Benzene-derived carbon nanothreads

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Supplementary Materials:

Materials and Methods

Supplementary Discussion of Raman Spectroscopy (Supplementary Table 1)

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Supplementary Materials:

Materials and Methods:

Synthesis of sp³ hybridized carbon nanotreads: Polymerized benzene samples were synthesized with large-volume high-pressure equipment at the SNAP beamline of the Spallation Neutron Source. In several different sample runs four possible hydrogen-carbon isotopic combinations of benzene (¹²C-benzene, ¹³C-benzene, perdeuterated ¹²C-benzene and perdeuterated ¹³C-benzene) were loaded as solids at low temperature into encapsulated metal gaskets to avoid evaporation. These different isotopic combinations facilitated analysis by neutron diffraction and solid-state NMR and assisted in the identification of Raman vibrational modes with isotopic shift experiments. The atmosphere was kept dry to avoid condensation. TiZr, Zr, and stainless steel gasket materials were used. No differences in properties suggestive of any catalytic effect were observed between the reaction products synthesized in the different gaskets. The samples were then placed into a VX3 Paris-Edinburgh press¹ equipped with double-toroid polycrystalline diamond anvils². The system was driven by an automatic hydraulic oil syringe
pump, allowing for controlled pressure ramps. Pressure-load curves, previously calibrated, indicated that the sample pressure was at approximately 20 GPa at the maximum oil pressure of 1650 bar that was used. The sample was kept at this maximum pressure for one hour and then slowly decompressed at average rates varying from 7 GPa/hr to 2 GPa/hr to ambient pressure. The encapsulated gaskets were cut open to reveal a white to off-white/yellow solid. The solid was characterized by x-ray and neutron diffraction measurements as well as solid-state nuclear magnetic resonance spectroscopy (SSNMR) and transmission electron microscopy (TEM) without further purification. For certain additional analyses, as described below, the samples were exposed to various light hydrocarbon solvents beforehand.

**Gas Chromatography-Mass Spectrometry (GC-MS):** Samples of $^{12}$C and $^{13}$C hydrogenated and perdeuterated benzene-derived solids were extracted with hexane after recovery. The hexane was then analyzed using an Agilent 6890 GCMS equipped with a 30 meter 5% phenyl PDMS column and an Agilent 5973 quadrupole mass analyser covering the mass range from 50 to 500 amu. As described below, the presence of various soluble small alkanes and diamondoid structures could be ruled out by this analysis.

**Transmission Electron Microscopy:** Images for Figure 1 were collected using a JEOL 2010-F field emission transmission electron microscope at an accelerating voltage of 200 kV. A wide beam was used to avoid sample damage. Samples for the field emission microscope were prepared by dispersing them dry on a grid and by dispersing them in pentane followed by casting onto a grid. The image for Supplementary 12, was collected with a JEOL 2010-LaB$_6$ microscope at an accelerating voltage of 200 kV. Samples for the LaB$_6$ microscope were prepared by dispersing them in n-pentane followed by casting onto a lacey-carbon-covered copper grid.
**X-Ray Diffraction:** Angle dispersive, x-ray diffraction patterns were collected at beamlines 11 ID-C and 16 ID-B of the Advanced Photon Source at Argonne National Laboratory in a transmission geometry. Data for the perdeuterated $^{12}$C benzene sample decompressed at an average rate of 7 GPa/hr were collected at 11 ID-C for supplementary 4. Data for both the $^{12}$CD sample decompressed at an average rate of 2 GPa/hr (2) and another sample, $^{12}$CH, quickly decompressed in a DAC (supplementary 1) were collected at 16 ID-B.

At 11-ID-C a high (115 keV) x-ray energy was used with an unfocused beam 1 mm × 1 mm in size and a Perkin Elmer area detector. This configuration allowed for a $Q_{\text{max}}$ of approximately 21 Å$^{-1}$. The sample was 2 mm in diameter and roughly 2 mm thick. Both experiments at 16-ID-B beamline were performed at 30.5 keV with the beam focused to 8 µm × 8 µm with Kirkpatrick-Baez (KB) mirrors. Two different detectors, a Pilatus and MAR IP were used. Ambient pressure data were collected on recovered samples approximately 800 µm in diameter and 250 µm thick or 100 µm in diameter and 30 µm thick. In both cases $Q_{\text{max}}$ was ~8 Å$^{-1}$.

