Structure of Cyclohexamantane

Isolation and Structural Proof of the Large Diamond Molecule, Cyclohexamantane ($C_{26}H_{30}$)

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In this report, we describe the first isolation and structural verification of the diamondoid cyclohexamantane, $C_{26}H_{30}$, a material that has probably never previously existed anywhere in crystalline form. Since the diamond surface can terminate in hydrogen,[1] cyclohexamantane may be thought of as a nanometer-sized diamond of approximately 10^{-21} carats. In fact, the cyclohexamantane structure has been used to represent a small diamond in theoretical investigations.[2–4] Here we present the experimentally determined properties of cyclohexamantane isolated from petroleum, which includes its single-crystal X-ray structure, and analysis by NMR and laser Raman spectroscopy, as well as mass spectrometry.

Diamondoids of the adamantane series are hydrocarbons composed of fused cyclohexane rings, all in stable chair conformations, which form interlocking cage structures that can be superimposed on the diamond crystal lattice.[5] The lower diamondoids have chemical formulas of $C_{4n+6}H_{4n+12}$, where n equals the number of diamond-cage subunits. The stability of diamondoids is illustrated by the heat of formation of adamantane (the smallest diamondoid) which is far lower than any other hydrocarbons of comparable carbon quantity and ring number. While there is only one form of adamantane, diamantane, and triamantane, there are four possible isomeric tetramantanes (*iso*-, *anti*-, and two enantiomeric *skew*-tetramantanes). There are ten possible pentamantanes,[6,7] nine isomers with the formula $C_{26}H_{32}$, and one with formula $C_{25}H_{30}$. Likewise, there are 39 postulated hexamantanes, 28 of which are isomers of $C_{30}H_{36}$, and ten of which are $C_{29}H_{34}$ isomers.[6,7] The pericondensed hexamantane, also named cyclohexamantane, is the only diamondoid structure with the formula $C_{26}H_{30}$.

The most efficient syntheses of all of the lower diamondoids (from adamantane through to triamantane) involve the carbocation-mediated superacid equilibration reaction discovered by von R. Schleyer.[8] However, this route to the higher diamondoids (that is, tetramantane and higher) is blocked by severe kinetic (mechanistic) constraints, and all attempts to synthesize the higher diamondoids have proven futile. Only one of the tetramantanes (*anti*-tetramantane) has been prepared by an elegant, complex, but low-yielding alternative synthetic pathway devised by McKervey's research group.[9]

Diamondoids occur naturally in virtually all petroleum.[10] In most crude oils, diamondoid concentrations are in the order of 1–100 ppm, and occur predominantly as substituted and unsubstituted adamantanes and diamantanes.[10] Although it is not clear how diamondoids are formed in the geosphere, we believe they may be created through carbocation-mediated rearrangements arising when newly generated petroleum, which contains functionalized molecular species (for example, double bonds), reacts with superacid sites on naturally occurring clay minerals, such as montmorillonite, in petroleum source rocks. Although macroscopic diamonds are less stabile than graphite under oil reservoir conditions, this is not true of nanometer-sized hydrogen-terminated diamonds, such as cyclohexamantane.[11–13] Therefore, the formation of diamondoids from petroleum precursors is thermodynamically favored and this helps to explain their surprising existence.

The number of different carbocation-mediated pathways to adamantane from only one starting material (*endo*-tetrahydrodicyclopentadiene) has been calculated to be 2897.[14] Similar treatments for diamantane yield numbers orders of magnitude higher.[15] With this increasing number of

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pathways and intermediates, it is clear that the natural synthetic route to cyclohexamantane from petroleum precursors must include an astronomical number of pathways and intermediate species. The low concentration of cyclohexamantane (less than 1 ppb in most oils) suggests that yields are extremely low. The amount of time required to arrive at the end product may be many millions of years (that is, the time involved in oil generation) thus overcoming the kinetic impediments that block syntheses on laboratory timescales. If this assertion is correct, petroleum may be the only possible source of cyclohexamantane.

Crystals of cyclohexamantane were obtained from a distilled Gulf Coast petroleum by reverse-phase high-performance liquid chromatography (HPLC).[16] Although it remained a minor component in HPLC fractions (dissolved in acetone), cyclohexamantane spontaneously crystallized from the acetone/HPLC complex mixture after several weeks (Figure 1). The crystals are transparent with a pronounced luster or brilliance.

Figure 1. SEM image of a cyclohexamantane crystal magnified 150×.

