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Structure and Opto-Electronic Behavior of Diamondoids, with Applications as MEMS and at the Nanoscale Level

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Abstract

Diamondoids have been of great interest in recent years due to their role in nanotechnology, drug-delivery and medicine. Due to their six or more linking groups, they have found major applications as templates and as molecular building blocks in nanotechnology, polymers synthesis, drug delivery, drug targeting, DNA-directed assembly, DNA-amino acid nanostructure formation, and in host-guest chemistry. In this paper, the molecular nature of diamondoids, their molecular specificities, their intermolecular interactions and their opto-electronic properties are introduced. These will help in the understanding of the structure-property relations and self-assembly of diamondoids, which is essential for designing functional molecular gears for micro-electro-mechanical systems (MEMS) and sensitive bionanosensors, and for developing new nanodrugs, just to name a few.

Diamondoid Molecules

Diamondoid molecules are cage-like, ultra-stable, saturated hydrocarbons. These molecules are ringed compounds, which have a diamond-like structure consisting of a number of six-member carbon rings fused together (see Figure 1). More explicitly, they consist of repeating units of ten carbon atoms forming a tetra-cyclic cage system [1-3]. They are called "diamondoids" because their carbon-carbon framework constitutes the fundamental repeating unit in the diamond lattice structure. The diamondoid carbon skeleton is a basic portion of diamond as shown in Figure 2. This structure was first determined in 1913 by Bragg and Bragg [4] using X-ray diffraction analysis.

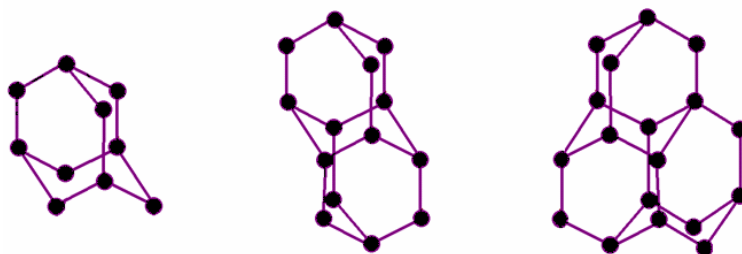


Figure 1: Molecular structures of adamantane, diamantane and trimantane (the smaller diamondoids) with chemical formulas $C_{10}H_{16}$, $C_{14}H_{20}$ and $C_{18}H_{24}$ from left to right.

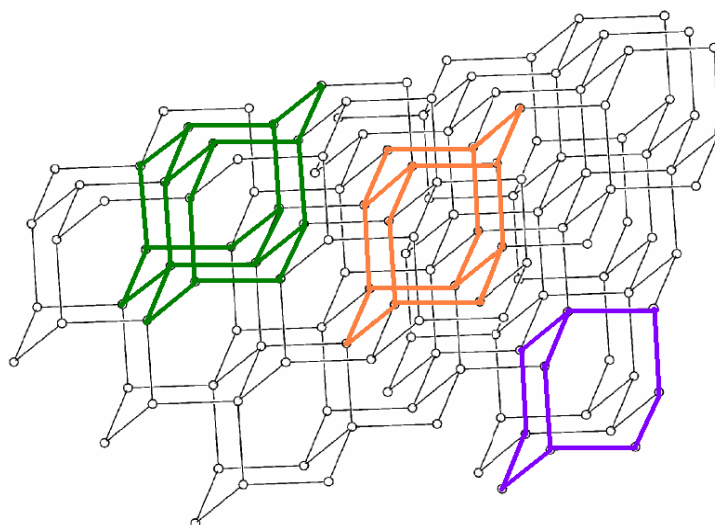


Figure 2: Structures of adamantane, diamantane and triamantane superimposed over the three-dimensional diamond network

The first and simplest member of the diamondoids group, adamantane, is a tricyclic saturated hydrocarbon (tricyclo[3.3.1.1]decane). Adamantane is followed by its polymantane homologues (adamantologues): diamantane, tria-, tetra-, penta- and hexamantane. Figure 1 illustrates the smaller diamondoid molecules, with the general chemical formula $C_{4n+6}H_{4n+12}$: adamantane

($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$) and triamantane ($C_{18}H_{24}$). Each of these lower adamantologues has only one isomer.

Depending on the spatial arrangement of the adamantane units, higher polymantanes ($n \geq 4$) can have several isomers and non-isomeric equivalents. There are three possible tetramantanes, all of which are isomeric. They are depicted in Figure 3 as iso-, anti- and skew-tetramantane, respectively. Anti- and skew-tetramantanes each possess two quaternary carbon atoms, whereas iso-tetramantane has three.