Empty container datasets were also collected to permit reduction to $S(Q)$ using the PDFgetX2 software package$^3$. A high resolution pair distribution function was obtained using established techniques within the PDFgetX2 software package for the data collected from the 11 ID-C beamline. The low $Q_{\text{max}}$ at 16 ID-B did not allow for determination of a high resolution pair distribution function.

The x-ray data in Fig. 1c were fitted with multiple Lorentzian peaks, whose positions could be indexed with a simple hexagonal two-dimensional lattice. These peak positions were compared with calculated peak positions from a variety of other candidate structures, including a
series of graphane layered structures, and possible contaminants from the high pressure cell, including the encapsulating metal gasket and diamond. Bragg peak positions were consistent from sample to sample.

Beamline 16 ID-B was also used to collect high-pressure diffraction data for supplementary 3 on the perdeuterated C_{12} benzene sample after it had been compressed in the PE cell. A symmetric DAC was used with 300 µm diameter culets and a T301 stainless steel gasket with a 100 µm hole and no pressure transmitting medium. Pressure was monitored using ruby fluorescence. In view of the small sample size, low Z of the elements, and substantial Compton scattering background of the diamond anvils, only the (100) and (200) Bragg peaks could be observed. The maximum Q range was limited to approximately 3.5 Å\(^{-1}\) by the diamond cell geometry. Additional information on beamlines 16-ID-B\(^{5}\) of HPCAT and 11-ID-C\(^{6}\) can be found in references 5 and 6, respectively.

**Neutron Diffraction:** Time of flight, energy dispersive, neutron diffraction data were collected on the Nanoscaled-Ordered Materials Diffractometer (NOMAD) of the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The sample decompressed at an average rate of 7 GPa/hr was mounted in a glass capillary and placed into the beam; an empty glass capillary dataset was used for a background measurement. Diffraction data with acceptable signal-to-noise were obtained from 0.5 – 25 Å\(^{-1}\). These data were corrected using standard procedures for scattering and absorption of both the sample and the container as well as multiple and inelastic scattering events. The samples were normalized to the isotropic incoherent scattering from vanadium and put on an absolute scale using the known scattering cross-sections of the sample nuclei. The resulting total scattering structure factor was truncated at 21 Å\(^{-1}\) to match the high-
energy x-ray data and Fourier transformed to generate a high-resolution pair distribution function using established techniques. Additional information about the NOMAD instrument can be found in reference 7.

**Raman Spectroscopy:** Raman spectra were collected with both 633 nm and 785 excitation using Renishaw inVia Raman microscopes. A 50×, 0.75 numerical aperture objective was used to collect the scattered light for unpolarized spectra. A lower numerical aperture (0.5) 50× objective was used for the polarized Raman analysis. The Raman scattered light was separated from the Rayleigh scattered light by a holographic notch filter, then dispersed by a 1200 g/mm grating onto a thermoelectrically cooled CCD. The incident power was kept below 1mW to avoid sample damage. Polarized Raman spectra were collected on reference materials to verify that the depolarization ratios were accurately measured.

**Solid State NMR:** 

¹³C solid state nuclear magnetic resonance (SSNMR) spectra were collected using a Varian 400MHz wide bore spectrometer equipped with a 4mm triple resonance probe configured for ¹H-¹³C double resonance mode. ¹³C MAS SSNMR of ¹³C isotopically enriched nanothread samples were collected using a 4.0 µs 90° pulse with a recycle delay of 60 seconds, 512 scans, approximately 83kHz ¹H TPPM decoupling, and magic angle sample spinning (MAS) with a frequency of 15 kHz. The ¹³C chemical shifts were referenced indirectly to TMS by setting the upfield ¹³C resonance of adamantane to 38.48ppm.

¹³C SSNMR spectra were also collected on a second sample containing both ¹³C and ²H using a Varian-Chemagnetics CMX Infinity 300 spectrometer equipped with a 5mm double resonance probe. To suppress any carbon background signal, BN inserts were used in addition to the DEPTH pulse sequence which suppresses all signal arising from carbon outside the RF coil. The
experimental parameters included a 4 μs excitation (90°) pulse, a recycle delay of 30 seconds, 4800 acquisitions, and a MAS frequency of 12 kHz.

