the formation of nanotubes from the smallest icosahedral nanoball, dodecahedron ($Al_{20}O_{30}$). Larger nanotubes could be derived in a similar way. The tubes are capped by the halves of ball, between which $(Al_{10}O_{15})_n$ units are added by forming the preferred Al_6O_6 rings. Depending on the number of added $(Al_{10}O_{15})_n$ units, the symmetries of tubes alternate between D_{5h} and D_{5d}. For even values of n, D_{5d}-symmetry is obtained, whereas odd values of n produce tubes with D_{5h}-symmetry.

Relative stabilities of alumina nanotubes derived from $Al_{20}O_{30}$ dodecahedron are shown in Table 4. To enable comparisons with Tables 2 and 3, the energies are given relative to truncated icosahedron ($Al_{60}O_{90}$). The stabilities systematically improve as a function of tube length, owing to the proportional increase in the number of favorable Al_6O_6 rings. The stability of an infinitely long tube was estimated by hyperbolic fitting of E/n as a function of n. The relative stability of the infinitely long tube is 7.7 kJ/mol/n higher than the stability of truncated icosahedron ($Al_{60}O_{90}$), hence also 4.5 kJ/mol/n higher than that of $Al_{80}O_{120}$ zonohedra. This indicates that long tubes are preferred owing to the significant number of Al_6O_6 rings. It does not, however, indicate that tubes are more stable than balls. This becomes apparent by comparing the energies of icosahedral balls, $Al_{60}O_{90}$ and $Al_{80}O_{120}$, with their tubular D_{5d}-symmetric isomers. In each case, ball is more stable, $Al_{60}O_{90}$ by 99 kJ/mol and $Al_{80}O_{120}$ by 153 kJ/mol. The low stabilities of thin nanotubes compared to nanoballs are predictable. Folding to a thin tube causes strain, simultaneously hindering the stabilizing π-electron donation from the lone pairs of oxygen to the vacant p-orbital of aluminum. The strain would be insignificant in thicker tubes, which should therefore possess closely similar stabilities with their ball-shaped congeners having the same molecular formula.

