

# *Supporting Information Appendix*

to

## **Graphanes: Sheets and stacking under pressure**

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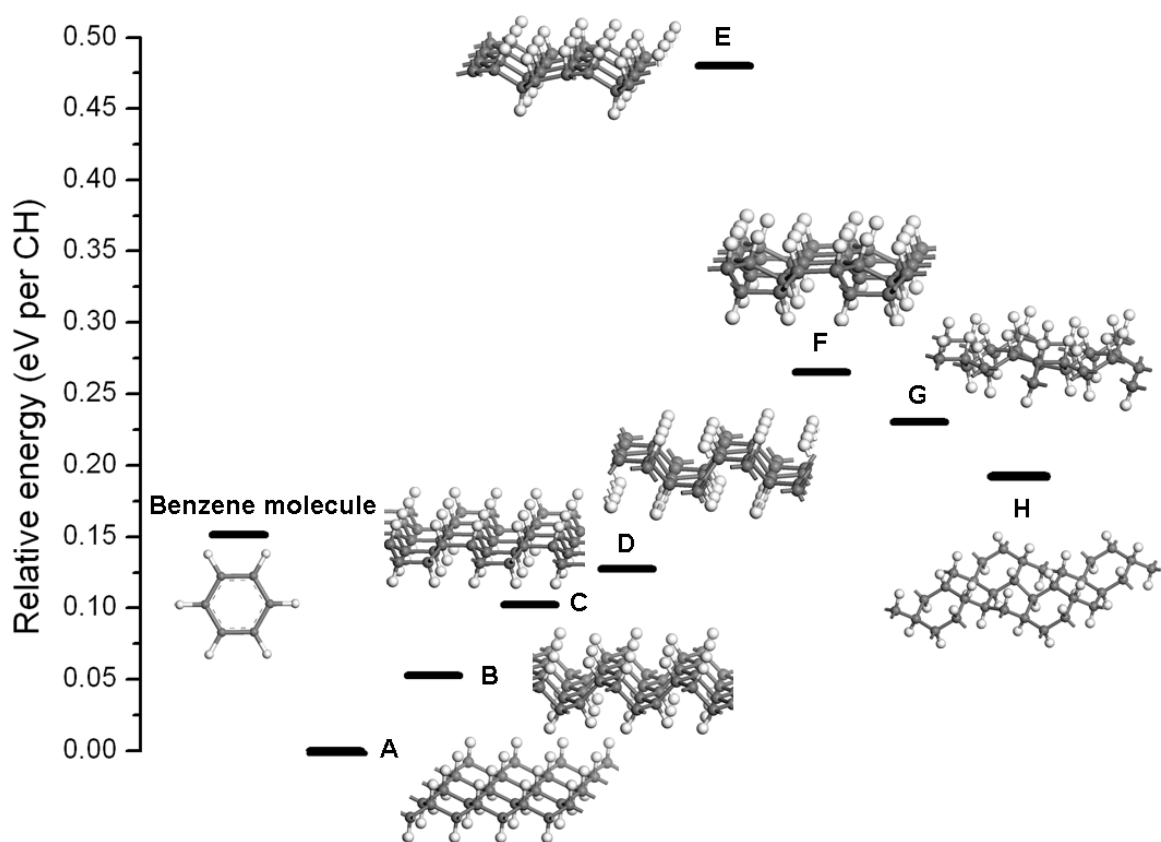