**Crystal Structure Modeling:** Two well-ordered one-dimensional sp³ carbon structures were considered as archetypes: the (3,0) sp³ nanothread proposed as the smallest-diameter ‘nanotube’ possible⁹ and “polymer I” proposed as a possible reaction product for polymerized high-pressure benzene¹⁰. These two structures, plus the structure described in Supplemental Figure 10, can be interconverted by Stone-Wales transformations; thus they are representatives of a single structural family. We calculated structural parameters at various pressures within density functional theory (DFT) using the PBE¹¹ exchange correlation functional and PAW pseudopotential¹²,¹³ at an energy cutoff of 600 eV, as implemented in the VASP package¹⁴-¹⁷. Van der Waals interactions were included using the VASP implementation of the DFT-D2 method of Grimme¹⁸. The structure relaxation optimized all atom positions as well as the unit cell shape using conjugate gradients.

The (3,0) tube at zero pressure assumes a triclinic lattice with four tubes in the unit cell (a=12.543 Å, b=12.166 Å, c=4.281 Å, alpha=82.55°, beta=75.74°, gamma=59.02°). When viewed along the tube axial direction the system assumes an oblique lattice with near-hexagonal symmetry in the transverse direction: the two lattice constants (inter-tube distances) are 6.04 Å and 6.08 Å with a 59.02° angle in between; neighboring tubes are shifted relative to each other axially to allow hydrogen inter-digitation for efficient packing. For a single tube, the lattice constant in the axial direction is 4.28 Å; the unit cell hosts twelve carbon and twelve hydrogen atoms, originating notionally from two benzene rings. Polymer I in the transverse direction also assumes an oblique lattice with near-hexagonal symmetry: the two transverse (i.e. inter-strand)
lattice constants are nearly equal (5.62 and 5.64 Angstroms) and the angle between them is close to sixty degrees (65.3°). The axial lattice constant is 4.9 Angstroms, and this structure also hosts twelve carbon and twelve hydrogen atoms within the unit cell.

These two ideal end-state structures have slightly smaller inter-tube separations than is observed experimentally. However, the (3,0) tube and polymer I are related by a sequence of two Stone-Wales transformations (as depicted in Fig. 3 of the main text) and the actual material obtained experimentally is apparently in a partially ordered intermediate state. For example, performing only one of the two Stone-Wales rotations that interconvert these two ideal structures yields a lower symmetry intermediate structure with less efficient hydrogen inter-digitation and a larger inter-tube separation. When an axially oriented carbon-carbon bond of the (3,0) nanotube is Stone-Wales rotated, the transverse lattice constant expands to 6.53 Angstroms and the axial lattice constant shrinks to 4.06 Angstroms; if the off-axis carbon-carbon bond is rotated instead, the transverse lattice expands to 6.21 Angstroms while axial periodicity expands to 4.60 Angstroms. We anticipate that a more disordered or heterogeneous state similar to experiment would have an inter-tube packing efficiency similar to that of these two ordered intermediates.

Coordinates for all relaxed structures are included in the supplementary information.

The lattice parameters of the (3,0) sp³ tube and polymer I from zero to 25 GPa were also calculated at the density functional level. The compression curves follow the same trend as the experiment results of Supplementary Fig. 2 which suggests that the long-range order observed experimentally is due to a structural direction that is defined by a soft (i.e. van der Waals) interaction.
Modeling Radial Distribution Function of Partially Ordered Systems: The (3,0) sp³ tube and polymer I can be interconverted by two Stone-Wales transformations, suggesting that the actual experimental material contains some partially ordered admixture of rotated bonds. Thus we generate nanothreads with controllable degrees of disorder by implementing a Monte Carlo bond rotation algorithm. The algorithm begins with a (3,0) tube within a long (50 Angstrom) axial supercell, with periodic boundary conditions. Stone-Wales transformations are performed on randomly selected carbon-carbon bonds (by rotating the carbon atoms and associated hydrogen atoms of that bond by 90 degrees about a local normal (the averaged orientations of the four planes defined by these carbons and their nearest neighbors)). After each rotation, the structure is relaxed using a classical force field (ReaxFF¹⁹, as implemented in LAMMPS²⁰,²¹), using a very brief molecular dynamics anneal (ramping from 300 K to 0 K over 100 fs) followed by conjugate gradient relaxation to the local minimum. The move is then accepted or rejected based on the difference in total energy. The effective temperature used for the Monte Carlo acceptance decision (3500, 5000 or 6000 K) is intended to reflect kinetic effects; it should not be interpreted as an actual equilibrium temperature. For simplicity, any move that created a less-than-threefold coordinate carbon atom or a square or triangular carbon ring is rejected. The Monte Carlo bond rotations continue until the radial distribution function converged. As a final step the structure is relaxed within density functional theory, since the empirical potential used in the Monte Carlo process slightly overestimates the carbon-carbon bond length.