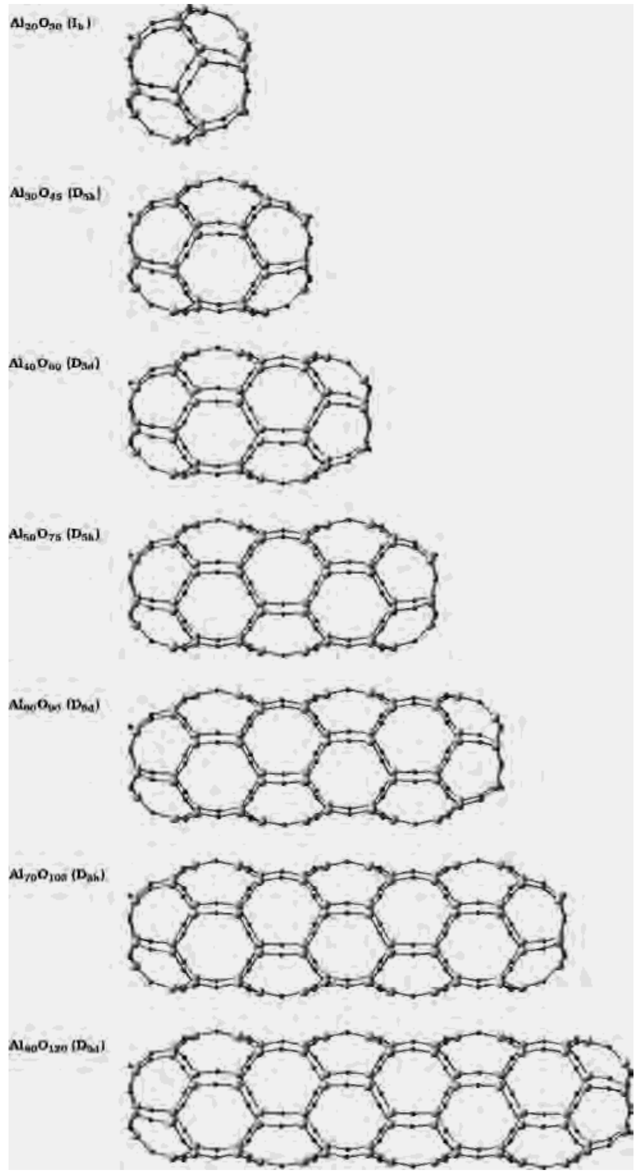

Figure 4. Formation of alumina nanotubes from the icosahedral $Al_{20}O_{30}$ nanoball.

Conclusions

Alumina nanostructures were derived from Platonic solids and Archimedean polyhedra and were optimized by quantum chemical HF/3-21G*, B3LYP/6-31G*, and MP2/6-311G* methods to determine the preferred structural characteristics and relative stabilites. I_h-symmetric nanoballs, being isoelectronic with icosahedral fullerenes, are preferred. Alumina nanoballs consist of 12 Al_5O_5 rings in combination with a variable number of Al_6O_6 rings. Generally, Al_6O_6 rings are

(14) For definition of zonohedra, see ref 10.

Table 4. Relative Stabilities (kJ/mol) of Alumina Nanotubes $(Al_2O_3)_n$ Derived from $Al_{20}O_{30}$ Dodecahedron[a]

symm	formula	n	rings	E_{HF}/n (au)	$\Delta E_{HF}/n$
I_h	$Al_{20}O_{30}$	10	12 × Al_5O_5	−705.1303	26.6
D_{5h}	$Al_{30}O_{45}$	15	12 × Al_5O_5 5 × Al_6O_6	−705.1350	14.4
D_{5d}	$Al_{40}O_{60}$	20	12 × Al_5O_5 10 × Al_6O_6	−705.1371	8.8
D_{5h}	$Al_{50}O_{75}$	25	12 × Al_5O_5 15 × Al_6O_6	−705.1383	5.5
D_{5d}	$Al_{60}O_{90}$	30	12 × Al_5O_5 20 × Al_6O_6	−705.1392	3.3
D_{5h}	$Al_{70}O_{105}$	35	12 × Al_5O_5 25 × Al_6O_6	−705.1398	1.7
D_{5d}	$Al_{80}O_{120}$	40	12 × Al_5O_5 30 × Al_6O_6	−705.1402	0.6
D_{5h}/D_{5d}	$Al_{2n}O_{3n}$[b]	∞	12 × Al_5O_5 ∞ × Al_6O_6	−705.1434	−7.7

[a] The stabilities are given relative to the energy of truncated icosahedron ($Al_{60}O_{90}$). [b] Extrapolated to infinity by hyperbolic fit: $E/n = a + b/n$, where $E/n = a$, when $n \to \infty$. Parameters: $a = -705.1434$; $b = 0.1259$; correlation coefficient = 0.999 98; data range $n = 15-40$.

preferred. The preference is due to π-electron donation from the lone pairs of oxygen to the vacant p-orbital of aluminum, which cannot be properly achieved by smaller rings. This results in stability increase as a function of the size of the ball.

Alumina nanotubes can be derived from their parent icosahedral nanoballs. The D_{5d}- or D_{5h}-symmetric tubes are capped by halves of the balls, and the tubular section consists of adjacent Al_6O_6 rings. Long tubes are preferred, owing to the larger proportion of favorable Al_6O_6 rings. To be stable, alumina nanotubes need to be thick. Thin tubes are destabilized due to strain and hindered π-coordination between oxygen and aluminum. Chemical and physical properties of alumina nanostructures should differ significantly from their parent carbon analogues, especially due to the high polarity of the Al−O bond. This novel group of materials is expected to provide its contribution to the field of nanotechnology in the near future.

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Supporting Information Available: Listings of input and output Cartesian coordinates and input keywords. This material is available free of charge via the Internet at http://pubs.acs.org.

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