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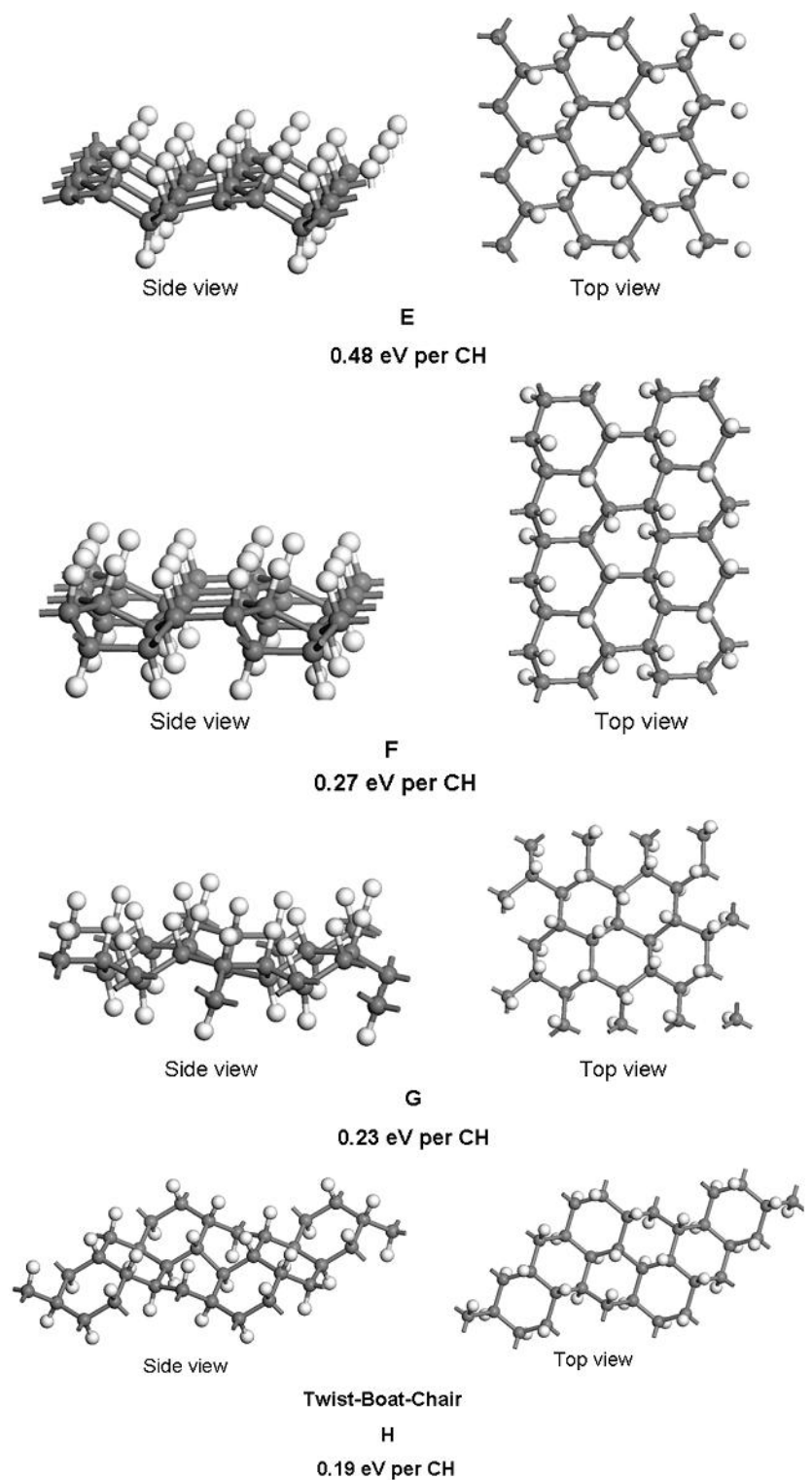
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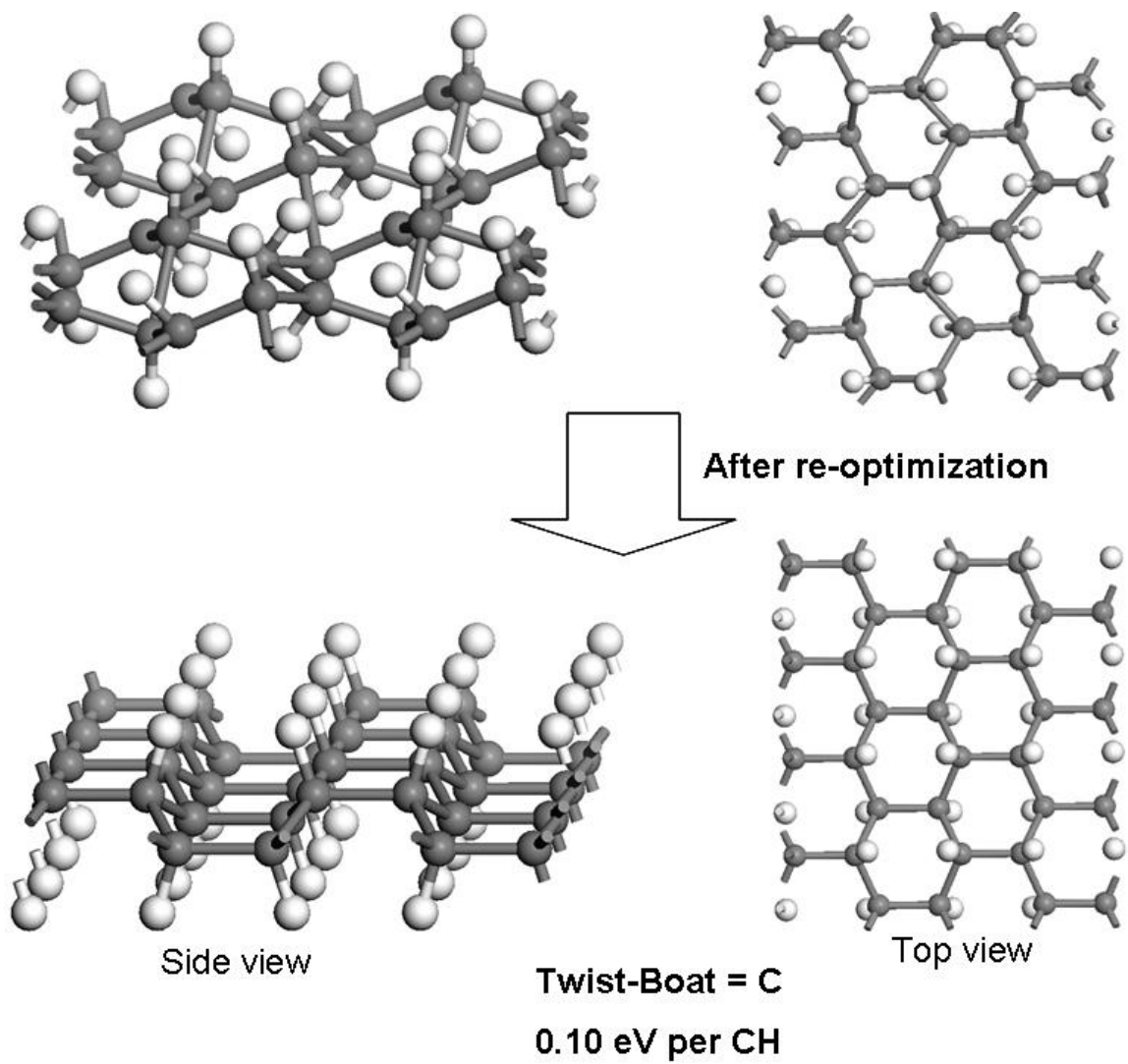
## 1. More single-layer graphanes at ambient pressure



