Theoretical Studies of Aluminoxane Chains, Rings, Cages, and Nanostructures

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Abstract: Alumina nanostructures and three families of aluminoxanes, linear, cyclic, and cagelike structures, have structures that resemble their isovalent electronic hydrocarbon analogues. Specific examples of each family are the counterparts of fullerene, allene, benzene, and cubane, respectively. The aluminoxanes and alumina nanostructures are related to each other; the latter can be regarded as a hydrogen- or alkyl-free form of aluminoxane. By exploiting this relationship, the relative stabilities of the three families of aluminoxanes, alumina nanostructures, and alumina crystal lattices have been estimated. According to ab initio calculations, aluminoxane cages, which take the form of a truncated octahedron and related polyhedra, are favored. The stability of the preferred cage, *T*-symmetric $Al_{28}O_{28}H_{28}$, is practically equal to that of the α-alumina crystal lattice.

Keywords: ab initio calculations · aluminoxanes · cage compounds · nanostructures · structure elucidation

Introduction

The rich chemistry of the main group compounds originates from their ability to form various chains, rings, cages, and clusters. In the case of carbon, the infinite number of combinations and permutations leads to organic chemistry. While the chemistry of aluminoxanes has been explored less, they can form linear, cyclic, and cage structures as well. From an industrial point of view, an important class of aluminoxanes is methylaluminoxanes (MAOs), which are excellent co-catalysts for olefin polymerization by metallocene catalysis.[1] The exact structure of the MAOs is unknown, which has caused a substantial barrier to the understanding of the polymerization process. MAO is prepared by controlled hydrolysis of $AlMe_3$; the complex product solution, which contains MAO together with free and associated $AlMe_3$, acts as a co-catalyst in the process. While the exact structure of MAO is unknown, it has been suggested that it contains linear chains, cycles, and cagelike clusters, consisting of approximately 5–20 Al−O−Me units.[2] The works of Sinn[3] and Barron and co-workers[4] suggest that cage structures are the most plausible. The latter group has successfully crystallized cagelike *tert*-butyl analogues of MAO. An extensive computational study by Ziegler et al. has shown that $AlMe_3$-free MAO should consist of a mixture of cages of variable size, of which $(AlOMe)_{12}$ is the most abundant.[5]

The well-known chemistry of carbon enables the structures of many other compounds to be rationalized. The structural analogy between hydrocarbons and boron nitrides is known, and originates from the location of boron and nitrogen on either side of carbon in the periodic table. A distinct example of the similarity between hydrocarbons and boron nitrides is provided by borazine,[6] an inorganic analogue of benzene. Whereas these isoelectronic compounds have practically identical structures, they differ from each other owing to the polarity of the B−N bond. Consequently, benzene is aromatic, whereas borazine is not.[7] Several isovalent electronic analogues can be considered, for instance, by moving down the periodic table (Si_6H_6, Ge_6H_6).[8,9] Recently, the similarity between benzene and one form of methylaluminoxane, $Al_3O_3Me_3$,[10] was discussed.

In the theoretical approach described herein, the structures of aluminoxanes were explored by using the analogy between hydrocarbons and aluminoxanes. The analogy is extended beyond benzene, and shows how aluminoxanes can be constructed on the basis of the analogous parent hydrocarbons. We start with linear, branched, and cyclic structures, followed by the analogues of cages, such as fullerenes and nanotubes. Throughout the work reported herein, the focus is not on methylaluminoxanes, but on unsubstituted aluminoxanes. As a consequence, conclusions on the struc-

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tures of aluminoxanes are drawn at a general level, without consideration of the substitution pattern.

Computational Details

The aluminoxanes were fully optimized by using the Hartree–Fock method, which has been shown to be suitable for organoaluminum complexes.[10,11] For aluminum and oxygen, we employed the 8-5-11G* and 8-411G* basis sets, respectively, which have been optimized for aluminum oxides by Catti et al.[12] For hydrogen, the standard 6-31G** basis set was applied. Linear, branched, and cyclic aluminoxanes were optimized without symmetry constraints, whereas cagelike structures were constrained to the symmetry in question. Frequency calculations were performed to confirm the character of the stationary point, and to obtain Gibbs free energies. Geometry optimizations and frequency calculations were carried out by Gaussian 03 quantum chemistry software.[13] Periodic Hartree–Fock calculations on α-alumina and aluminum hydride were performed with the CRYSTAL03[14] program using 65 K points in the irreducible part of the first Brillouin zone, and convergence criteria of 10^{-8} Hartree for both eigenvalues and total energies.

Results and Discussion

The structural families: The boron nitride analogues of hydrocarbons together with the corresponding aluminoxanes are illustrated in Figure 1. Four structural families, allene, benzene, cubane, and fullerene, were considered. The aluminoxane counterpart of allene is Al_2OH_4, which possesses a linear D_{2d}-symmetric structure. This structure arises from π-electron donation from the oxygen lone pair to the vacant p orbital of aluminum, as has been reported previously.[10,15] While such a π interaction is weaker than the strong π bond of allene, it is sufficient to define the structure of the aluminoxane, and the Al–O bond order can be considered to be greater than one. The valence electron count of 16 is equal to that of allene. For boron nitrides, the corresponding 16 valence electron species is a linear D_{2d}-symmetric $[B_2NH_4]^-$ anion.[16]

The aluminoxane counterpart of benzene is the D_{3h}-symmetric $Al_3O_3H_3$. The planarity of the structure originates from the π interaction between oxygen and aluminum, similar to that in the allene analogue. Unlike benzene, $Al_3O_3H_3$ is not aromatic owing to the significant difference in the electronegativities of aluminum and oxygen which prevents the delocalization of electrons.[10] This is also the case for the D_{3h}-symmetric borazine ($B_3N_3H_6$), which is known to be nonaromatic.[7] Each compound possesses 30 valence electrons.

The equal valence electron count also applies to the T_d-symmetric boron nitride and aluminoxane counterparts of cubane, each species containing 40 valence electrons. Similar to the C–C single bonds in the saturated cubane, the aluminoxane cage also contains Al–O single bonds. This is apparent from the calculated Al–O bond distances of 1.817 Å, which is within the typical Al–O single bond length range of 1.8–2.0 Å.[17] It is notable that the calculated Al–O bond lengths in the allene and benzene analogues are much shorter, 1.662 Å and 1.681 Å, respectively, owing to the π-electron donation from oxygen to the electron-deficient three-coordinated aluminum.