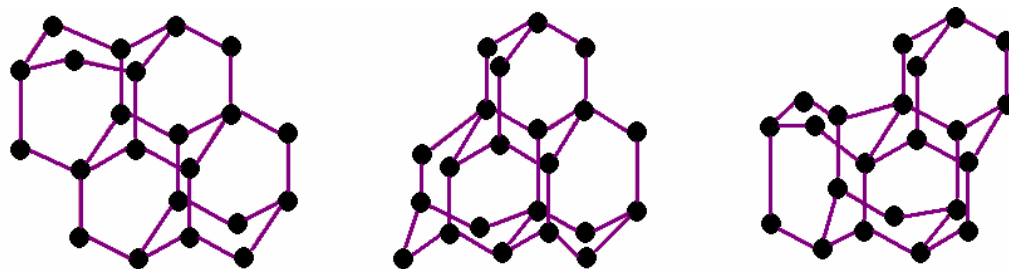


Figure 3: The three possible tetramantanes, all of which are isomeric, as anti-, iso- and skew-tetramantane from left to right. Anti- and skew-tetramantanes each possess two quaternary carbon atoms, whereas iso-tetramantane has three quaternary carbon atoms. The number of diamondoid isomers increases appreciably after tetramantane.

With regards to the remaining members of the diamondoids group, there are seven possible pentamantanes, six of which are isomeric ($C_{26}H_{32}$) and obeying the molecular formula of the homologous series, and one is non-isomeric ($C_{25}H_{30}$). For hexamantane, there are 24 possible structures: 17 are regular cata-condensed isomers with the chemical formula ($C_{30}H_{36}$), six are irregular cata-condensed isomers with the chemical formula ($C_{29}H_{34}$), and one is peri-condensed with the chemical formula ($C_{26}H_{30}$), as shown in Figure 4.

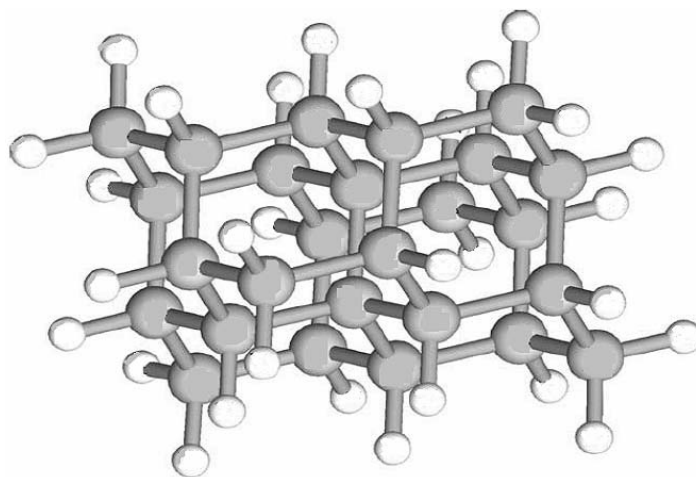


Figure 4: Molecular structure of (peri-condensed) cyclohexamantane ($C_{26}H_{30}$). The darker spheres represent carbon atoms, while the lighter spheres are hydrogen atoms.

Diamondoids, when in the solid state, melt at much higher temperatures than other hydrocarbon molecules with the same number of carbon atoms in their structure. Since they also possess low strain energy, they are more stable and stiff, resembling diamond in a broad sense. They contain dense, three-dimensional networks of covalent bonds, formed chiefly from first- and second-row atoms with a valence of three or more. Many of the diamondoids possess structures rich in tetrahedrally-coordinated carbon. They are materials with superior strength-to-weight ratios.

It has been found that adamantane crystallizes in a face-centered cubic lattice, which is extremely unusual for an organic compound. The molecule therefore should be completely free from both angle strain (since all carbon atoms are perfectly tetrahedral) and torsional strain (since all C-C bonds are perfectly staggered), making it a very stable compound and an excellent candidate for various applications, as will be discussed later.

At the initial point of growth, crystals of adamantane show only cubic and octahedral faces. The effects of this unusual structure on physical properties are interesting [5].

Many of the diamondoids can be brought to macroscopic crystalline forms with some special properties. For example, in its crystalline lattice, the pyramidal-shape [1(2,3)4]pentamantane has a large void in comparison to similar crystals. Although it has a diamond-like macroscopic structure, it possesses the weak, non-covalent, intermolecular van der Waals attractive forces involved in forming a crystalline lattice [6,7]. Another example is the crystalline structure of 1,3,5,7-tetracarboxy adamantane, which is formed via carboxyl hydrogen bonds of each molecule with four tetrahedral nearest-neighbors. The similar structure in 1,3,5,7-tetraiodoadamantane crystal would be formed by I...I interactions. In 1,3,5,7-tetrahydroxyadamantane, the hydrogen bonds of hydroxyl groups produce a crystalline structure similar to inorganic compounds, like the cesium chloride (CsCl) lattice [8] (see Figure 5).

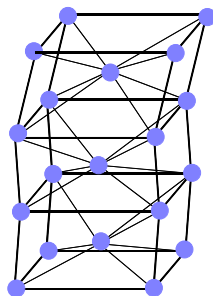


Figure 5: Quasi-cubic units of the crystalline network for 1,3,5,7- tetrahydroxyadamantane, taken from [8]. The molecules have been shown as blue spheres and hydrogen bonds as solid linking lines. This crystalline structure is similar to that of CsCl.

The presence of chirality is another important feature in many derivatives of diamondoids. It should be pointed out that tetramantane [123] is the smallest of the lower diamondoids to possess chirality [6].