**Figure S1.** Relative energy (eV per CH) of benzene and graphanes. Graphane A is taken as a reference. Drawings of graphane structures E, F, G, H are shown below.

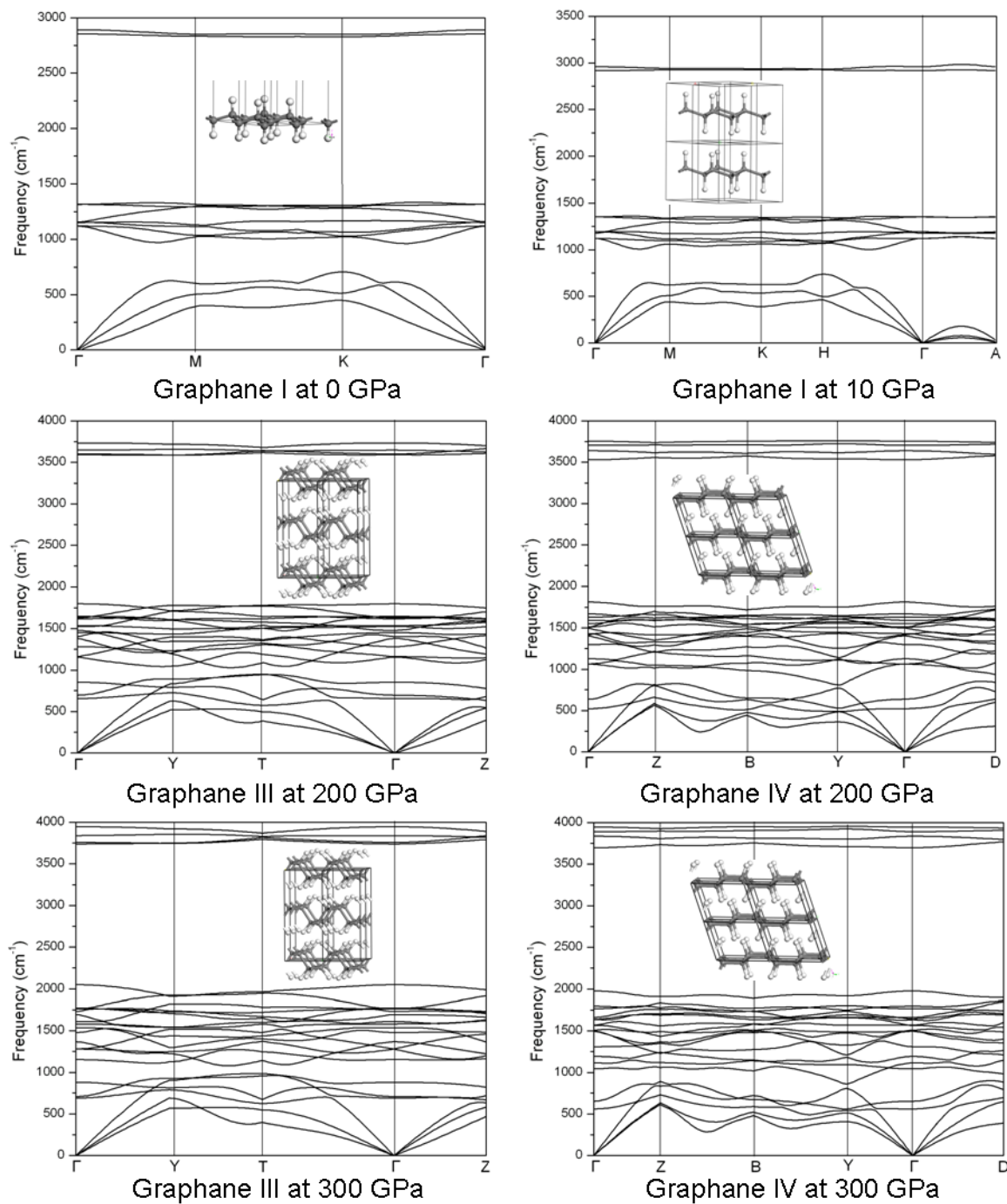


**Figure S2.** Graphanes E, F, G, H. The Twist-Boat Chair graphane from the work of D. K. Samarakoon and X.-Q. Wang is H.