The structural and electronic similarities between fullerenes and alumina nanostructures have recently been demonstrated.[18] Similar to fullerenes, the alumina nanostructures, being made of Al_5O_5 and Al_6O_6 rings, prefer to adopt the shape of I_h-symmetric balls. A link exists between alumina nanostructures and aluminoxanes, but it is not a simple link. The molecular formula of aluminoxanes is typically $(AlOR)_n(AlR_3)_m$, with the trialkylaluminum moieties being incorporated into the basic framework of the aluminoxane. In the case of the chain, ring, and cage structures, the relationship is apparent. The isovalent electronic aluminoxane analogue of allene has a molecular formula of $(AlOH)(AlH_3)$, whereas the benzene and cubane counterparts are free of trialkylaluminum groups, having molecular formulae of $(AlOH)_n$, where $n=3$ and 4, respectively. By using the same ex-

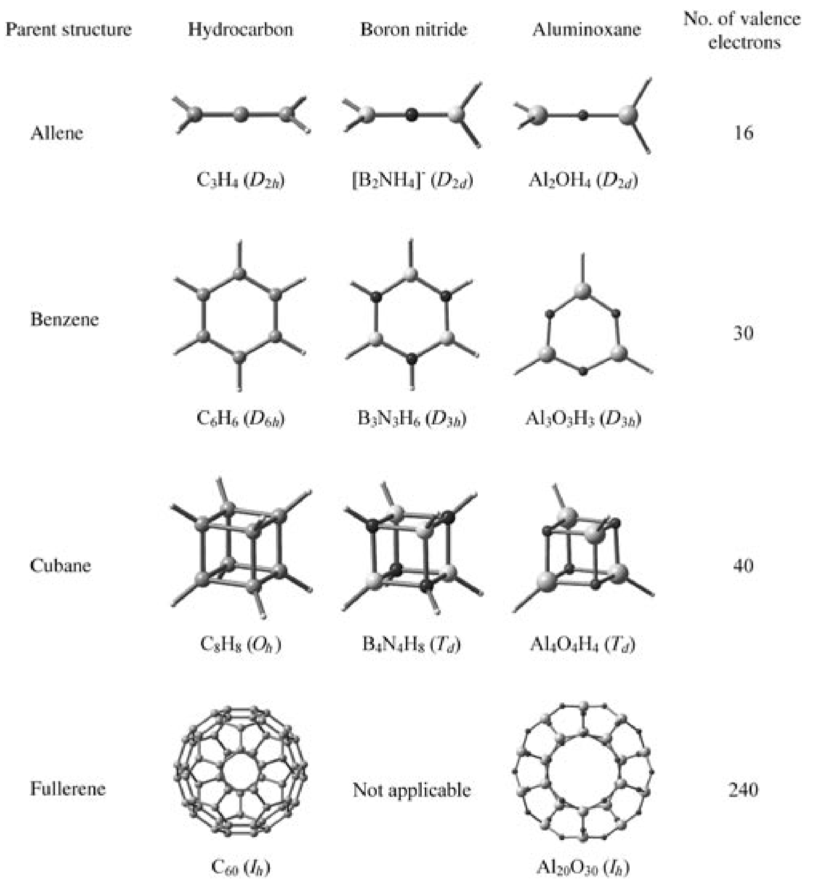


Figure 1. Isovalent electronic boron nitride and aluminoxane analogues of allene, benzene, cubane, and fullerene.

pression for the alumina analogue of C_{60} fullerene, its molecular formula would be $(AlOH)_{30}(AlH_3)_{-10}$, which is $Al_{20}O_{30}$, and it would contain 240 valence electrons, which is equal to the valence electron count of C_{60} fullerene. Hence, alumina nanostructures can be considered to be aluminoxanes from which hydrogen atoms or alkyl groups have been completely removed in the form of trialkylaluminum. The molecular formulas of the allene, benzene, cubane, and fullerene analogues of aluminoxanes are summarized in Table 1. For boron nitrides, the corresponding 240 valence-electron structure is not applicable as it would necessitate the presence of five-membered rings which cannot be fulfilled without introducing unstable B–B and N–N bonds[19] into the nanostructure. Instead, boron nitride fullerenes favor alternating four-membered B_2N_2 and six-membered B_3N_3 rings.[20]

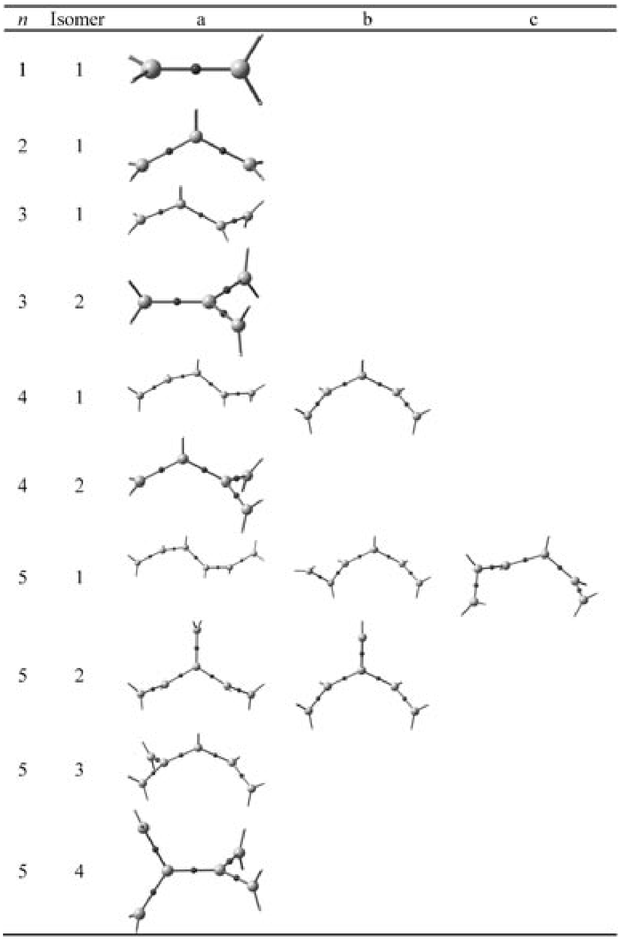
Table 1. Molecular formulae of the allene, benzene, cubane, and fullerene analogues of aluminoxanes.

Hydrocarbon analogue	Molecular formula	$(AlOH)_n(AlH_3)_m$ n	 m
allene	Al_2OH_4	1	1
benzene	$Al_3O_3H_3$	3	0
cubane	$Al_4O_4H_4$	4	0
fullerene	$Al_{20}O_{30}$	30	−10

The isovalent electronic analogy between hydrocarbons and aluminoxanes was then used to explore the structures beyond the allene, benzene, cubane, and fullerene counterparts. We examined the four aluminoxane groups in detail, determining the lowest energy structures within each group. Finally, the stabilities of the groups were compared with each other, and conclusions on the preferred structural characteristics of the studied aluminoxanes were drawn at a general level.

Linear and branched aluminoxanes: The $(AlOH)(AlH_3)$ allene analogue was systematically built up to $(AlOH)_5(AlH_3)$ to investigate the corresponding higher oligomers. Note that several other structures would be obtained if the number of AlH_3 units was increased as well. Such structures, however, have no electronic analogy with hydrocarbons, and were therefore not considered in this work. All the conformations of each isomer were considered, these conformations arising from the possibility that the four consecutive aluminum atoms have a dihedral angle of either 90 or −90°.[10] The structures of the isomers and their conformations together with their total energies and Gibbs free energies at 298.15 K are illustrated in Figure 2.