Molecular Structure of Diamondoids

Diamondoid molecules show unique properties due to their exceptional atomic arrangements. Adamantane consists of cyclohexane rings in ‘chair’ conformation. These molecules are chemically and thermally stable, strain-free and non-biodegradable.

Adamantane {(CAS No: 281-23-2) 1-tricyclo[3.3.1.1^{3,7}]decane }

Diamantane {(CAS No: 2292-79-7) pentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane } also known as {decahydro-3,5,1,7-[1.2.3.4]-butanetetraylnaphthalene }

Each successively-higher diamondoid family shows increasing structural complexity and varieties of molecular geometries. *Sui generis* properties of diamondoids have provoked an extensive range of inquiries in different fields of science and technology [9], including exploring these as molecular building blocks in nanotechnology.

Intermolecular Interactions

Knowledge about intermolecular interactions is very critical to designing and fabricating organic nanostructure-based devices such as organic thin film transistors, organic light-emitting devices, organic semiconductor nanorods, composites, etc. However, the nature and role of intermolecular interactions in such organic nanostructures as diamondoids is very challenging and not well understood [10-13,14].

The molecular structural characteristics of macroscopic systems based on the knowledge of statistically-averaged (effective) pair-interparticle interactions have already been defined and formulated in the thermodynamic limit [15-23]. As a result, the available atomic and molecular interaction database for macrobodies by means of effective-pair-intermolecular potentials is only an approximation [10-13]. Since the number of particles are finite in organic nanostructures,

those statistical-averaging tools are not well-suited for this purpose. As a result, the theory of intermolecular potential functions of such systems and their relationship with their structural characteristics need to be formulated [10-13]. It is important to develop a phenomenological as well as mathematical foundation of intermolecular interactions for diamondoids which are presently non-existent, and to develop connections between intermolecular interactions and structural characteristics of diamondoid organic nanoscale systems [24-28].

It should be pointed out that structural characteristics in nanoscale systems are a dynamic phenomenon, not the static equilibrium of macroscopic phases. Coexistence of phases is expected to occur over bands of temperature and pressure, rather than at just sharp points [10,24-26]. The Gibbs phase rule loses its meaning, and many phase-like forms may occur for nanoscale systems that are unobservable in the macroscopic counterparts of those systems.

For atoms and rather simple molecules, quantum mechanical *ab initio* calculational methods [29-33] have been successful in producing accurate intermolecular potential functions. For complex molecules and macromolecules, computations are prohibitively difficult to produce accurate potential data. Therefore, a joint theoretical and experimental effort is necessary. Experimentally, we use atomic force microscopy (AFM) and microelectrophoresis measurements to study the intermolecular interactions and structural characteristics in diamondoid-based organic nanosystems. These two different tools complement each other and measure levels of interactions on two different scales: The microelectrophoresis measurements reveal the information on a microscopic scale, while AFM investigates the interaction between atoms and the tip of the apparatus (for details, see the next section).

We have recently performed a first-principles simulation of the interaction between adamantane and an atomic force microscope tip made up of gold [34]. Our simulation results demonstrate quantitatively how an AFM tip interacts with adamantane. It is found that the AFM tip is able to detect the sharp potential change in adamantane. For instance, along different directions, the detailed morphology of the molecular structure can be probed directly. If the tip scans across the [111] direction, the potential change directly follows the sharp structural difference in two kinds of carbon atoms. This is an excellent starting point for our experimental effort, as one can see a large force change in the vicinity those atoms. In addition, if the scan is close to the tetragonal direction, a four-fold symmetry emerges. For the scan along the [111] direction, we estimate the force constant to be about 1.5 times that of C₆₀, which is an indication of the excellent mechanical properties of adamantane. We expect real experiments can probe these detailed changes. However, if the experimental tip contains more atoms, then the experimental results would be an average of the theoretical results.

To be more specific about our theoretical work, we directly compute the *xy*-scan image by scanning across two different surfaces, where one is hexagonal and the other is square surface. The probed atoms are the outside hydrogen atoms. We first hold our tip above adamantane and move along the *x*-direction. At each of the point, we do three radial scans and then use the finite difference method to compute the forces at each point. The number of calculations is huge. Figure 6(a) shows the force along the *z*-direction, where we use the intensity to show the magnitude of the force. One sees that there are two bright spots, which we know from the geometry of adamantane to correspond to the two outermost hydrogen atoms. Figure 6(b) shows

a scan over the hexagonal surface. Different from the square scan, there are three bright spots in this picture, corresponding to the three hydrogen atoms. These distinctive features are expected to show up in real experiments.