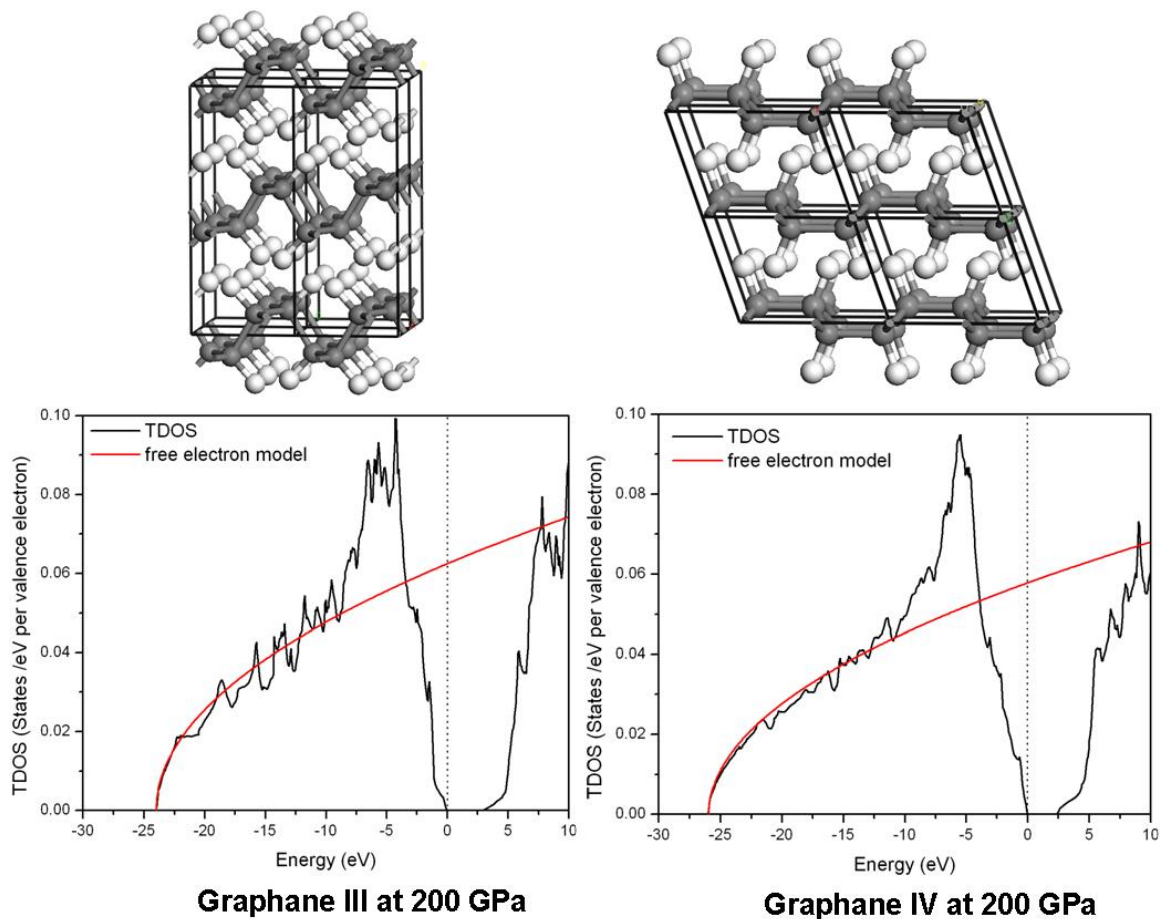
**Figure S3.** The twist-boat structure of D. K. Samarakoon and X.-Q. Wang optimizes to graphane raft C.

## 2. Calculated phonon dispersion of graphane structures



**Figure S4.** The computed phonon dispersion of graphane I at 0 and 10 GPa, graphane III at 200 and 300 GPa, and graphane IV at 200 and 300 GPa.