To calculate the PDF the resulting disordered thread is assembled into a hexagonal lattice and each thread is randomly shifted axially to model inter-tube disorder. This is essentially equivalent to calculating the PDF for a single thread; the lattice is created as a convenient mechanism to
ensure that the PDF asymptotes to one. The PDF is then convolved with a Gaussian to account for instrumental and thermal broadening (any additional broadening due to e.g. the minor sp² component of the sample can also be captured in part by this procedure). Although thermal broadening could be explicitly included at the empirical potential level, the final density functional relaxation noted above precludes this. The partial radial distribution functions for C-C, C-H, and H-H pairs are weighed by 0.2509, 0.249, and 0.50 respectively to produce the neutron-scattering radial distribution function. PDFs from all three effective temperatures provide good matches to experiment; the 5000 K simulation is chosen for plotting in Fig. 2. The slight overestimate of the nearest-neighbor carbon-carbon distance in the simulation may reflect a weak admixture of residual sp² bonding in the experimental samples.

**Auto-Correlation of HRTEM Images:** Image auto-correlation is used to extract information about periodicities in the high-resolution transmission electron microscopy. One image in particular appears to represent an especially well-ordered portion of the sample where medium-range axial order is present. The greyscale image intensities for the indicated region of the image were centered about a zero average, normalized, and then auto-correlated as a function of horizontal and vertical shifts. Maxima and minima in the autocorrelation function correspond to incipient periodicities in the original image. The minima perpendicular to the center diagonal in Supplementary Fig. 11 correspond to a ~6.2 Angstrom transverse separation between striations in this image; values in this range are consistently observed across multiple images for the inter-thread separation. This particular image also shows axial “beading”, which appears in the autocorrelation as a feature around approximately ±3.8 Å in the diagonal (i.e. axial) direction. This axial periodicity is close to the range of unit cell lengths calculated for ordered nanothread
structures examined (4.0 – 5.0 Å). At the current level of precision, the precise periodic structure observed cannot be resolved.

**Optical Spectrum Calculation:**

Raman spectra were calculated using density functional perturbation theory implemented in the Quantum Espresso package, together with norm-conserving pseudo-potential and LDA exchange-correlation functionals.

**Supplementary Discussion of Exclusion of Graphane and Diamondoids:**

Multiple allotropes of graphane could provide alternative low-enthalpy high-pressure phases with a 1:1 C:H stoichiometry. However all known variants of graphane are clearly inconsistent with the measured ~6.4 Å lattice spacing between weakly bonded structural subunits (Supplementary Fig. 5). Although the measured correlations in the first and second neighbor shells of G(r) are similar to those in diamondoids such as adamantane, PDFs of these molecules do not match at longer distances (Supplementary Fig. 6). In addition, diamondoid crystals are difficult to reconcile with the strong 1D striations observed in TEM. Diamondoids are also more hydrogen-rich than benzene and compressed benzene is unlikely to lose carbon relative to hydrogen, especially under the strong topochemical constraints of high pressure.

**Supplementary Discussion of Raman Spectra:**

We calculated the spectra for five one-dimensional sp\(^3\) carbon structures: the (3,0) sp\(^3\) ‘nanotube’, the polymer I structure, and three structures constructed by Stone-Wales bond rotations on the (3,0) sp\(^3\) nanotube. One of these three had an off-axis bond rotated at a rate of one rotation per unit cell, one had an off-axis bond rotated at a rate of one rotation per three unit cells, and the other had an axial bond rotated at a rate of one rotation per three unit cells. All five
structures have Raman-active radial breathing modes in the region from 690 cm\(^{-1}\) to 820 cm\(^{-1}\), which is consistent with the experimental observation of a mode at 805 cm\(^{-1}\). The radial breathing mode of these sp\(^3\) structures is at much higher frequencies than similar modes in sp\(^2\) carbon nanotubes\(^{25}\) because their diameter is much smaller. The vibrational frequency of the radial breathing mode of the polymer I at 818 cm\(^{-1}\) is closest to the experimental value. The radial breathing mode frequency shifts up with increasing pressure. We calculated its position for the (3,0) ‘nanotube’ at various pressures and found that the frequency shifts from 747 cm\(^{-1}\) at ambient pressure to 814 cm\(^{-1}\) at 20 GPa. The slight discrepancy between theoretical calculation and experiment observation could come from structure disorder, local environment strain, or the computational limits of density functional theory.