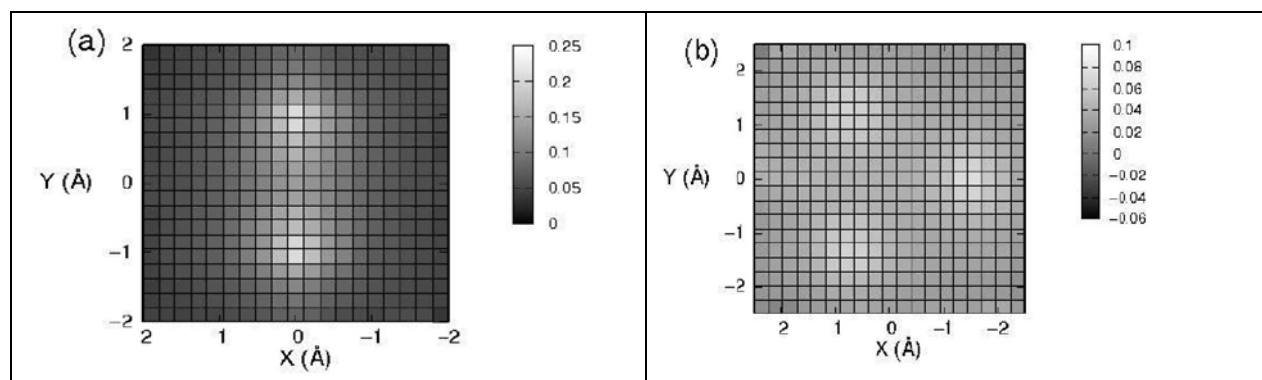


Figure 6: xy -scan image for (a) square surface and (b) hexagonal surface. The bright spots represent where the hydrogen atoms are located. For (a), the tip is 1.2 Å away from the center carbon atom; for (b), the tip is 1.8 Å away from the center of the triangle formed by the three outermost carbon atoms

Diamondoids as Molecular Building Blocks in Nanotechnology

Nanotechnology is the branch of engineering that deals with the manipulation of individual atoms, molecules and systems smaller than 100 nanometers. Two different methods are envisioned for nanotechnology to build nanostructured systems, components and materials: one method is named the “top-down” approach, and the other method is called the “bottom-up” approach. In the top-down approach, the idea is to miniaturize the macroscopic structures, components and systems towards the nanoscale. In the bottom-up approach, the atoms and molecules constituting the building blocks are the starting point to build the desired nanostructure [36-38].

Various illustrations are available in the literature depicting the comparison of the top-down and bottom-up approaches [37,38]. In the former, a macro-sized material is reduced in size to reach the nanoscale dimensions. The photolithography used in the semiconductor industry is an example of the top-down approach. The bottom-up nanotechnology is the engineered manipulation of atoms and molecules in a user-defined and repeatable manner to build objects with certain desired properties. To achieve this goal, a number of molecules are identified as the molecular building blocks (MBBs) of nanotechnology, among which diamondoids are the most important ones owing to their unique properties [6,39-44]. Diamondoids can be divided into two major clusters based upon their size: lower diamondoids (1-2 nm in diameter) and higher diamondoids (> 2 nm in diameter).

The building blocks of all materials in any phase are atoms and molecules. Their arrangements and how they interact with one another define many properties of the material. The nanotechnology MBBs, because of their sizes of a few nm’s, impart to the nanostructures created from them new and possibly preferred properties and characteristics heretofore unavailable in

conventional materials and devices. These nanosize building blocks are intermediate in size, lying between atoms and microscopic and macroscopic systems, and contain a limited and countable number of atoms. They constitute the basis of our entry into new realms of bottom-up nanotechnology [37,38].

The controlled and directed organization of MBBs and their subsequent assembly into nanostructures is one fundamental theme of bottom-up nanotechnology. Such an organization can be in the form of association, aggregation, arrangement or synthesis of MBBs through non-covalent van der Waals forces, hydrogen bonding, attractive intermolecular polar interactions, electrostatic interactions, hydrophobic effects, etc. [37].

The ultimate goal of assemblies of nanoscale molecular building blocks is to create nanostructures with improved properties and functionality heretofore unavailable to conventional materials and devices. As a result, one should be able to alter and engineer materials with desired properties. For example, ceramics and metals produced through controlled consolidation of their MBBs are shown to possess properties substantially improved and different from materials with coarse microstructures. Such different and improved properties include greater hardness and higher yield strength in the case of metals and better ductility in the case of ceramic materials [42].

Considering that nanoparticles have much higher specific surface areas, in their assembled forms there are large areas of interfaces. One needs to know in detail not only the structures of these interfaces, but also their local chemistries and the effects of segregation and interaction between MBBs and their surroundings. The knowledge of ways to control nanostructure sizes, size distributions, compositions and assemblies are important aspects of the bottom-up nanotechnology [37].

In general, nanotechnology MBBs are distinguished for their unique properties. They include, for example, graphite, fullerene molecules made of various numbers of carbon atoms (C_{60} , C_{70} , C_{84} , C_{240} , etc.), carbon nanotubes, nanowires, nanocrystals, amino acids and diamondoids [37]. All these molecular building blocks are candidates for various applications in nanotechnology.