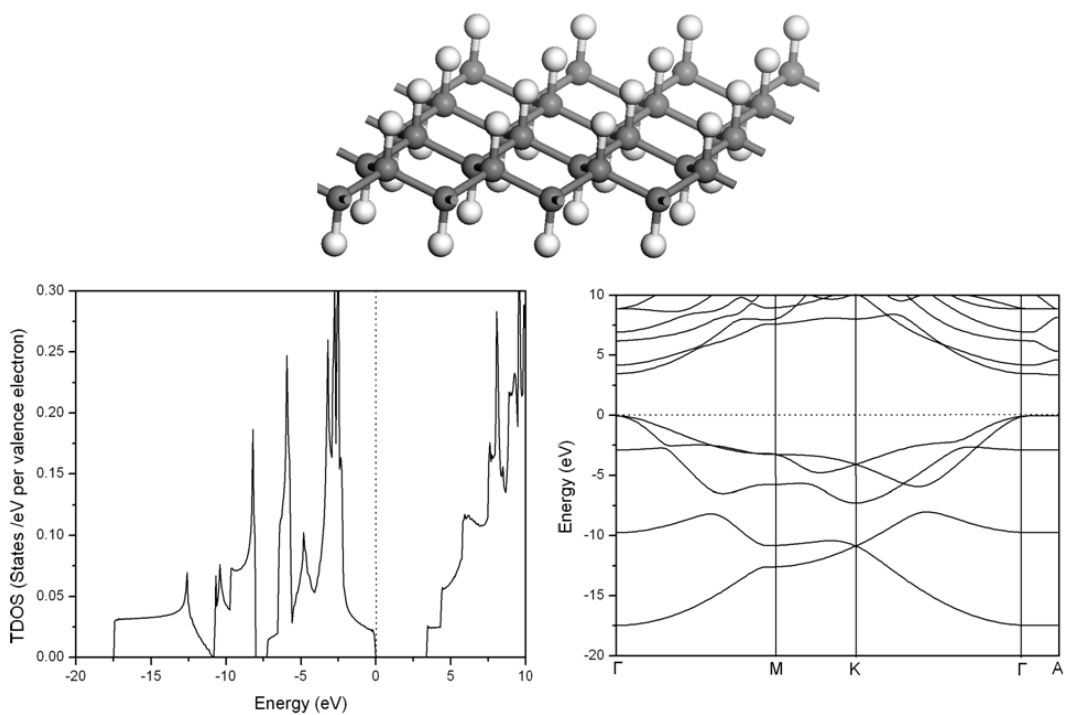
### 3. Computed total density of states for graphane III and IV at 200 GPa.



**Figure S5.** Computed total density of states for graphane III and graphane IV at 200 GPa.

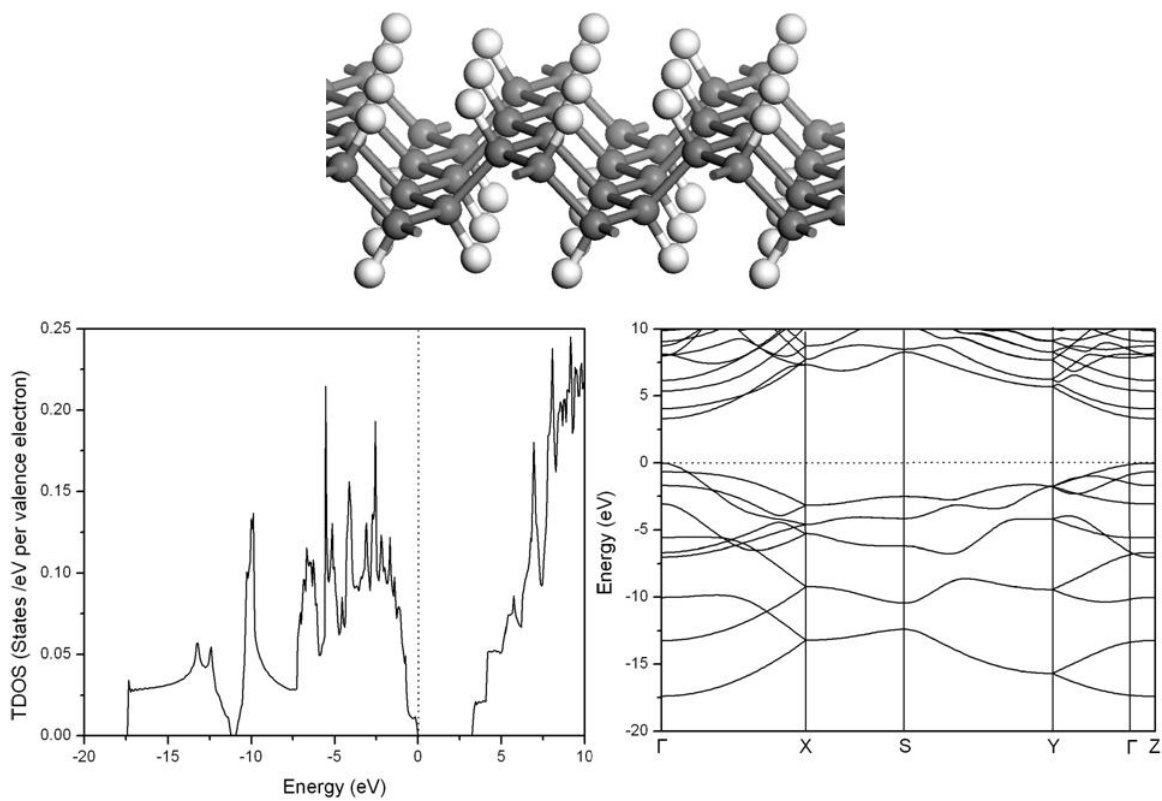
A free electron parabola is superimposed. The dotted line indicates the highest occupied level.