The two smallest structures, the allene counterparts $(AlOH)(AlH_3)$ and $(AlOH)_2(AlH_3)$, have only one linear isomer.



n	Isomer	ΔE [kJmol^{-1}]	ΔG [kJmol^{-1}]
1	1a	0.0	0.0
2	1a	0.0	0.0
3	1a	0.0	0.0
3	2a	9.6	6.4
4	1a	0.0	0.0
4	1b	0.3	-0.9
4	2a	9.5	5.8
5	1a	0.0	0.0
5	1b	0.2	-0.8
5	1c	0.4	0.8
5	2a	9.4	7.2
5	2b	9.7	5.4
5	3a	9.7	7.3
5	4a	18.9	13.5

Figure 2. Structures, relative total energies, and relative Gibbs free energies ($T = 298.15$ K) for the isomers of $(AlOH)_n(AlH_3)$ aluminoxanes, where $n = 1–5$.

The Al–O–Al angles are 180° and the hydrogen atoms bonded to adjacent aluminum atoms are perpendicular to each other. These structural characteristics have been reported previously for linear methylaluminoxanes,[10] and are due to π interactions between the oxygen lone pairs and the vacant p orbitals of the aluminum atoms. Note that the structural analogy to hydrocarbons is lost when moving to $(AlOH)_2(AlH_3)$, which is isovalent electronic with vinylallene (1,2,4-pentatriene). The next smallest structure, $(AlOH)_3(AlH_3)$, has two isomers, linear (1a) and branched (2a). In terms of the total energy, the linear structure is favored by 9.6 kJ mol^{-1}, but this difference is reduced to 6.4 kJ mol^{-1} after vibrational and thermal corrections, as can be seen in the Gibbs free energy. In the case of the branched isomer, the π-electron donation to the middle aluminum atom is distributed over three oxygen atoms, which apparently is not preferable. The same also applies to the isomers of $(AlOH)_4(AlH_3)$, the branched isomer (2a) being approximately 10 kJ mol^{-1} higher in total energy than the linear isomers. The two conformations of the linear $(AlOH)_4(AlH_3)$ are distinguished by the dihedral angles of the adjacent Al-Al-Al-Al torsions, which are 90° in 1a, but 90 and −90° in 1b. The possible combination of dihedral angles (±90°) for Al-Al-Al-Al torsions give three linear conformations for $(AlOH)_5(AlH_3)$ with very similar energies (1a–c). Successive branching of the linear chain appears to have a constant destabilizing effect of approximately 10 kJ mol^{-1}. Consequently, structures that contain one side chain (2a, 2b, and 3a) are 10 kJ mol^{-1} higher in energy than the linear isomers, while the doubly branched 4a is destabilized by approximately 20 kJ mol^{-1}. Gibbs free energies are generally in line with the total energies. While none of the aluminoxane structures has been experimentally characterized, the structural analogue of $(AlOH)(AlH_3)$ with $CH(SiMe_3)_2$ substituents has been determined.[21] Furthermore, several corresponding aluminoxanes that contain two-coordinate oxygen atoms and four- or five-coordinate aluminum atoms have been structurally characterized.[4a,22]

Comparison of the relative stabilities of the linear and branched aluminoxanes of formula $(AlOH)_n(AlH_3)$ as a function of n is not straightforward because of the extra AlH_3 unit. An attempt to perform this comparison is presented later when the relative stabilities of the four structural families of aluminoxanes are compared.

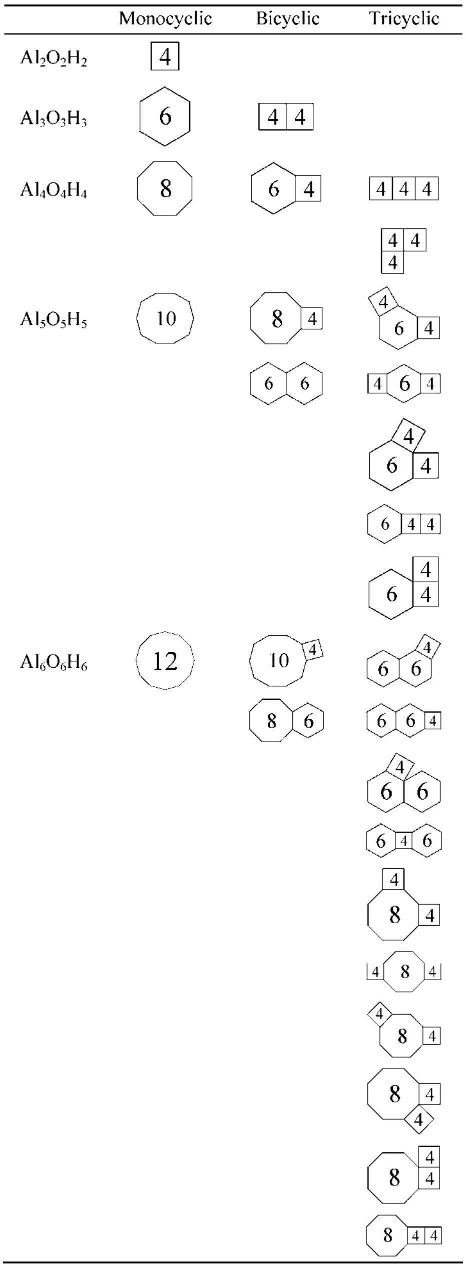
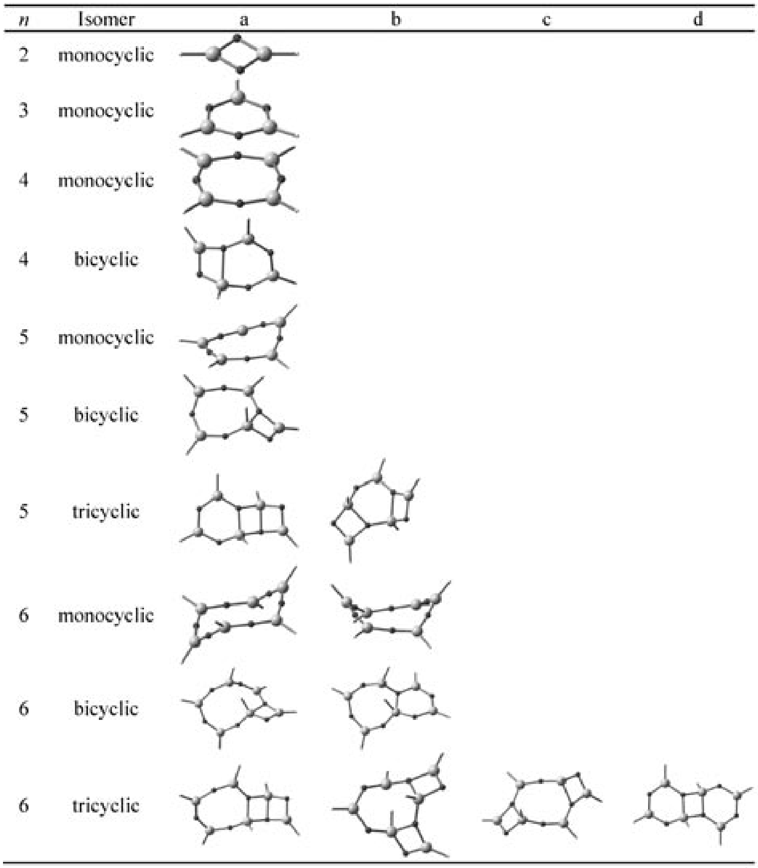


Figure 3. Schematic structures of conceivable mono-, bi-, and tricyclic $(AlOH)_n$ aluminoxanes, where $n = 2$–6.