One of the properties used to distinguish MBBs from one another is the number of their available linking groups. MBBs with three linking groups, like graphite, can only produce planar or tubular structures. MBBs with four linking groups can form three-dimensional diamond lattices. MBBs with five linking groups can create three-dimensional solids and hexagonal planes. The ultimate possibility at present would be MBBs with six or more linking groups. Adamantane with six linking groups (see Figure 7) and higher diamondoids are of the latter category, which can be used to construct many complex three-dimensional structures [41]. Such MBBs can have numerous applications in nanotechnology, and they are of major interest in designing shape-targeted nanostructures, including the synthesis of supramolecules with manipulated architectures [45-49].

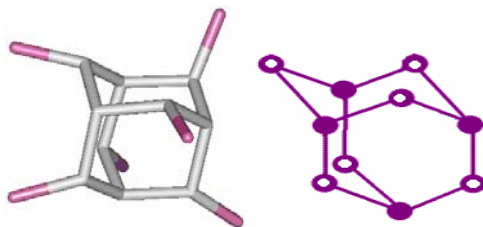


Figure 7: Demonstration of the six linking groups of adamantane.

In addition to possessing six or more linking groups, diamondoids have high strength, toughness and stiffness when compared to other known MBBs. They are tetrahedrally-symmetric stiff hydrocarbons. Strain-free structures of diamondoids give them high molecular rigidity, which is quite important for an MBB. High density, low surface energy and oxidation stability are some other preferred properties of diamondoids as MBBs. Diamondoids have noticeable electronic properties [50]. In fact, they are H-terminated diamond and the only semiconductors which show a negative electron affinity [6].

Since diamondoids possess the capability for derivatization, they can be utilized for reaching suitable molecular geometries needed for molecular building blocks of nanotechnology. Functionalization by different groups can produce appropriate reactants for desired reactions, microelectronics, optics, employing polymers, films and crystal engineering. Over 20,000 variants of diamondoids have been identified and synthesized, and even more are possible [42], providing a rich and well-studied set of MBBs.

Adamantane can be used in molecular studies and preparation of fluorescent molecular probes [51,52]. Because of its incomparable geometric structure, the adamantane core (adamantyl) can impede interactions of fluorophore groups, and self-quenching would diminish due to steric hindrance. Hence, mutual quenching would be diminished, allowing the introduction of several fluorescent groups to the same molecular probe in order to amplify their signals.

Due to their demanding synthesis, diamondoids are helpful models to study structure-activity relationships in carbocations (carbonium ions, which have a positively-charged carbon atom) and radicals, to develop empirical computational methods for hydrocarbons, and to investigate orientational disorders in molecular crystals [5,35].

Atomic force microscope (AFM) is a powerful nanotechnology tool for molecular imaging and manipulations. One major factor limiting resolution in AFM to observe individual biomolecules such as DNA is the low sharpness of the AFM tip that scans the sample. Nanoscale 1,3,5,7-tetrasubstituted adamantane is found to serve as a molecular tip for AFM and may also find application as chemically well-defined objects for calibration of commercial AFM tips [53].

Opto-Electronic Properties of Diamondoids

Opto-electronics, a sub-field of photonics, refers to the study and applications of electronic devices that interact in general with invisible light (such as gamma ray, x-ray, ultraviolet and

infrared). Optoelectronic devices are electrical-to-optical or optical-to-electrical transducers, or instruments that use such devices in their operation.

Diamondoids are generally optically transparent in visible light and have high electrical insulating properties as does diamond. In a recent study, it is found that the large gaps between the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO gaps) in diamondoids are the molecular counterparts of a large fundamental gap in diamond, which is responsible for its optical transparency in the visible range and its insulating properties [41]. The difference between the HOMO and LUMO energy levels is called the band gap energy, which can serve as a measure of the excitability of a molecule: the larger the energy, the harder it will be for excitation to occur. The highest occupied molecular orbital (HOMO) level for organic semiconductors is similar to what the valence band is to inorganic semiconductors. The same analogy is used between the lowest unoccupied molecular orbital (LUMO) level and the conduction band.

The bond lengths and angles in the carbon skeletal structure of diamondoids are essentially the same as in bulk diamond (see Figure 2).

The average bond length of C-C bonds in diamondoids is around 1.545 Å, and the average value of C-H bond lengths is about 1.10 Å. The former matches the C-C bond length in bulk diamond quite well. Upon an increase of the diamondoid size, the average C-C and C-H bond lengths will increase slightly, whereas the average bond angle decreases as the diamondoid size increases. Overall, the average bond angles of most diamondoids are less than the bond angle 109.47° of C-C-C in the bulk diamond structure. This is because the C-H bonds existing in the diamondoids make contributions of smaller bond angles of C-C-H or/and H-C-H to the average bond angles. It is also found that the similarity in bonding between diamondoids and diamond extends also to their bond strength and resistance to deformations [40,54].

The electronic density distribution in diamondoids is important to study for theoretical as well as general chemistry purposes. An explanation and prediction of the reactivity (including reaction mechanisms) and possible existence and stability of related compounds are based on the knowledge of the valence electron density distribution in the diamondoids molecular framework.