**4. Computed band structure and density of states of single-sheet graphanes at ambient pressure.**

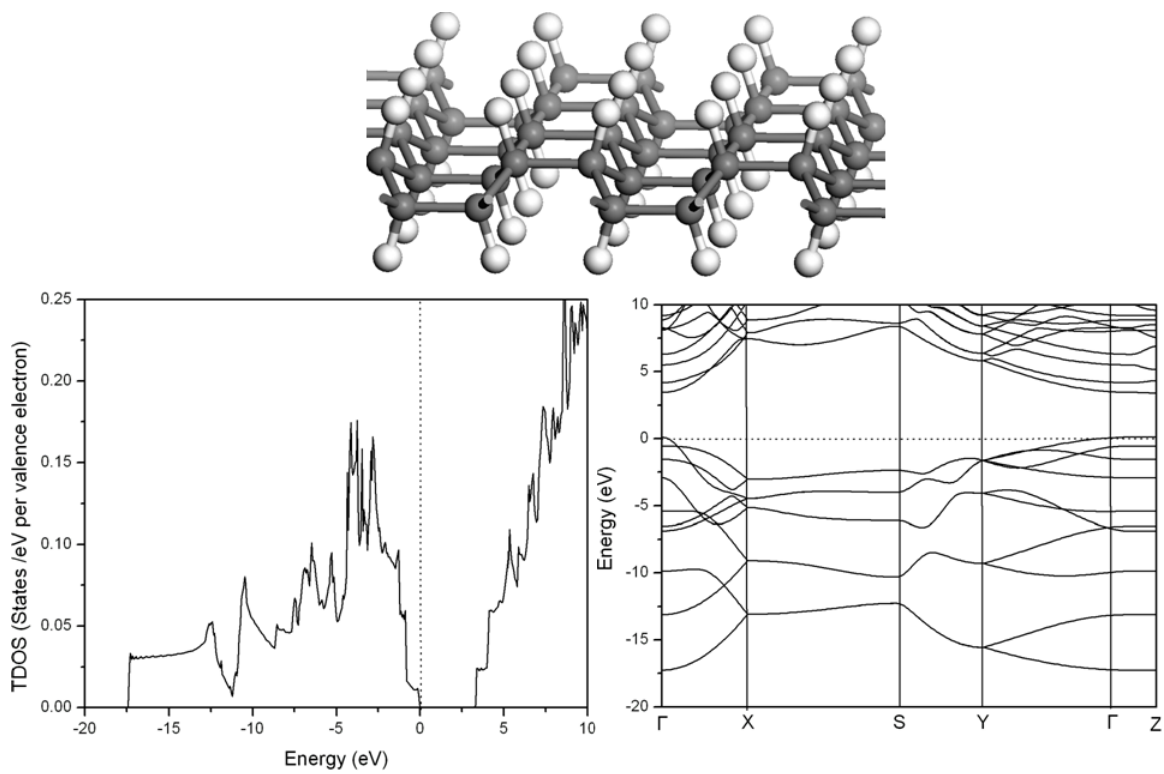


**Figure S6.** Computed band structure and density of states for single-sheet graphane I at ambient pressure. The dotted line indicated the highest occupied level.





**Figure S7.** Computed band structure and density of states for single-sheet graphane III at ambient pressure. The dotted line indicates the highest occupied level.



**Figure S8.** Computed band structure and density of states for single-sheet graphane IV at ambient pressure. The dotted line indicates the highest occupied level.

**5. Computed Wigner-Seitz radius  $r_s$  of diamond, graphane I, II, III, IV, V and CH<sub>4</sub> and H<sub>2</sub>.**

**Table S1.** Calculated Wigner-Seitz radius  $r_s$  of diamond, graphane I, II, III, IV, V and solid CH<sub>4</sub> and H<sub>2</sub>.

$r_s$	Diamond	I	II	III	IV	V	CH <sub>4</sub>	H <sub>2</sub>
0GPa	1.32	1.65	1.67	1.63	1.60	1.67	2.34	2.79
50GPa	1.28	1.42	1.42	1.40	1.40	1.41	1.55	1.69
100GPa	1.25	1.35	1.35	1.33	1.33	1.35	1.44	1.55
200GPa	1.21	1.27	1.27	1.26	1.26	1.27	1.33	1.41
300GPa	1.17	1.23	1.23	1.21	1.21	1.22	1.27	1.33

The dimensionless Wigner-Seitz radius  $r_s$  is defined by  $4\pi(r_s a_0)^3/3=1/\rho$ , where  $\rho$  is the average valence-electron density and  $a_0$  the Bohr radius. Since  $\rho=N/V$ , where  $N$  is the number of valence electrons in the unit cell and  $V$  is the volume of the unit cell,  $\rho$  scales as  $V^{-1/3}$ .