Cyclic aluminoxanes: Mono-, bi-, and tricyclic aluminoxanes of the formula $(AlOH)_n$ were studied up to $n = 6$. The structures were systematically constructed from combinations of rings containing even numbers of atoms, hence forming structures similar to annulenes and polycyclic aromatics. The combinations that were studied are schematically presented in Figure 3. Notwithstanding several theoretical choices, the number of resulting isomers is rather small. Most of the polycyclic aluminoxanes either open up to form monocyclic structures, or alternatively begin to transform towards cagelike structures. The obtained geometry minima and relative stabilities are shown in Figure 4.

The two smallest cyclic aluminoxanes, $(AlOH)_2$ and $(AlOH)_3$, both have one unique isomer. The D_{2h}-symmetric $(AlOH)_2$, which consists of a four-membered Al_2O_2 ring, is the isovalent electronic analogue of cyclobutadiene, both having 20 valence electrons. The D_{3h}-symmetric $(AlOH)_3$ is the isovalent electronic analogue of benzene, as was discussed above. The aluminoxane analogue of cyclooctatetraene, or [8]annulene, differs somewhat from its hydrocarbon counterpart. Whereas $(AlOH)_4$ adopts a planar D_{4h}-symmetric structure, [8]annulene prefers the D_{2d}-symmetric tub conformation.[23] Wehmschulte and Power have determined the crystal structure of a planar tetrakis(μ_2-oxo)(2,4,6-tri-*tert*-butylphenyl)aluminum, which is an analogue of monocyclic $(AlOH)_4$ with bulky *tert*-butyl substituents.[24] The bicyclic isomer of $(AlOH)_4$, which consists of fused Al_2O_2 and Al_3O_3 rings, corresponds to the C_s-symmet-



n	Isomer	ΔE [kJmol^{-1}]	ΔG [kJmol^{-1}]	$\Delta E/n$ [kJmol^{-1}]	$\Delta G/n$ [kJmol^{-1}]
2	mono	0.0	0.0	0.0	0.0
3	mono	0.0	0.0	-94.1	-84.8
4	mono	0.0	0.0	-112.7	-100.7
4	bi	45.7	44.3	-101.3	-89.7
5	mono	0.0	0.0	-116.6	-105.1
5	bi	22.8	35.4	-112.0	-98.1
5	tri (a)	-38.8	-16.1	-124.4	-108.4
5	tri (b)	36.1	57.1	-109.4	-93.7
6	mono (a)	0.0	0.0	-118.5	-105.0
6	mono (b)	3.4	-3.5	-117.9	-105.6
6	bi (a)	-98.9	-72.1	-135.0	-117.0
6	bi (b)	-3.4	19.1	-119.0	-101.8
6	tri (a)	-67.6	-46.9	-129.7	-112.8
6	tri (b)	-19.9	11.9	-121.8	-103.0
6	tri (c)	30.3	48.5	-113.4	-96.9
6	tri (d)	-142.7	-116.9	-142.3	-124.4

Figure 4. Structures, relative energies of the isomers (ΔE, ΔG), and relative energies per AlOH unit ($\Delta E/n$, $\Delta G/n$) for the isomers of cyclic $(AlOH)_n$ aluminoxanes, where $n=2$–6. The stabilities per AlOH unit are given relative to the $(AlOH)_2$ monocycle. Gibbs free energies are given at $T=298.15$ K.

ric isomer of [8]annulene. The monocyclic aluminoxane is preferred by 44 kJ mol^{-1} over its bicyclic isomer.

The planarity of the monocycle is lost when switching to $(AlOH)_5$, which is the isovalent electronic analogue of [10]annulene. The same applies to [10]annulene itself, which has been extensively studied by theoretical methods. Nevertheless, its preferred isomer has not been unambiguously determined, the nonplanar boat, azulene-like, heart, naphthalene-like and twist isomers being among the favored structures.[25] The $(AlOH)_5$ monocycle is C_s-symmetric, and corresponds to the boat conformation of [10]annulene. The distortion of the monocycle from the planar arrangement is due to sp^2-hybridized aluminum atoms, which prefer O-Al-O bond angles of approximately 120°. Interestingly, the $(AlOH)_5$ monocycle is not the preferred isomer. The tricycle (a), which consists of a six-membered and two four-membered rings, is favored by 39 kJ mol^{-1} in terms of the total energy and 16 kJ mol^{-1} in terms of the Gibbs free energy. Two other polycycles, bicyclic with Al_2O_2 and Al_4O_4 rings, and tricyclic (b), with one Al_3O_3 and two Al_2O_2 rings have much higher energies. The difference between the (a) and (b) isomers of the tricycles is the position of the four-membered rings, which, in the case of the preferred (a) isomer, are connected to each other, and in the case of (b), which is higher in energy, are separated by an Al–O bond.

The $(AlOH)_6$ monocycle can adopt two conformations: A D_{3d}-symmetric chair (a) and a C_2-symmetric boat (b) structure. The chair conformer is slightly favored in terms of the total energy. Entropy effects, however, cause the order of stability to be reversed. The isovalent electronic hydrocarbon analogue is [12]annulene, which has several low-energy isomers, the C_1- and D_2-symmetric structures being preferred.[26] In addition to the monocycle, we found two bicycles, (a) and (b), as well as four tricycles, (a–d). The bicycle prefers a combination of Al_2O_2 and Al_5O_5 rings, instead of Al_3O_3 and Al_4O_4 rings. The tricyclic (d) isomer, in which two six-membered rings are connected through two Al–O bonds, is the clearly favored hexamer. The three other tricyclic isomers (a–c) are combinations of two Al_2O_2 and one Al_4O_4 rings. Similar to the corresponding pentamers, their stabilities systematically decrease as the separation between the four-membered rings increases.