Cyclohexamantane has a surprisingly high melting point (> 314 °C in a sealed capillary tube) that reverses the melting-point trend observed among lower diamondoids. Cyclohexamantane sublimes in an open capillary tube at around 293 °C.

Single-crystal X-ray diffraction was carried out on an isolated cyclohexamantane crystal (the structure is shown in Figure 2 and the packing is shown in Figure 3).[17] The molecule is disc shaped and utilizes the $\bar{3}$ (S_6) crystallographic symmetry of space group $R\bar{3}$, but it has effective $\bar{3}m$ ($D3d$) symmetry. The mean C–C distance is 1.538(7) Å, and the central C–C bond is 1.568(6) Å, significantly longer; the mean C-C-C angle is 109.7(10)°.

A mass spectrum of cyclohexamantane (Figure 4 b) shows a large molecular ion (m/z 342), typical of unsubstituted diamondoids, and a doubly charged molecular ion at m/z 171, along with a number of minor fragment ions.

The laser Raman spectrum of crystalline cyclohexamantane displays a variety of peaks between $\tilde{\nu} = 300$ and 2920 cm^{-1} (Figure 4 a; Table 1). The spectrum was compared with the data reported for adamantane,[18] diamond,[19] and nanophase or "amorphous" diamond[20] (Table 1). CH and CH_2 stretching modes are observed between $\tilde{\nu} = 2840$ and 2920 cm^{-1}. Vibrations at $\tilde{\nu} = 445$ and 652 (CCC deformation), 985 (CH_2 rocking), 1219 and 1311 (CH bending), and 1451 cm^{-1} (CH_2 scissor) are comparable with those observed in adamantane. Peaks at $\tilde{\nu} = 498$ and 1142 cm^{-1} for cyclohexamantane correspond to peaks observed in the Raman spectrum of nanocrystalline diamond.[20] A number of peaks are observed between $\tilde{\nu} = 1330$ and 1380 cm^{-1} (Figure 4 a) which may be related to various weak CH bending and CH_2 wagging and twisting vibrations seen in the spectrum of adamantane. A more attractive possibility is that these vibrations are related to the breathing mode observed in diamond[18] at 1332 cm^{-1}, which corresponds to vibrational

Table 1: Observed Raman frequencies for crystalline cyclohexamantane and reference substances used to help with assignments. Data for adamantane is taken from Bistiricic et al.,[18] for diamond from Solin and Ramdas[19], and for amorphous diamond from Prawer et al.[20]

Raman Frequencies [cm^{-1}]				Possible assignments for cyclohexamantane
Cyclohexamantane	Reference Substances			
	Adamantane	Nanophase diamond	Diamond	
340, w				
347, w				
445, m	441, m			CCC deformation
498, s		500		
652, m	638, vw			CCC deformation
674, w				
814, w	800, vw			CC stretch
817, w	800, vw			CC stretch
985, m	972, m			CH_2 rock
1029, s				
1048, m				
1056, w				
1074, w	1098, s			CH_2 rock
1142, m		1140		
1181, s		1200		CC stretch
1203, w		1200		CC stretch
1219, w	1220, s			CH bend
1256, w				
1292, w				
1311, w	1312, w		1332	CH bend, CC stretch
1337, w		1332	1332	CC stretch
1352, w	1352, vw		1332	CH_2 wag, CC stretch
1359, w			1332	CC stretch
1375, w	1371, w		1332	CH_2 twist, CH bend, CC stretch
1451, w	1436, m			CH_2 scissor
2848, s	2849, m			CH_2 stretch
2860, vs				CH stretch, CH_2 stretch
2877 vs				CH stretch, CH_2 stretch
2907, s (sh)	2907, s (sh)			CH_2 stretch
2916, vs	2916, vs			CH stretch

Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

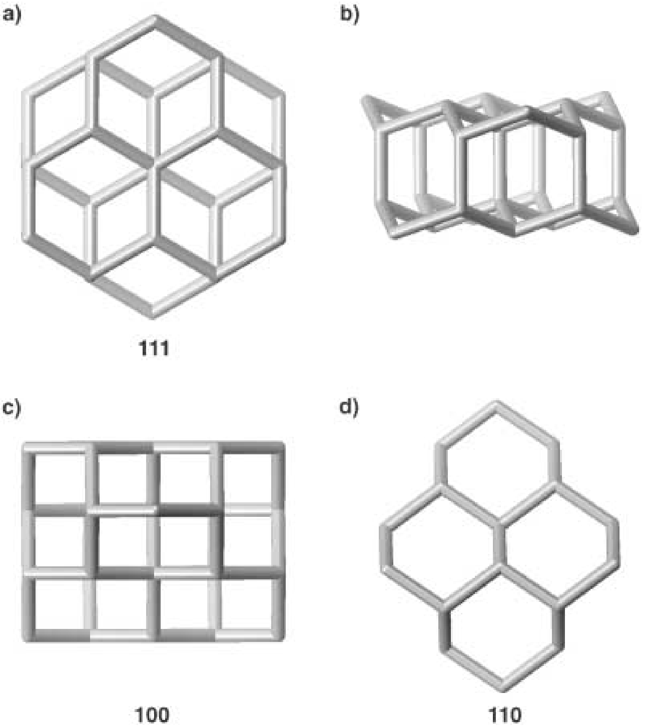

Figure 2. The carbon framework structure of cyclohexamantane based on single-crystal X-ray diffraction. a) View along a diamond (111) crystal-lattice plane; b) side view of this "wheel-like" molecule; c) and d) views along the (100) and (110) diamond crystal-lattice planes, respectively.

modes of the quaternary carbon atoms, in accord with a diamond-like coordination. The very strong peak at $\tilde{\nu} = 2860\,\mathrm{cm^{-1}}$ for cyclohexamantane is also observed in the Raman spectrum of the hydrogenated diamond C⟨111⟩ surface.[21] Additional important peaks in the Raman spectrum of cyclohexamantane appear at 498, 1029, 1048, 1142, 1181, and 1256 $\mathrm{cm^{-1}}$. The peak at 1181 $\mathrm{cm^{-1}}$, along with a weaker one at 1203 $\mathrm{cm^{-1}}$ may represent other vibrational modes of sp^3-bonded carbon atoms, as reported for nanophase diamond.[22]

The ^{1}H-decoupled ^{13}C NMR spectrum of cyclohexamantane (Figure 5 a) shows three of the expected four signals with the signal for the two equivalent quaternary carbon atoms (atoms 11 and 12; Figure 5 c) being absent. This feature is not surprising given the small amount of sample used and the expected long longitudinal relaxation times, as demonstrated for the quaternary carbon in triamantane. A DEPT spectrum (Figure 5 b) allowed assignment of all the CH_2 carbon atoms (atoms 4, 8, 15, 19, 23, and 26; Figure 5 c) to $\delta = 38.6$ ppm. This corresponds with the value of $\delta = 38.6$ ppm reported for the structurally related triamantane.[23] Similarly, the CH resonance at $\delta = 37.8$ ppm can be assigned to the twelve equivalent CH carbon atoms (atoms 1, 3, 5, 7, 9, 14, 16, 18, 20, 22, 24, and 25; Figure 5 c) and that at $\delta = 47.3$ ppm to the six equivalent CH carbon atoms (atoms 2, 6, 10, 13, 17, 21; Figure 5 c) on the basis of the similarities in chemical environment with carbon atom 2 ($\delta = 46.9$ ppm) and atom 3 ($\delta = 38.1$ ppm) in triamantane.[23]

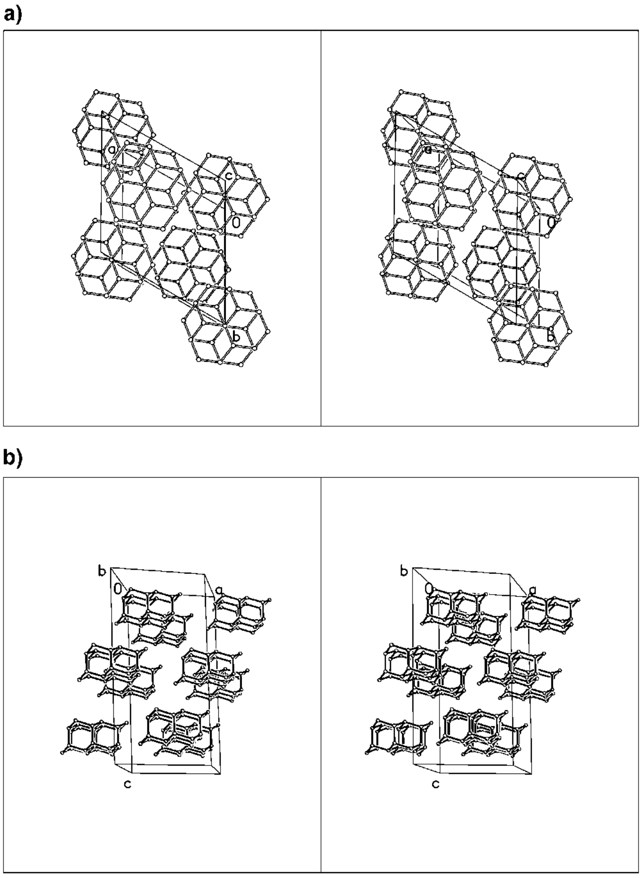

Figure 3. a) and b) Two stereoscopic projections showing different views of the crystal packing of cyclohexamantane.