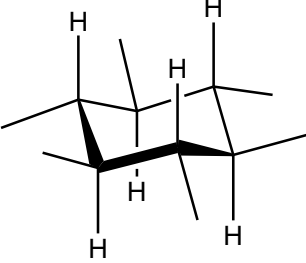
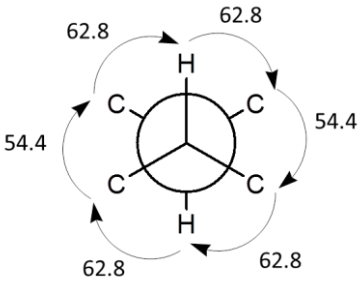
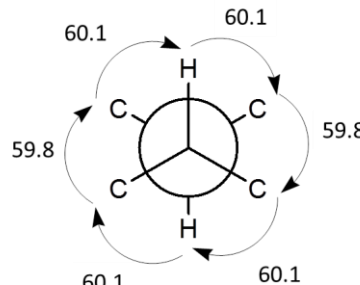
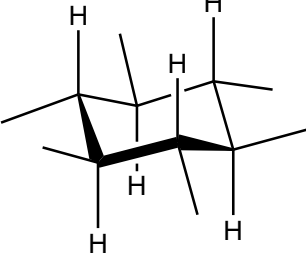
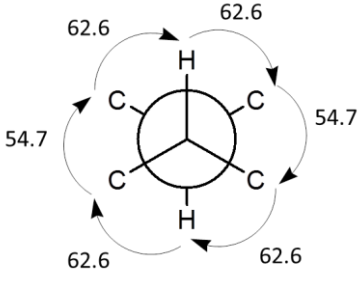
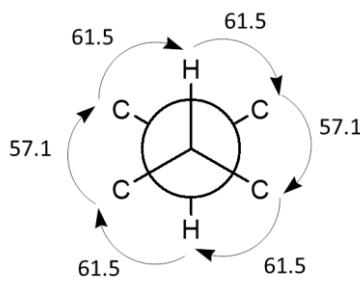
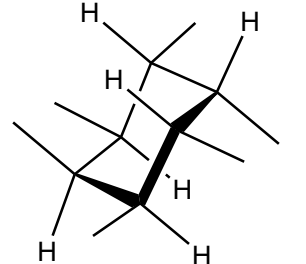
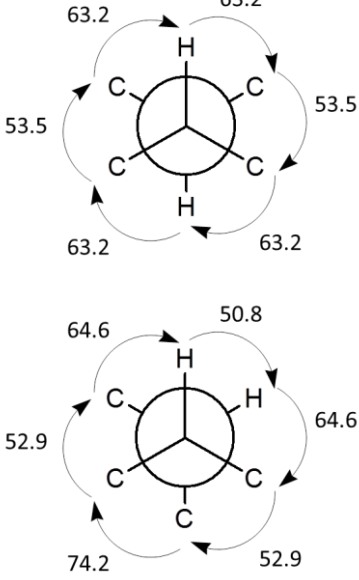
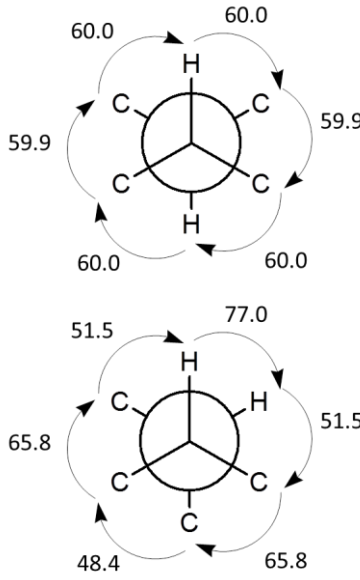
**6. C-C and C-H distances in diamond, graphane I, II, III, IV, V and CH<sub>4</sub> at 0 -300 GPa.**