The observed stability orders can be interpreted by means of two competing effects: 1) Reorganization of the ring system, which is a destabilizing effect, and 2) the formation of four-coordinated aluminum centers, which is a stabilizing effect. This is best seen by comparing the stabilities of monocycles with bicycles as a function of the number of AlOH units. In the case of the tetramer and pentamer, the monocycle is preferred over the bicycle owing to the preference of $(AlOH)_3$ and $(AlOH)_4$ rings to adopt a planar arrangement of atoms. This planarity is lost in the bicycles, and the energy lost in the reorganization of the ring system is somewhat larger than that gained by the formation of a four-coordinated aluminum center. The situation is very different for the bicyclic (a) isomer of the hexamer, in which four- and ten-membered rings are connected to each other. Since the ten-membered $(AlOH)_5$ monocycle does not prefer a planar arrangement, it does not suffer from reorganization of the ring. However, it does benefit from the resulting four-coordinated aluminum, and therefore it has a higher stability. These competing effects, the reorganization of the ring and four-coordination of aluminum, dominate the stabilities of tricycles as well. Starting from $n=5$, the formation of tricycles is preferred to the formation of monocycles. The tricyclic (d) isomer of the hexamer, in which two four-coordinate aluminum centers are formed without loss of the planarity of the six-membered rings, is clearly the preferred structure of the whole series of ring systems. Consequently, six-membered rings, which are connected by two Al–O bonds, appear to be the basic structural elements of cyclic aluminoxanes.

Aluminoxane cages: Cagelike aluminoxane clusters are derived from Platonic solids and Archimedean polyhedra. Five Platonic solids exist: tetrahedron, cube, octahedron, dodecahedron, and icosahedron. As far as the analogy with hydrocarbons is concerned, only those polyhedra in which three faces meet at each vertex are applicable owing to the tetravalence of sp^3-hybridized carbon atoms. Three Platonic solids meet this criterion: tetrahedron, cube, and dodecahedron. In the case of aluminoxanes, polyhedra that consist of odd-numbered polygons are ruled out since they would require the formation of Al–Al and O–O bonds. These two criteria leave us with only one Platonic solid, that is, the cube. The same criteria apply to the Archimedean polyhedra as well. Of a total of 13 Archimedean polyhedra, three meet the required conditions. These are the truncated octahedron, the truncated cuboctahedron and the truncated icosidodecahedron. The structures of hydrocarbon polyhedranes together with their applicable aluminoxane counterparts are illustrated in Figure 5.

Owing to the composition of the polyhedron framework of two distinct atoms, aluminum and oxygen, the symmetries of the aluminoxane cages are lower than their parent polyhedra. The aluminoxanes are, however, isovalent electronic with their polyhedrane analogues. The analogue of the O_h-symmetric cubane is the T_d-symmetric $(AlOH)_4$, both possessing 40 valence electrons. As far as the Archimedean polyhedra are concerned, the simplest aluminoxane is the T_h-symmetric $(AlOH)_{12}$, which is the analogue of the O_h-symmetric truncated octahedrane. This structure consists of a combination of six Al_2O_2 and eight Al_3O_3 rings and has a total of 120 valence electrons, that is, the same as its polyhedrane counterpart. With 240 valence electrons the O-symmetric $(AlOH)_{24}$ is the isovalent electronic analogue of the O_h-symmetric truncated cuboctahedrane. The structure consists of twelve Al_2O_2, eight Al_3O_3 and six Al_4O_4 rings. The I-symmetric $(AlOH)_{60}$ is derived from the largest Archimedean polyhedra, the truncated icosidodecahedron. It is the isovalent electronic analogue of the I_h-symmetric truncated icosidodecahedrane, both containing 600 valence electrons. The cage consists of 30 Al_2O_2, 20 Al_3O_3 and 12 Al_5O_5 rings.

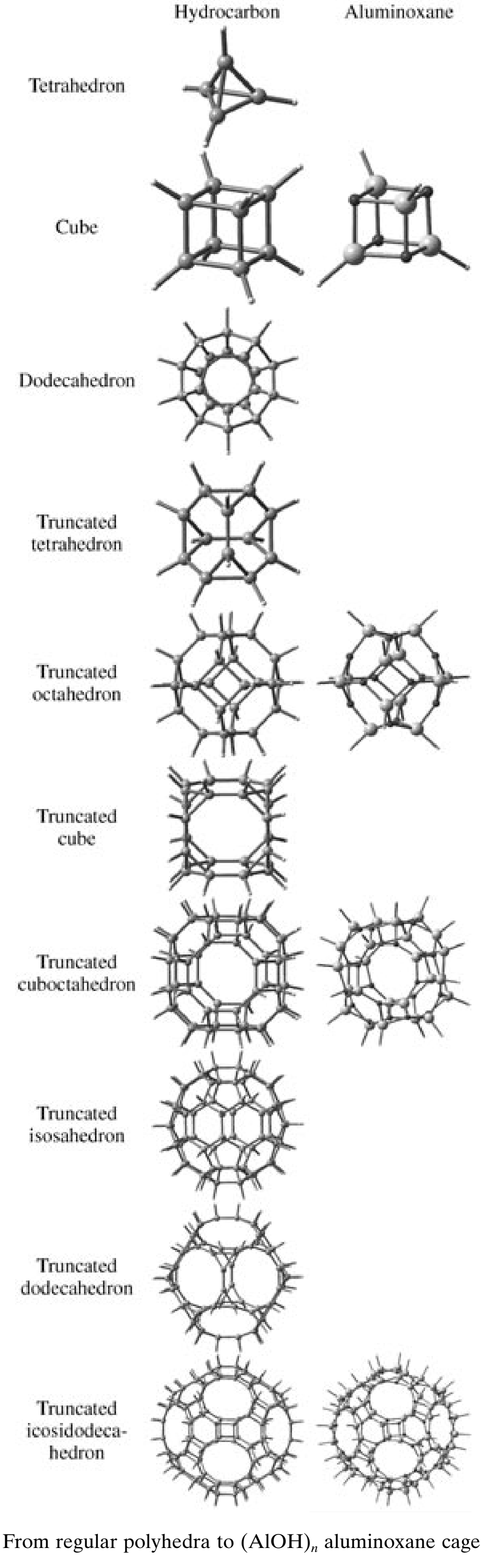


Figure 5. From regular polyhedra to $(AlOH)_n$ aluminoxane cages.

The relative stabilities of the aluminoxane cages derived from regular polyhedra are given in Table 2. The analogue

Table 2. Relative total energies and Gibbs free energies ($T = 298.15$ K) of $(AlOH)_n$ aluminoxane cages derived from Platonic solids per AlOH unit. The energies are given relative to the$(AlOH)_2$ monocycle.