Some opto-electronic properties of adamantane, the first and the smallest of diamondoid molecules, has been studied in recent years. For example the geometry and electronic structure of adamantane and related molecular cations has been studied with the emphasis on the electron density distribution on the face planes and in the carbon cage on the basis of *ab initio* molecular orbital calculations. Figure 8 provides charts for the distribution electron density in adamantane across its C1-C7-C10 and C1-C2-C3 planes and along the C1-C4 line as calculated by Korolkov and Sizova [55].

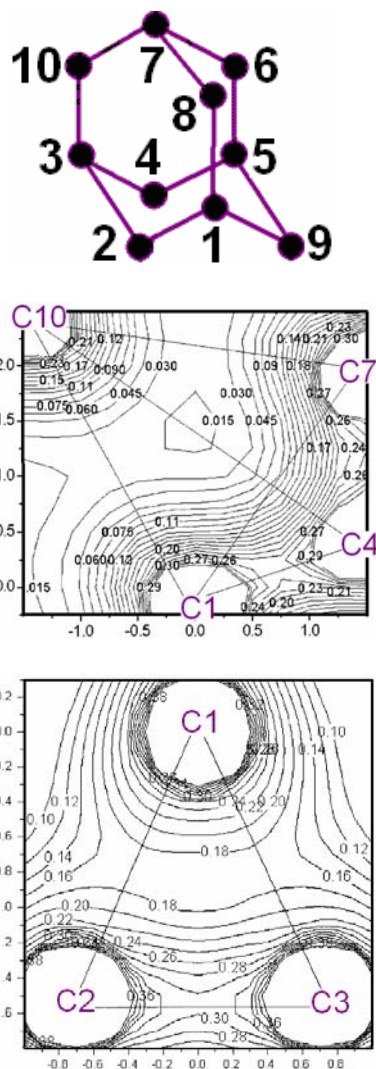


Figure 8: Charts of the distributions of the electron density in adamantane across the C1–C7–C10 and across the C1–C2–C3 planes and along the C1–C4 line [55].

These calculations [55] indicate very low electronic density in the inner parts of the adamantane molecule and its increase in the corresponding adamantyl cations. It is believed that the differences in the electronic density distribution in saturated hydrocarbon–adamantane, and in polyhedral boron hydrides are caused by their different abilities to form additional weak bonds. The carbon atoms of saturated hydrocarbons have no vacant $2p$ orbitals in their valence structure, and that makes any additional interactions with the electron pairs on bonding orbitals impossible. As a result, the valences of the carbon atoms in saturated adamantane hydrocarbon are close to the usual value of four [55].

A group of investigators in Germany [56] have measured synchrotron-based carbon K-edge x-ray absorption (XAS) of diamondoids (starting from adamantane and continuing to hexamantane) together with that of a bulk diamond reference as it is shown by Figure 9. Near-

edge x-ray absorption is a useful spectroscopy tool to probe electronic and structural properties of fine structure of thin organic films and liquids [57].

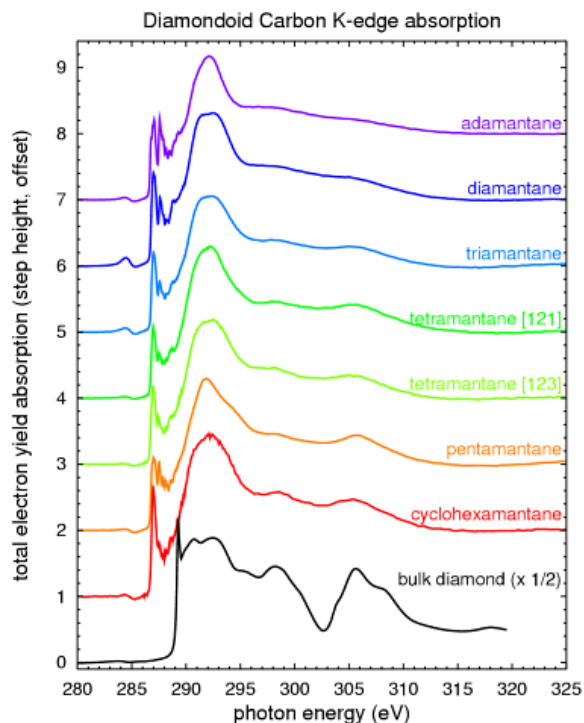


Figure 9: Carbon K-edge x-ray absorption of diamondoids (from adamantane to hexamantane) and of a bulk diamond

According to this figure, practically all the diamondoids possess the general features of the diamond band structure. The larger diamondoid sizes exhibit band structures much closer to that of bulk diamond as the second absolute gap at 303 eV emerges.

Adamantane is considered an ideal molecule for the study of basic NMR spectroscopy mechanisms [58]. In solid-state NMR spectroscopy, adamantane is used as a common standard for chemical shift referencing (see, e.g., [59]). In dye lasers (i.e., which use an organic dye as a lasing medium), adamantane may be used to prolong their life. This is because adamantane cannot be photoionized since it lacks ultraviolet absorption bands [60]. In another study, adamantane molecule has been used in the design of a novel photoswitching single molecular tip for chemical identification through noncontact atomic force microscopy [61]. The synthesis of novel thermally reversible photochromic spiro is yet another interesting recent photonic application of adamantane [62]. In another study the electronic and vibrational properties of small diamondoids are investigated using an *ab initio* molecular orbital method [54].