In addition, the (3,0) ‘nanotube’ and its two Stone-Wales variants with the lowest bond rotation density have Raman-active modes in the region from 930 cm\(^{-1}\) to 990 cm\(^{-1}\) that are associated with a flexure of the nanothread. Two neighboring six-membered rings along axis tilt with respect to each other, such that two of the linking bonds extend when the third bond contracts. These modes are close to the experimentally observed mode at 1005 cm\(^{-1}\) (i.e. within the accuracy of the calculation). Unlike the flexure modes of sp\(^2\) nanotubes, which are not Raman active,\(^{26}\) these modes are Raman active with optical character within the primitive unit cell. Raman modes that are totally symmetric, such as the radial breathing modes for the (3,0) ‘nanotube’ and polymer I structure, should exhibit Raman depolarization ratios \((\rho = I_{\text{perpendicular}}/I_{\text{parallel}})\) less than 0.75.\(^{27}\) A depolarization ratio of 0.65 is observed experimentally (Supplementary Figure 7). A partially disordered structure derived from both these ideal structures is the best match to the experimental pair distribution functions, but it appears that the totally symmetric
character of the radial breathing mode is at least partially preserved (although a heterogeneous mixture of different species of more well-ordered nanotreads could provide an alternative explanation). The flexure mode is not totally symmetric and is observed to be depolarized with $\rho=0.75$ (Supplementary Figure 7).

Supplementary Table 1 shows relevant characteristic frequencies in the spectral region of 750 cm$^{-1}$ to 1100 cm$^{-1}$, part of the single bond C-C spectral fingerprint region, for hydrocarbon vibrations reported in the Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules and also for candidate diamondoid molecules which have multiple adamantane-like cages.$^{28,29}$ The presence of molecules arising from reaction of benzene under pressure and exhibiting these vibrations can be ruled out from several lines of evidence, thus providing further support for the respective assignments of the observed Raman modes at 805 and 1005 cm$^{-1}$ to radial breathing and flexure modes characteristic of sp$^3$ nanotreads. None of the small molecular species in Supplementary Table 1 were observed in mass spectrometry experiments performed on a hexane extract (see gas chromatography-mass spectrometry section above). Hexane dissolves small alkanes, adamantane, and diamondoids and so would extract these molecules and deliver them to the mass spectrometer. Furthermore, the Raman polarization analyses are inconsistent with the presence of alkane chains, including long-chain alkanes, which would not exhibit totally symmetric modes in the region of 800 cm$^{-1}$. Cyclohexane, benzene, certain diamondoids, and adamantane would exhibit totally symmetric modes, but are not observed in the mass spectrometry experiments or have Raman shifts inconsistent with those observed (e.g., benzene, cyclobutane, larger diamondoids). Moreover benzene and cyclohexane are liquids that would evaporate upon sample recovery. The presence of isopropyl tertiary
carbons would require the formation of methyl groups from benzene, which would require hydrogen shifts that appear unlikely. Moreover, these carbons would not have the requisite Raman polarization properties. As diamonoid size increases, the cage breathing mode decreases in frequency to values much below that observed at 805 cm\(^{-1}\).