Parent polyhedra	Formula	n	Symm.	E/n [a.u.]	G/n [a.u.]	$\Delta E/n$ [kJ mol^{-1}]	$\Delta G/n$ [kJ mol^{-1}]
cube	$Al_4O_4H_4$	4	T_d	−317.508173	−317.500819	−154.8	−136.5
truncated octahedron	$Al_{12}O_{12}H_{12}$	12	T_h	−317.539546	−317.528199	−237.2	−208.4
truncated cuboctahedron	$Al_{24}O_{24}H_{24}$	24	O	−317.537327	−317.525190	−231.4	−200.5
truncated icosidodecahedron	$Al_{60}O_{60}H_{60}$	60	I	−317.530619	−317.518123	−213.7	−181.9

of cubane, $(AlOH)_4$, is clearly the least stable, followed by the counterparts of truncated icosidodecahedrane, $(AlOH)_{60}$, and truncated cuboctahedrane, $(AlOH)_{24}$. Consisting of four- and six-membered rings, the analogue of truncated octahedrane, $(AlOH)_{12}$, is favored in terms of both the total energy and the Gibbs free energy. This is in line with cyclic aluminoxanes, which prefer fused four- and six-membered rings, and also with experimental structure determinations. Barron and co-workers have synthesized $(AlO\textit{t}Bu)_n$ cages, where $n = 6$, 8, 9, and 12.[4] Each of the structures consists of a combination of four- and six-membered Al_2O_2 and Al_3O_3 rings. The $(AlO\textit{t}Bu)_{12}$ cage has a similar structure to that of the analogue of truncated octahedrane, $(AlOH)_{12}$, and is the smallest cage not to contain square-square edges. These aluminoxane cages, with methyl substituents instead of *tert*-butyl groups, have been studied theoretically by Ziegler and co-workers,[5] who demonstrated that the analogue of truncated octahedrane, $(AlOMe)_{12}$, is favored.

The preference for a combination of four- and six-membered rings with no square-square edges is apparently due to the minimization of angular strain. In the case of hydrocarbon polyhedranes, dodecahedrane has the lowest total angular strain per carbon atom followed by truncated octahedrane.[27] This is also the case for the aluminoxanes, which however cannot adopt a dodecahedron structure as it is composed of pentagons. Hence, the aluminoxanes adopt the structure with the next lowest strain, that is, truncated octahedrane. The truncated octahedrane hydrocarbon has not been synthesized, although the dodecahedrane with the least strain has been[28] along with the polyhedranes derived from other appropriate Platonic solids, that is, cubane[29] and tetrahedrane[30] hydrocarbons.

Owing to the preference of aluminoxanes to adopt the truncated octahedron structure, we systematically derived and optimized larger tetrahedral aluminoxane zonohedra[31] up to $(AlOH)_{64}$, each consisting of a combination of six Al_2O_2 and $n-4$ Al_3O_3 rings. The structures, molecular formulae, and symmetries of the aluminoxane cages together with their relative stabilities are presented in Figure 6.

The tetrahedral complexes have T_h, T_d, or T symmetries. The analogue of the T_h-symmetric truncated octahedron, $(AlOH)_{12}$, is followed in size by the T_d-symmetric $(AlOH)_{16}$, which is favored by 5.0 kJ mol^{-1} per AlOH unit in terms of the total energy, and by 3.6 kJ mol^{-1} per AlOH unit in terms of the Gibbs free energy. The congener of $(AlOH)_{16}$ with methyl substituents has been studied by Ziegler and co-workers,[5] who found that $(AlOH)_{16}$ is favored in terms of the total energy, and $(AlOH)_{12}$ in terms of the Gibbs free energy. We verified these results by B3LYP calculations, which gave practically the same energy differences as given above, $(AlOH)_{16}$ being favored by 5.1 kJ mol^{-1} per AlOH unit in total energy, and 3.9 kJ mol^{-1} per AlOH unit in Gibbs free energy. Apparently, the reversed stability order noted by Ziegler and co-workers does not arise from the level of theory, but may be due to the substitution pattern. We also compared the performance of the Hartree–Fock (HF) method with that of the MP2/6-311G** calculations in the case of the three smallest monocyclic aluminoxanes, $(AlOH)_n$, where $n = 2$–4, and the two smallest cages, T_d-symmetric $(AlOH)_4$ and T_h-symmetric $(AlOH)_{12}$. The total energies of the structures relative to the smallest ring are −94.1, −112.7, −154.8, and −237.2 kJ mol^{-1} per AlOH unit by the HF method, and correspondingly −84.2, −97.8, −140.0, and −221.4 kJ mol^{-1} per AlOH unit

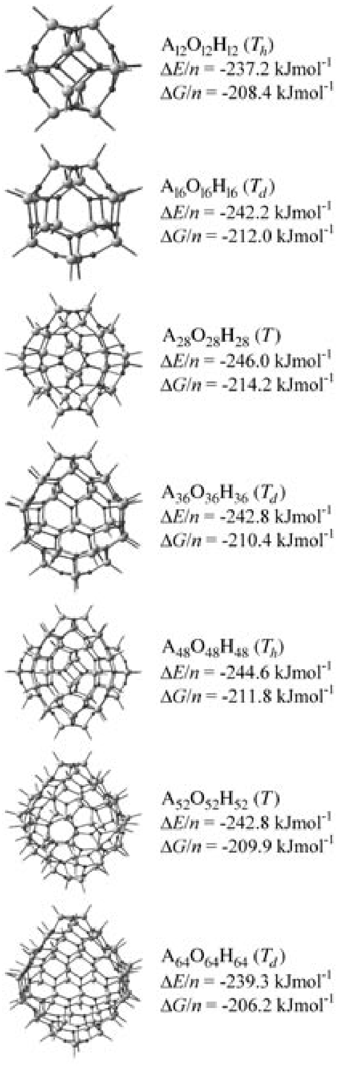


Figure 6. Structures, relative total energies, and relative Gibbs free energies ($T = 298.15$ K) for tetrahedral $(AlOH)_n$ aluminoxane zonohedra consisting of Al_2O_2 squares and Al_3O_3 hexagons. The energies are given relative to the $(AlOH)_2$ monocycle.

by the MP2 method. The qualitative trends obtained by HF are, therefore, in good agreement with those obtained by the MP2 method. Interestingly, the *T*-symmetric $(AlOH)_{28}$, which has a framework that has not been reported for aluminoxanes before, is the most stable cage structure in terms of both the total energy and the Gibbs free energy. Compared with the analogue of truncated octahedrane, $(AlOH)_{12}$, it is favored by 8.8 kJ mol^{-1} per AlOH unit in total energy, and 5.8 kJ mol^{-1} per AlOH unit in Gibbs free energy. As *n* in $(AlOH)_n$ increases upwards of 28, the relative energies begin to rise, the larger structures up to $(AlOH)_{64}$ still being quite stable, and generally with higher stabilities than the T_h-symmetric $(AlOH)_{12}$.

Alumina nanostructures: The nanostructures of aluminum oxides can be considered to be aluminoxanes from which hydrogen or alkyl groups have been completely removed in the form of trialkylaluminum. By using the expression frequently applied to the molecular formula of aluminoxanes, the alumina nanostructures are of the form $(AlOR)_{3n}(AlR_3)_{-n}$. The molecular structures of alumina nanoballs and nanotubes have recently been studied.[18] Their structural characteristics are briefly summarized below.

