DIAMOND MOLECULES FOUND IN PETROLEUM
New Members of the H-Terminated Diamond Series

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Abstract: We recently reported [1,2] the discovery and isolation of new members of the hydrogen-terminated diamond series, ~1 to ~2 nm sized higher diamondoids from petroleum. Crystallographic studies [1,2] revealed a wealth of diamond molecules that are nanometer-sized rods, helices, discs, pyramids, etc. Highly rigid, well-defined, readily derivatizable structures make them valuable molecular building blocks for nanotechnology. We now produce certain higher diamondoids in gram quantities. Although more stable than graphite particles of comparable size, higher diamondoids are extraordinarily difficult to synthesize. Attempts to synthesize them were abandoned in the 1980’s. We examined extracts of diamond-containing materials synthesized by CO₂ laser-induced gas-phase synthesis [3] and commercial CVD in an attempt to detect diamantane to undecamantane. However, high-sensitivity GCMS detected no diamondoids in these materials.

Keywords: diamondoids, polymantanes, adamantane, CO₂ laser, CVD, nanotechnology

1. INTRODUCTION

We begin this paper by examining the enormous size range of hydrogen-terminated diamond crystals, focusing on the tiniest possible ultrananano-
crystals of cubic diamond. We next discuss how structures of the diamond series are conceptually built-up from the smallest member to give the lower diamondoids. We then describe the newly discovered higher diamondoids, and show how they differ from the lower diamondoids. This includes a discussion of the many interesting structural features of higher diamondoids pertinent to the emerging field of nanotechnology. We briefly review past efforts to synthesize higher diamondoids by synthetic organic chemists (efforts ending in the 1980’s), and discuss the surprising occurrence of higher diamondoids in petroleum. Finally, we describe our (unsuccessful) attempts to detect the formation of diamondoid hydrocarbons by two methods used to produce synthetic diamond, and discuss possible implications of these findings to the formation of higher diamondoids.

2. THE SMALLEST ULTRANANOCRYSTALLINE DIAMOND

Ultrananocrystalline diamonds possess a myriad of interesting and useful properties, as the proceedings of this conference readily attest. With modern technologies pushing the size of diamond crystals needed in newer applications to smaller and smaller ranges, it is worthwhile reexamining the limits of this miniaturization progression. This is particularly true with the growing interest in the fields of nanotechnology and nanomaterials. These fields aim to “engineer” and “build” structures and devices using components having nanometer dimensions [4]. Moreover, there is a fundamental understanding that diamond is a prized material for such applications [5–7].

The well-known unit cell of cubic diamond [8] is shown in Figure 1a. The 10-carbon cage, characteristic of the cubic diamond structure, is shown excised from the lattice in Figure 1b. When dangling carbon bonds are terminated with hydrogen atoms, this 10-carbon diamond crystal cage becomes a molecule of adamantane, the C_{10}H_{16} hydrocarbon (molecular weight, MW 136). Adamantane is in the Td point group. Octahedral symmetry is displayed by the spatial relationship of its secondary carbon atoms, Figures 1c and 1d. The faces of the adamantane octahedron (Figure 1c) correlate with the (111) lattice faces of larger octahedral diamond crystals (e.g., the 455-carbon octahedral diamond drawn in Figure 2). The vertices of the octahedron in adamantane, and a perfect H-terminated macroscopic octahedral diamond crystal (if such a thing existed), as well as all of the intermediate members of the diamond