<table>
<thead>
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<th>Peak Position (cm)</th>
<th>Vibrational Mode</th>
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<tr>
<td>837-905</td>
<td>C-C Skeletal stretch in n-Alkanes</td>
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<tr>
<td>800-900</td>
<td>Longitudal Acoustic mode in n-Alkanes</td>
</tr>
<tr>
<td>800-810</td>
<td>C-C(CH)</td>
</tr>
<tr>
<td>802</td>
<td>Ring breathing of cyclohexane</td>
</tr>
<tr>
<td>1001</td>
<td>Ring breathing of cyclobutane</td>
</tr>
<tr>
<td>992</td>
<td>Ring breathing of benzene</td>
</tr>
<tr>
<td>1040-1100</td>
<td>CCC antisymmetric stretch in n-Alkanes</td>
</tr>
<tr>
<td>800</td>
<td>C-C Stretch in adamantane</td>
</tr>
<tr>
<td>758</td>
<td>C-C Stretch (Cage breathing) in adamantane</td>
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<tr>
<td>&lt; 758</td>
<td>C-C Stretch (Cage breathing) in larger diamondoids ,</td>
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**Supplementary Table 1: Characteristic Raman Frequencies of Hydrocarbon Vibrations in the Raman Fingerprint Region.\(^{28,29}\)**
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**Supplementary Figure 1:** Total scattering x-ray structure function of \(^{12}\)CH benzene downloaded at 20 GPa/hr in a DAC. Only diffuse scattering and no Bragg peaks are observed up to 7 Å\(^{-1}\) in this more rapidly decompressed sample.
**Supplementary Figure 2:** Variation in interplanar spacings derived from Bragg peaks upon compression. The nanothread 2-D lattice (100) and (200) Bragg peaks shift too rapidly to be associated with strong covalent bonding (exemplified by the shift in the in-plane a axis of graphite shown at the top). Rather, their shift is characteristic of van der Waals bonding (exemplified by the shift upon compression observed in graphite along its c axis and the simulated nanothread lattice shown). Disorder in the experimental threads may prevent them from packing as efficiently as predicted for the ideal, ordered (3,0) nanotubes with an axial bond rotated, thus increasing their compressibility.
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Supplementary Figure 3: Total scattering structure functions of nanothreads determined from high-energy angular dispersive x-ray diffraction and energy dispersive neutron diffraction data. Bragg reflections are observed at low Q and diffuse scattering is present at high Q. A shared cutoff $Q_{\text{max}}$ of 21 Å$^{-1}$ was used when transforming both of these S(Q) to real space, this was dictated by the highest Q value at which the usable portions of the S(Q) cross 1.0.
**Supplementary Figure 4: $^{13}$C solid-state NMR of sp$^3$ carbon nanothreads.** NMR analyses of two different samples of carbon nanothreads ($^{13}$CD red and $^{13}$CH black curves) reveal a high sp$^3$ carbon content, 80-84%. The sp$^2$ and sp$^3$ carbon spectral regions are colored red and blue, respectively.
Supplementary Figure 4: 13C solid-state NMR of sp³ carbon nanothreads. NMR analyses of two different samples of carbon nanothreads (13CD red and 13CH black curves) reveal a high sp³ carbon content, 80-84%. The sp² and sp³ carbon spectral regions are colored red and blue, respectively.

Supplementary Figure 5: Comparison of experimental x-ray diffraction pattern and five theoretically predicted graphane structures. None of the layered graphane structures are a good match to the experimental data. Moreover, none of the interlayer spacings match the separation of the striations observed in HRTEM images (Fig. 1a)
Supplementary Figure 6: Comparisons between pair distribution functions calculated for three diamondoids and experiment. Thick and thin lines show neutron and X-ray pair distribution functions $G(r)$, respectively. The reasonable agreement found at short distances is to be anticipated, considering that all structures share a local sp$^3$ bonding geometry. However, all three diamondoids produce a clear shoulder in the neutron patterns at around 1.75 Å that is not observed. The diamondoid structures also exhibit strong peaks at 3.0 Å in both $G(r)$ functions that arise from C-C pairs. The experimental x-ray $G(r)$ exhibits only a weak peak and none is observed in the neutron $G(r)$. The diamondoid neutron $G(r)$ functions are weighted the same as disordered tubes in Fig. 4. The diamondoid lattices were relaxed/equilibrated with a classical force field (ReaxFF) at 300K.
Supplementary Figure 7: Polarization analysis of 785 nm Raman spectra collected from a sample synthesized from $^{13}$C benzene. Depolarization ratios observed for the radial breathing mode and flexure mode are 0.65±0.03 and 0.75±0.03 respectively. The radial breathing mode is thus polarized while the flexure mode is depolarized. The depolarization ratios were determined from Voigt fits to the Raman peaks with a cubic spline background fit to account for the fluorescence background. This fluorescence is polarization dependent, as is typically observed for solid state materials. Both $^{13}$C Raman modes are downshifted relative to the modes observed in $^{12}$C spectra. The radial breathing mode remained polarized as both the position of the excitation spot on the sample and the excitation wavelengths (633 and 785 nm) were varied. Raman mode intensities did not vary as the sample was rotated, indicating that there was no preferred orientation of the nanothreads within the volume probed by the laser excitation.
Supplementary Figure 8: Views down crystallographic axes of the high-pressure benzene II phase: a, b, Views down a and b axes showing nearly-hexagonally-packed columns of tilted benzene molecules. c, View down c axes showing lack of nearly-hexagonally-packed columns and interleaving of adjacent columns with different tilts. One set of interleaved C-H bonds from adjacent columns is shown by the arrow. This direction appears less likely to be able to form a well-developed thread upon reaction.
Supplementary Figure 9: Nanothread formed by cycloaddition and intramolecular reaction. Top: A reaction mechanism that forms a sp³ nanothread from benzene molecules arranged in the benzene II crystal. Benzene molecules are oriented in a slipped stack along both the a and b axes of the benzene II crystal structure. An a axis stacking extracted from this crystal structure is shown in the leftmost column. A series of [4π+2π] cycloaddition reactions can form a benzene polymer (second and third columns). Aligned olefin functions are then well oriented for a zipper cascade⁴⁰ to give a fully sp³ hybridized nanothread (fourth column). The cycloaddition and zipper reactions both have negative activation volumes and would thus be promoted under high pressure. The zipper reaction is very exothermic; the slow decompression employed in our experiments may aid in controlling this reaction. Tight binding relaxation of the [4π+2π] cycloaddition reaction product spontaneously forms the fully sp³ thread in view of its considerable thermodynamic stability. This structure can interconvert to the (3,0) and polymer I structures discussed in the main text by Stone-Wales transformation: all three structures should be considered members of a single structural family, since current scattering data does not provide a firm basis to distinguish between them. Although benzene dimers are prone to cycloreversion, benzene oligomers several repeat units long can be formed at hundreds of MPa pressures in the liquid state⁴¹. High pressure solid-state polymerization appears to facilitate formation of much longer structures. Bottom: Structurally relaxed nanothread formed by this process.
mechanism. In isolation it is curved, but within a crystal packing constraints could force linearity.