Similar to the aluminoxane cages, the structures of alumina nanoballs can also be derived from Platonic solids and Archimedean polyhedra (Figure 7). Because the nanostructures are composed of $(AlO)_n$ rings, where *n* is the type of polygon in the parent polyhedra, all those polyhedra in which three faces meet at each vertex are applicable. The I_h-symmetric $Al_{60}O_{90}$, which has the shape of a truncated icosahedron, is favored. Interestingly, the preferred structure is a structural analogue of the I_h-symmetric C_{60} fullerene, consisting of 12 Al_5O_5 rings and 20 Al_6O_6 rings, the same number of C_5 and C_6 rings in C_{60} fullerene. Furthermore, with 720 valence electrons, the I_h-symmetric $Al_{60}O_{90}$ truncated icosahedron is isovalent electronic with the C_{180} fullerene, whereas the C_{60} fullerene is isovalent electronic with a smaller alumina nanostructure, the I_h-symmetric $Al_{20}O_{30}$ dodecahedron. Alumina nanotubes can be derived from I_h-symmetric nanoballs. The resulting tubes have either D_{5d} or D_{5h} symmetries, and are capped by icosahedral hemispheres. While alumina nanoballs have not been synthesized, several alumina nanotubes have been.[32] Octahedral $Al_{24}O_{24}$ could also be a plausible structure.[33]

Relative stabilities of structural groups: Comparison of the stabilities of the four basic structural families of aluminoxanes is of interest, but not straightforward owing to the different stoichiometries of aluminum, oxygen, and hydrogen. Cages and cycles can be easily compared as both have molecular formula of the form $(AlOH)_n$. However, the comparisons with linear aluminoxanes of formula $(AlOH)_n(AlH_3)$, and with nanostructures of formula $(Al_2O_3)_n$ or $(AlOH)_{3n}(AlH_3)_{-n}$ are complicated: The linear aluminoxanes because of the extra AlH_3 unit, and the alumina nanostructures because of the absence of hydrogen. Since the only variable affecting the stoichiometries is the number AlH_3 units incorporated into the structures, elimination reactions can be used for qualitative energy comparisons. When all the hydrogen atoms are removed from the aluminoxanes, we end up with the composition $(Al_2O_3)_n$, each product having the same stoichiometry of Al/O = 2:3. The conversion of aluminoxanes to aluminum oxides through elimination of hydrogen enables comparisons with alumina crystal structures,

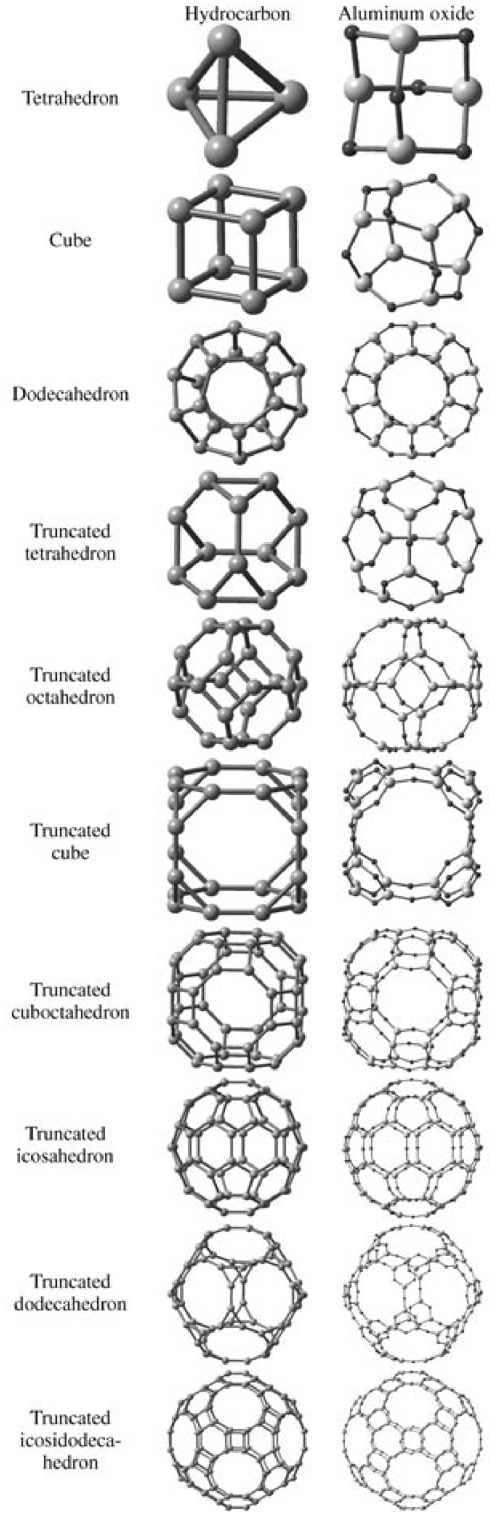


Figure 7. From regular polyhedra to $(Al_2O_3)_n$ alumina nanostructures. Reproduced from reference [18].

which are experimentally well-characterized. In this context, we selected α-alumina, that is, corundum,[34] as the reference, with which the alumina nanostructures and the three families of aluminoxanes were compared.

A practical issue, which needs to be addressed in the removal of hydrogen, is the form in which AlH_3 is eliminated. Knowledge of aluminum hydride compounds is limited, the recently detected dialane, $(AlH_3)_2$, being the only identified species.[35] This does not prove, however, that $(AlH_3)_2$ is the preferred structure. On the basis of computational studies, the trimer should also be stable,[36] as may other higher oligomers as well. The association of AlH_3 units ultimately leads to the solid-state structure of aluminum hydride,[37] which is thermodynamically unstable with respect to decomposition to the elements.[38] In terms of the total energy, however, aluminum hydride is favored over elemental aluminum and hydrogen. Since Gibbs free energies were not available from periodic calculations, we estimated the stabilities on the basis of the total energies. Hence, we ran a periodic calculation on the aluminum hydride crystal lattice to obtain the lowest total energy of AlH_3. The reaction for the elimination of hydrogen is given in Equation (1).

$$(AlOH)_n(AlH_3)_m \rightarrow (AlH_3)_x + (Al_2O_3)_y \quad (1)$$

The comparison of three types of aluminoxanes, alumina nanostructures, and the α-alumina crystal lattice is presented in Table 3. For each structural family, the preferred structure was selected. In the case of linear aluminoxanes, conformer 1a of $(AlOH)_5(AlH_3)$ is favored in terms of the total energy. Of the aluminoxane cycles and cages, the tricyclic (d) isomer of $(AlOH)_6$ and the *T*-symmetric $(AlOH)_{28}$ are preferred, respectively. We re-optimized the truncated icosahedral $Al_{60}O_{90}$ alumina nanoball, which is the favored alumina nanostructure as far as the regular polyhedra are concerned, by using the same basis sets as applied to the aluminoxanes. Furthermore, periodic Hartree–Fock calculations were carried out on α-alumina to quantify the stabilities of the complexes. Elimination of $^8/_3$ AlH_3 units from the linear $(AlOH)_5(AlH_3)$ leaves us with $^5/_3$ Al_2O_3 units. Since the energies are given per Al_2O_3 unit at the end, dealing with fractions does not affect the procedure. By following the same procedure for the cyclic $(AlOH)_6$ two AlH_3 units are eliminated, thus producing $(Al_2O_3)_2$, whereas the removal of $^{28}/_3$ AlH_3 units from the $(AlOH)_{28}$ cage results in $^{28}/_3$ Al_2O_3 units. The energy per Al_2O_3 unit is obtained by dividing the total energy of the structure, from which the energy derived from the periodic calculation of AlH_3 multiplied by the number of eliminated units is subtracted, by the number of Al_2O_3 units.