The ^{1}H NMR spectrum (Figure 5 c) is characterized by three second-order multiplets (indicating the presence of long-range couplings), which could be assigned on the basis of integration and homonuclear decoupling experiments. Thus, the multiplet at $\delta = 1.19$ ppm is assigned to six methine hydrogen atoms (associated with carbon atoms 2, 6, 10, 13, 17, and 21), that at $\delta = 1.59$ ppm to twelve methine hydrogens (associated with carbon atoms 1, 3, 5, 7, 9, 14, 16, 18, 20, 22, 24, and 25), and that at $\delta = 1.712$ ppm to the twelve methylene hydrogens (geminal on the carbon atoms 4, 8, 15, 19, 23, and 26).

Cyclohexamantane may be formed by an extremely large number of rearrangments of suitable 26-carbon-atom precursor molecules during oil generation. Another possibility suggested by Lin and Wilk[24] involves alkylation of lower diamondoids by clay-catalyzed reactions with methane gas, followed by cyclization to form higher diamdondoids. If this hypothesis is correct, then the formation of substantially larger diamondoids than cyclohexamantane could be postulated. In fact, one might hypothesize microcrystalline diamonds as a product. Because these diamonds would not be soluble in petroleum, they would remain in the petroleum source rock (a hypothesis we are currently exploring). Interestingly, there are microcrystalline black diamonds known as carbonados, which unlike other diamonds, are

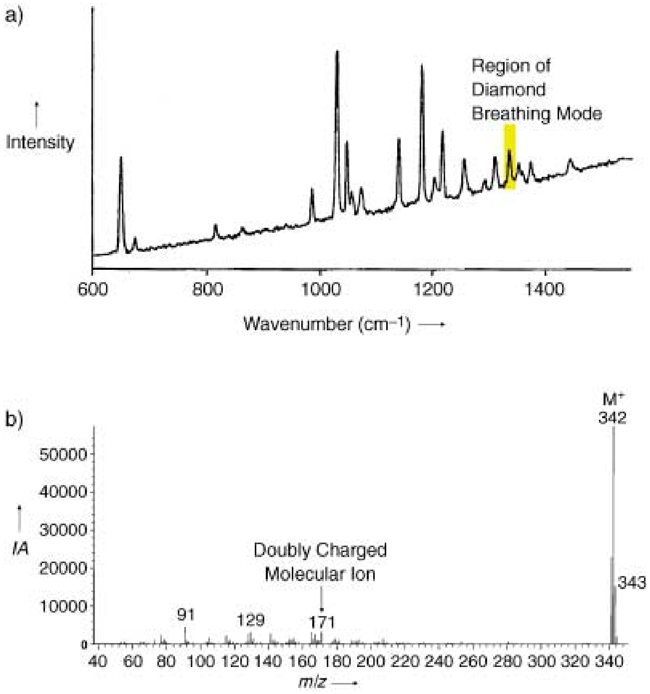

Figure 4. Laser Raman spectrum (a) and mass spectrum (b) obtained for cyclohexamantane. The laser Raman spectrum of crystalline cyclohexamantane was acquired on a Renishaw Raman system 2000 microscope using the 514 nm line from an argon ion laser. The power output was adjusted to 25 mW. A ×50 objective was used to produce a spot size of approximately 1.5 μm in diameter to collect the scattered light. The slit was adjusted to give a resolution of 1 cm^{-1} and a confocal sampling depth of approximately 3 μm. A full peak listing with possible assignments is given in Table 1. The GC/MS instrument was a VG Trio-1 mass spectrometer coupled to a HP 5890 gas chromatograph. Ionization was by electron impact (EI); the collision energy was 70 eV; IA = ion abundance.

believed to be formed in the Earth's crust, based on mineral inclusions.[25] The origin of these diamonds is enigmatic not only because of their crustal origin, but also their highly unusual $^{12}C/^{13}C$ isotopic ratios. Unlike other naturally occurring diamonds, which have isotopic signatures representative of mantle-derived carbon, carbonados have $\delta^{13}C$ values from (−25) to (−30) per mil,[26,27] which is in the same range as petroleum.