Diamondoids can be used to produce electric, electronic, and magnetic functional complexes and polymers (see, e.g., [63] and also [64,65]). In recent years, a few patents have been issued for the opto-electronic applications of diamondoids including a patent for application of adamantane as dye etching masks [66] and diamondoid-containing field emission devices [67].

Applications of Diamondoids in Micro-Electro-Mechanical Systems (MEMS)

Diamondoids are expected to be quite useful in the design of MEMS devices, as they have been also envisioned to be used in nanotechnology because of their stability, rigidity and strength. Due to the availability of multiple attachment sites (Figure 7), they are envisioned for the accurate design and building of durable and robust MEMS precision devices [68]. The exceptional hardness, fracture strength and inertness of diamondoids make them unique materials for miniaturized MEMS, such as rotors, propellers, ratches, gears, toothed cogs and cantilevers [69]. It has been estimated that MEMS constructed out of diamondoids should last many times longer than current silicon-based MEMS. Since diamondoids are chemically benign, they would not promote allergic reactions in biomedical applications.

Crystal Engineering: The branch of MEMS and nanotechnology called “crystal engineering” is a new concept through which the power of non-covalent intermolecular forces is used in the solid-state to design new nanomaterials with desired functions. The approach here is to learn from known crystalline structures of, for example, minerals in order to design compounds with desired properties. Crystal engineering is considered to be a key new technology with applications in pharmaceuticals, catalysis and materials science. The structures of adamantane and other diamondoids have received considerable attention in crystal engineering due to their molecular stiffness, derivatization capabilities and their six or more linking groups (see Figure 10 [70-74]).

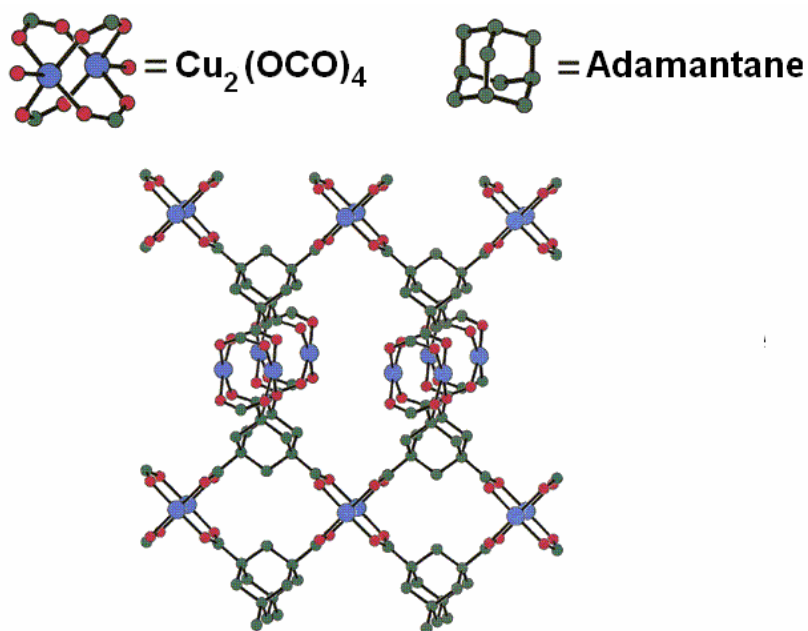


Figure 10: Crystal engineering example: design of a decorated framework made up of the $\text{Cu}_2(\text{OCO})_4$ cluster (Cu, blue; C, green; O, red) and adamantane [74].

Molecular Manufacturing: A concept called “molecular manufacturing,” which was originally proposed in 1992 by K. E. Drexler [39] has attracted the attention of some investigators [40,75-

78]. Molecular manufacturing is defined as “the production of complex structures via non-biological mechanosynthesis (and subsequent assembly operations)” [39]. Chemical synthesis controlled by mechanical systems operating on atomic scale, and with direct positional selection of reaction sites performed by atomic-precision manipulation systems, is known as mechanosynthesis.

Due to their strong stiff structures containing dense, three-dimensional networks of covalent bonds, diamondoids are one of the favorite sets of molecules considered for molecular manufacturing as originally proposed, described and analyzed in “nanosystems.” If diamondoid materials could be synthesized as proposed, they could be quite strong and yet light. For example, diamondoids are being considered to build stronger but lighter rockets and other space components and a variety of other earth-bound articles for which the combination of weight and strength is a consideration [39,40,78-80].

Some of the applications of molecular manufacturing based on diamondoids are: the design of an artificial red blood cell called respirocyte, nanomotors, nanogears, molecular machines and nanorobots [42,80-83]. As an example, the proposed design of nanogears is shown in Figure 11. Other potential applications of molecular manufacturing of diamondoids are in the design of molecular capsules and cages for various applications including drug delivery.