Table 3. Relative stabilities of the three forms of aluminoxanes, an alumina nanostructure and the alumina crystal lattice per Al_2O_3 unit.

	Linear	Cyclic	Cage	Nanostructure	Crystal lattice
aluminoxane	$(AlOH)_5(AlH_3)$	$(AlOH)_6$	$(AlOH)_{28}$		
isomer	1a	tri, d	*T*-symmetric	truncated icosahedron	α-alumina
no. of AlH_3 units (x)	$^8/_3$	2	$^{28}/_3$	0	0
parent aluminum oxide	$(Al_2O_3)_{5/3}$	$(Al_2O_3)_2$	$(Al_2O_3)_{28/3}$	$(Al_2O_3)_{30}$	$(Al_2O_3)_\infty$
no. of Al_2O_3 units (y)	$^5/_3$	2	$^{28}/_3$	30	∞
$E-xE(AlH_3)$[a] [a.u.]	−1181.349331	−1417.728092	−6617.170063	−21266.077966	
$[E-xE(AlH_3)]/y$ [a.u.]	−708.809598	−708.864046	−708.982507	−708.869266	−708.985951
$\Delta[E-xE(AlH_3)]/y$ [kJ mol^{-1}]	463.3	320.3	9.0	306.6	0.0

[a] Energy per AlH_3 unit from periodic calculation of aluminum hydride: $E(AlH_3) = -243.646186$ a.u.

The linear aluminoxane is clearly disfavored, the energy per Al_2O_3 unit being approximately 460 kJ mol^{-1} higher than that of the α-alumina crystal. The low stabilities of the linear aluminoxanes can be attributed to the presence of three-coordinated aluminum atoms, which are electron deficient. The electron deficiency is somewhat reduced by π-electron donation from the lone pairs of the oxygen atoms. This interaction, however, is relatively weak[10] and therefore insufficient to stabilize the compound. Since aluminoxanes with three-coordinated aluminum atoms generally tend to oligomerize, this type of compound can only exist in the presence of bulky substituents which prevent oligomerization.[39] The only crystallographically characterized structure that exactly matches the linear aluminoxanes of formula $(AlOR)(AlR_3)$ is the one with bulky $CH(SiMe_3)_2$ substituents.[21]

The $Al_{60}O_{90}$ alumina nanostructure, in terms of the electron deficiency of the aluminum atoms, basically belongs to the same category as the linear aluminoxanes. Each aluminum atom is three-coordinated, the relatively weak O–Al π interaction somewhat stabilizing the compound. While the stability of the alumina nanostructure is approximately 300 kJ mol^{-1} per Al_2O_3 unit lower than that of the α-alumina crystal, it is significantly more stable than the linear aluminoxane. Furthermore, it is notable that the alumina nanostuctures are stabilized as a function of the size of the structure.[18] This may account for the existence of large alumina nanostructures, such as the experimentally known long nanotubes.[32]

Whereas monocyclic aluminoxanes, owing to the presence of three-coordinated aluminum atoms, possess practically the same stabilities as their linear congeners,[10] polycycles have lower energies. This is due to the presence of the preferred four-coordinated aluminum atoms that connect the adjacent rings. The stabilities of the polycyclic aluminoxanes are still much lower than that of the α-alumina crystal, the preferred of the studied polycycles, the tricyclic (d) isomer of $(AlOH)_6$, being 320 kJ mol^{-1} per Al_2O_3 unit higher in energy. Furthermore, owing to the flexibility arising from the high ionic character of the aluminoxanes, the synthesis of linear and cyclic aluminoxanes could be considered much more difficult than the synthesis of the corresponding carbon compounds. As discussed above, the polycyclic aluminoxanes have a strong tendency to transform into cagelike structures, thereby maximizing the number of four-coordinate aluminum atoms. The stabilities of aluminoxane cages are incomparable to other aluminoxane families, being practically equal to that of the α-alumina crystal lattice. Apparently, aluminoxanes tend to form cages, but which type of cage is not evident. Since aluminoxanes generally have the formula $(AlOR)_n(AlR_3)_m$, several cagelike structures could be generated if a variable number of trialkylaluminum groups were taken into consideration. Within the scope of this work, where $m=0$, the aluminoxane cages prefer to adopt the form of a truncated octahedron and other related polyhedra.

Conclusions

Linear, cyclic, and cagelike aluminoxanes and alumina nanostructures were explored by ab initio methods. The four families of compounds can be rationalized by a topological analogy with hydrocarbons. Linear and branched aluminoxanes, which have a molecular formula of $(AlOH)_n(AlH_3)$, are isovalent electronic with allene and its derivatives. Correspondingly, cyclic and cagelike aluminoxanes of the formula $(AlOH)_n$ are the counterparts of annulenes and polyhedranes, respectively. Alumina nanostructures, which are isostructural and isovalent electronic analogues of fullerenes, are related to aluminoxanes through the elimination of hydrogen or alkyl groups in the form of trialkylaluminum. In general a similar analogy can also be made between boron nitrides and hydrocarbons, and could be considered for other isoelectronic systems. Note, however, that isoelectronic compounds, such as aluminum fluorides, may have a very different chemistry.

The structures of the linear and branched aluminoxanes are dominated by π-electron donation from the lone pairs of the oxygen atoms to the vacant p orbitals of the electron-deficient three-coordinated aluminum atoms. Linear structures are preferred to branched ones. Polycyclic aluminoxanes with fused Al_2O_2 and Al_3O_3 rings are preferred to monocyclic aluminoxanes due to the presence of the preferred four-coordinate aluminum centers that connect the adjacent rings. Cagelike aluminoxanes prefer to take the shape of a truncated octahedron and related polyhedra consisting of Al_2O_2 and Al_3O_3 rings. The T-symmetric $Al_{28}O_{28}H_{28}$, which is composed of six Al_2O_2 and 24 Al_3O_3 rings, is favored. The relative stabilities of the three classes of aluminoxanes, together with the alumina nanostructures and α-alumina crystal lattice, were compared by considering an elimination reaction in which hydrogen is removed from the aluminoxanes in the form of aluminum hydride. Aluminoxane cages are clearly favored over their linear and cyclic congeners and alumina nanostructures, the energies per Al_2O_3 unit being similar to that of the crystal lattice of α-alumina.

Acknowledgements

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