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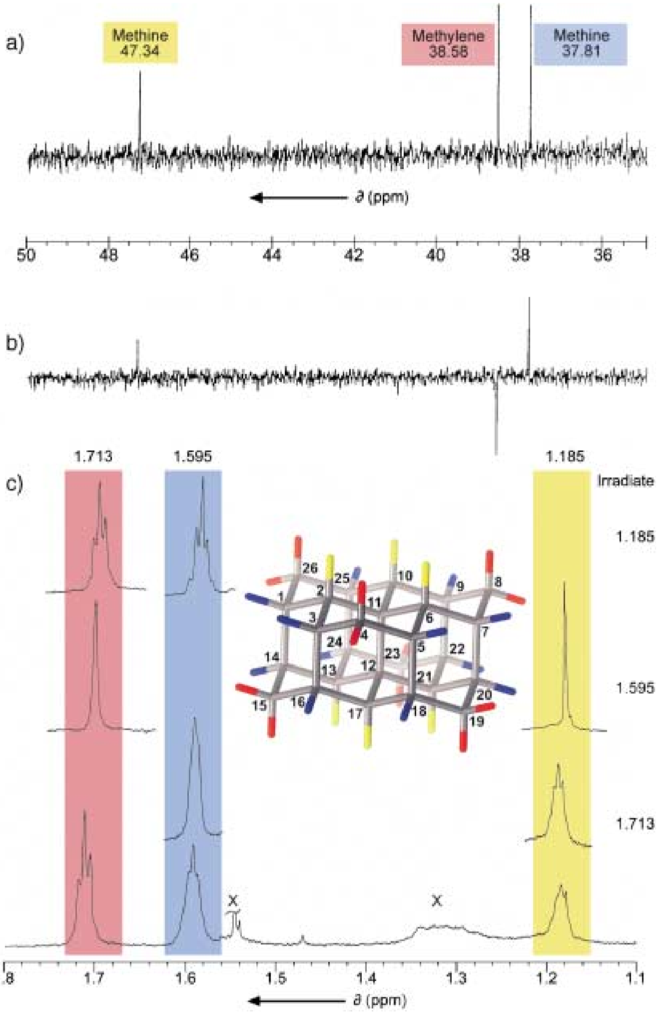

Figure 5. ^{13}C NMR (a) and DEPT (b) spectra were acquired on a JEOL Lambda 300 spectrometer operating at 75 MHz; c) ^{1}H NMR spectrum acquired on a JEOL GX400 spectrometer operating at 400 MHz. Spectra were recorded using C_6D_6 as solvent. In the ^{1}H NMR spectrum, "X" corresponds to impurities; the approved IUPAC numbering for cyclohexamantane is shown, namely, dodecacyclo-$[12.12.0^{2,11}.0^{3,16}.0^{5,18}.0^{6,11}.0^{7,20}.0^{9,22}.0^{10,25}.0^{12,17}.0^{12,21}.0^{13,24}]$hexacosane, according to the von Baeyer system.

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[16] High-performance liquid chromatography (IBM, instrument) was conducted on a Zorbax octadecyl silane (ODS) column (250 mm long, 4.6 mm internal diameter) using an acetone mobile phase at 1.5 mL min^{-1}. Cyclohexamantane-containing distillation residue (0.10 mL) was injected neat and fractions were monitored by GC-MS. Cyclohexamantane spontaneously crystallized out of complex mixtures in HPLC fractions in the acetone mobile phase.

[17] Crystal structure determination: $C_{26}H_{30}$, colorless, shiny fragment, crystal size $0.20\times0.15\times0.06$ mm^3, trigonal, space group $R\bar{3}$ (No. 148), $a=b=9.0630(10)$, $c=17.417(2)$ Å, $V=1238.9(2)$ Å^3, $Z=3$, $\rho_{\text{calcd}}=1.377$ g cm^{-3}, $2\theta_{\max}=109.7°$, $Cu_{K\alpha}$, $\lambda=1.54178$ Å, 2θ–ω scans, $T=293(2)$ K, 780 reflections collected, 352 unique ($R(\text{int})=0.014$), 301 observed ($I>2\sigma(I)$), σ limits 0.002–0.006 Å, Lorentz and polarization corrections applied, no absorption correction, $\mu(Cu_{K\alpha})=0.571$ mm^{-1}, solved by direct methods (SHELXS-90), refined by full-matrix least-squares on F^2, all non-H atoms anisotropic, H atoms constrained, (SHELXL-93), 41 parameters, $R_1=0.0447$ (observed data), $wR2=0.1404$ (all data), max./min. residual electron density 0.265/−0.100 e Å^{-3}. CCDC-202094 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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