Diamond Molecules Found in Crude Oil

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Hydrogen-terminated diamond is a continuous structural series ranging in size from macrocrystalline diamonds down to the smallest diamondoid hydrocarbon, adamantane, which contains a single diamond crystal cage. H-terminated diamonds with dimensions of 1 to 2 nanometers are higher diamondoids. We used the extraordinary thermal stability and shape variability of the higher diamondoids to isolate them from petroleum. Single-crystal x-ray studies reveal a wealth of diamond molecules that are nanometer-sized rods, discs, pyramids, and other structures, including resolvable chiral forms showing rare primary helicity. We find higher diamondoids (polymantanes) containing from four to eleven diamond cages, including various methylated analogs. Rigid, well defined structures that can be derivatized at specific structural sites make higher diamondoids valuable nanometer-sized molecular building blocks with potential applications in nanotechnology and new nanomaterials. We can now produce certain tetramantanes and pentamantanes in gram quantities.

The cubic-diamond cage structure gives diamondoids strength and stability, but also makes them extraordinarily difficult to synthesize by classical synthetic organic methods. A surprisingly effective way of preparing adamantane was discovered by von Schleyer in the 1950's. However, this method, which exploits diamondoid thermodynamic stability during carbocation rearrangements, cannot form diamondoids with more than three cages.

Nanodiamonds can be synthesized by a variety of chemical vapor deposition (CVD), ion-implant, and detonation techniques. We have used gas chromatography-mass spectrometry (GCMS) to analyze diamond materials prepared by a CO_2 laser induced gas-phase synthesis technique in an attempt to detect the presence of diamondoids (diamantane to undecamantane) as byproducts of this process. (Nanodiamonds with diameters of 10 nm and larger had been detected earlier in these materials using transmission electron microscopy.) Even using high-sensitivity selected ion monitoring GCMS methods, no diamondoids were detected, although aromatic hydrocarbons with from 3 to 6 fused aromatic rings were found. Diamondoid analyses of diamond powders produced by commercial CVD will also be presented. These results have implications to both diamondoid and diamond formation mechanisms.