Supplementary Figure 10: Full Raman spectrum of $^{13}$CH benzene after compression and relation to sp² carbon content. A “G” peak characteristic of a second sp² bonded hydrogenated amorphous carbon phase is observed. The broad fluorescence background observed can be attributed to small hydrogenated and aromatic sp² carbon clusters that must account for at least some of the sp² carbon content observed via NMR (Supplementary Fig. 4). A Tauc analysis of diffuse reflectance spectra collected on a compressed benzene sample reveals a gap of 2.3 eV, which places an upper bound of approximately 7 aromatic rings on the cluster size. If we assume that all of the sp² carbon were olefinic and associated with the nanothreads the position of the peak associated with the first C-C coordination sphere of 1.52 Å in the pair distribution function (Fig. 3) implies a sp² carbon content of 9% $\left(1.52 \text{ Å} = 0.91(1.54 \text{ Å}) + 0.09(1.31 \text{ Å})\right)$, where 1.54 Å and 1.31 Å are the bond lengths for carbon single and double bonds. However, some of the carbon must be aromatic or the G feature in the Raman spectrum (and the background fluorescence) would not be observed. This analysis suggests that the nanothreads alone cannot contain more than 9% sp² carbon. If no reaction of the olefinic bonds occurred, the sp² content of the nanothreads would be 33%. This appears to rule out a structure formed solely by $[4\pi+2\pi]$ cycloaddition reactions (Supplementary Fig. 9) without any
subsequent reaction of the olefinic bonds remaining after these reactions. A similar analysis of the position of the first peak in the pair distribution function assuming all sp² carbon is aromatic gives at most 15% sp² bonding \((1.52 = 0.85(1.54\text{Å}) + 0.15(1.41\text{Å}))\), where 1.41 Å is the bond length of an aromatic carbon bond) vs. 16-20% sp² content determined from NMR (Supplementary Fig. 4). This again suggests that there is not much sp² bonding in the nanothreads, as the sp² content is best accounted for by assuming it is aromatic. C-H Raman stretching modes associated with sp³ and sp² carbon are also observed.
Supplementary Figure 11: HRTEM image of carbon nanotreads (left) and contour plot of the image autocorrelation function (right). A spacing of ~6.2 Å is observed in the direction transverse to the nanotreads, close to that observed in Figure 1. Weak beading with a spacing of 3.5–3.8 Å is observed along the length of the threads and is suggestive of order in this direction. Local maxima in the axial direction are marked by + and the local minima in the transverse direction are indicated by *.
Supplementary Information

Supplementary References


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