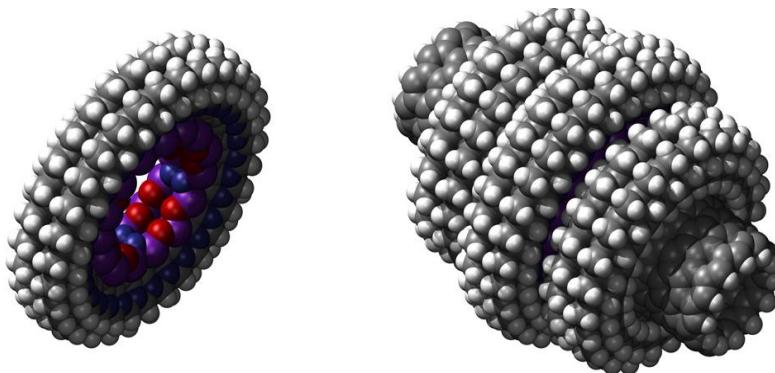


Figure 11: Low-friction nano-bearing assembly. In this design, two diamondoid rings replace small segments of a carbon nanotube, providing a lock for a third, larger ring. The larger ring includes a stitch-work of oxygens to create an electron-rich interior whose effective circular van der Waals packing just touches that of the nanotube framework [image taken from www.somewhereville.com].

For the concept of molecular manufacturing to become successful, among other requirements, a systematic study of the fundamental intermolecular interaction theory of the covalent and non-covalent molecular processes involved is needed [77].

DNA-Diamondoid Nanostructures: Due to the ability of adamantane and its derivatives to attach to DNA, it is possible to construct well-defined nanostructures consisting of DNA fragments as linkers between adamantane cores. This could be a powerful tool to design DNA-directed nanostructured self-assemblies [84]. A unique feature of such DNA-directed self-

assemblies is its site-selective immobilization, which makes possible the construction of well-defined nanostructures, as shown in Figure 12.

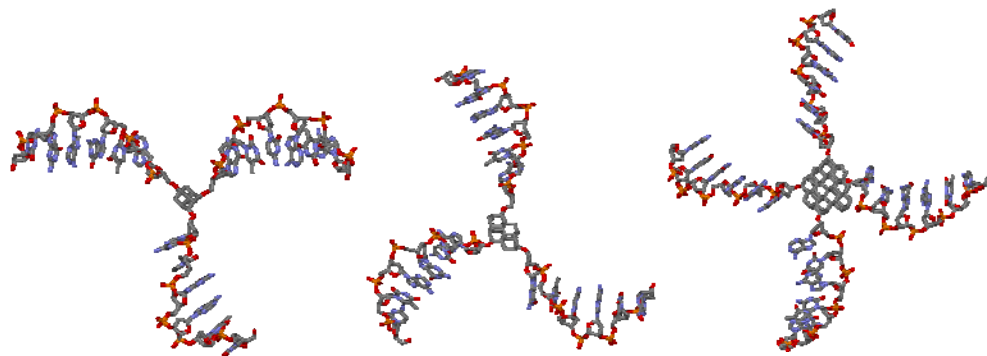


Figure 12: DNA fragments/diamondoid nanostructures left to right: (i) adamantane nucleus and three hexanucleotide linkers; (ii) tetramantane nucleus and three hexanucleotide linkers; (iii) undecamantane nucleus and four hexanucleotide linkers. The hydrogen atoms are removed for clarity [85].

On the other hand, the possibility of the introduction of a vast number of substitutes (like peptidic sequences, nucleoproteins, hydrophobic hydrocarbon chains, etc.) to an adamantane core (adamantyl) makes such a process capable of designing steric colloidal and supramolecular conformations via setting hydrophobic/hydrophilic and other interactions. In addition, the rigidity of adamantane structure can provide strength and rigidity to such self-assemblies [86].

Discussion

Diamondoids are a peculiar class of organic molecules (hydrocarbons) with unique structures and properties. They possess typical characteristics of diamond face-fused cages with hydrogen terminated dangling bonds. They may be used as molecular building blocks of complex functional nanostructures to be found in future NEMS devices. Diamondoids could have applications in self-assembly, immobilization, thin films, synthesis and characterization of MEMS and NEMS devices, ion-selective electrodes and cantilevers for scanning probe microscopy.

Diamondoids can be employed to construct molecular rods, cages and containers, and also for utilization in different methods of self-assembly. In fact, through the development of self-assembly approaches and utilization of diamondoids in these processes, it should be possible to design and construct novel nanostructures.

Diamondoids offer the possibility of producing a variety of MEMS and nanostructural devices, including molecular-scale and micro-scale components of machinery such as rotors, propellers, ratches, gears, toothed cogs, etc. We expect them to have potential for even more possibilities for applications in molding and cavity formation due to their organic nature and their sublimation properties. The diverse geometries and possibility of six or more attachment sites (linking groups) in diamondoids provide an extraordinary potential for the production of shape-derivatives in nanotechnology.

Despite many extensive investigations into properties of diamondoid, their opto-electronic properties are poorly studied. Our future work in this regard will involve joint experimental and theoretical studies of the opto-electric properties of diamondoids. These will be based on density functional theory (DFT) and *ab initio* quantum mechanical computations, collision-induced light scattering (CILS) and refractive index measurements.

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