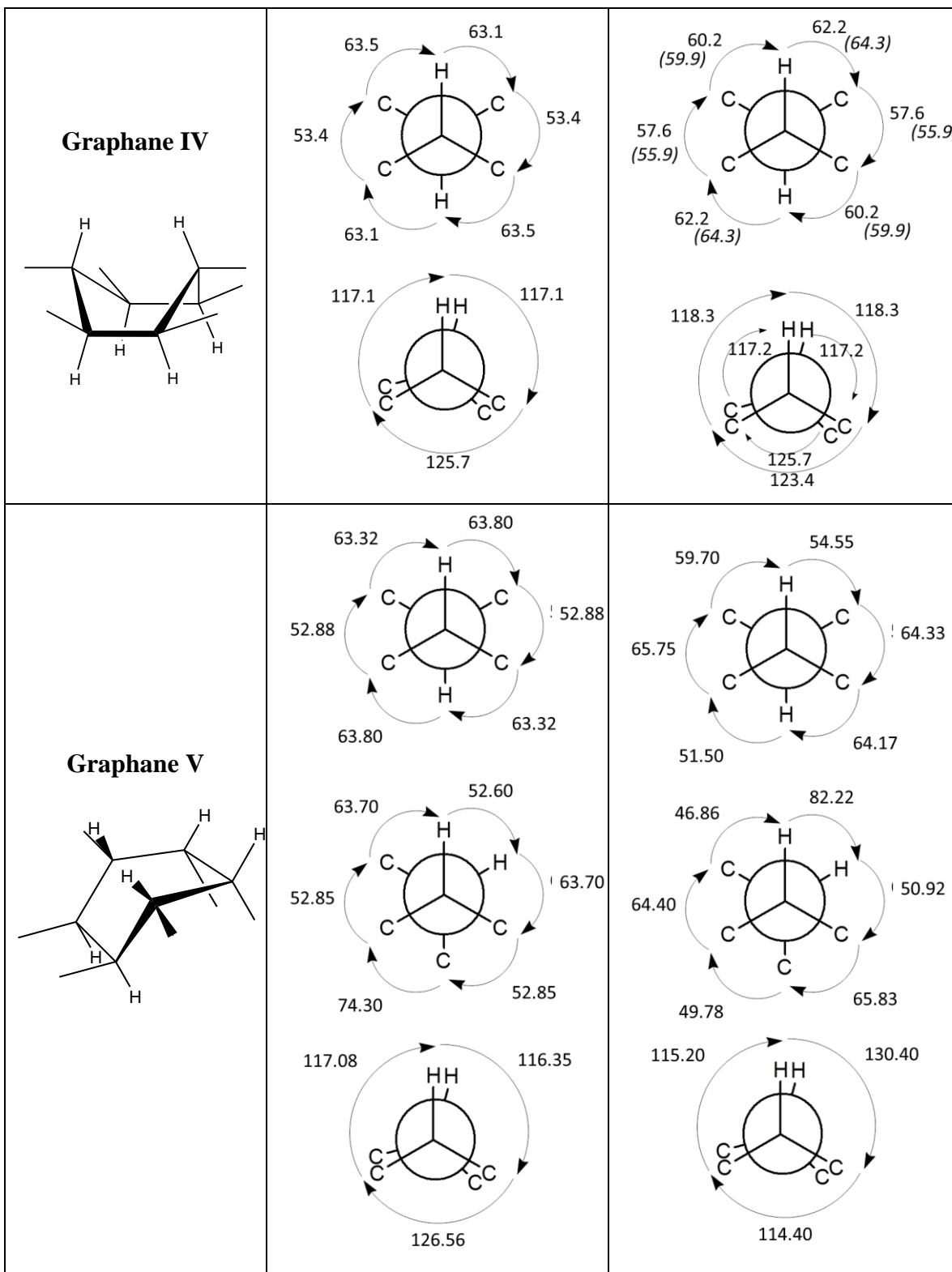
**Table S2.** C-C and C-H distances (in Å) in diamond, solid methane and five graphanes at 0GPa, 50GPa, 100GPa, 200GPa and 300GPa.

		0GPa	50GPa	100GPa	200GPa	300GPa
Diamond	C-C	1.549	1.500	1.464	1.412	1.374
	C-H					
Solid methane (for USPEX)	C-C					
	C-H	1.096	1.065	1.054	1.033	1.022
Graphane I	C-C	1.539	1.478	1.443	1.393	1.357
	C-H	1.112	1.081	1.060	1.032	1.012
Graphane II	C-C	1.540	1.479	1.445	1.398	1.364
	C-H	1.112	1.079/1.081	1.055/1.061	1.024/1.036	1.002/1.018
Graphane III	C-C	1.544	1.485/1.488	1.452/1.455	1.408/1.410	1.376/1.378
	C-H	1.106	1.079	1.060	1.033	1.015
Graphane IV	C-C	1.537/1.570	1.487/1.501	1.454/1.464	1.408/1.415	1.375/1.380
	C-H	1.105/1.106	1.074/1.081	1.054/1.064	1.027/1.039	1.008/1.020
Graphane V	C-C	1.542/1.545 /1.570	1.481/1.485 /1.496	1.447/1.453 /1.457	1.402/1.409 /1.409	1.376/1.378 /1.378
	C-H	1.103	1.074/1.079	1.054/1.059	1.026/1.033	1.006/1.014

## 7. Torsional angles in graphanes I, II, III, IV, and V at P= 1atm and P= 300 GPa

**Table S3.** Torsional angles in graphanes I, II, III and IV at P= 1 atm and P= 300 GPa

	<b>P=1atm</b>	<b>P=300GPa</b>
<p><b>Graphane I</b></p> 		
<p><b>Graphane II</b></p> 		
<p><b>Graphane III</b></p> 		

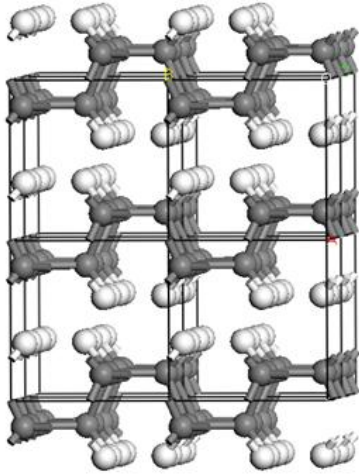


## 8. Enthalpy of stacked graphanes under high pressure

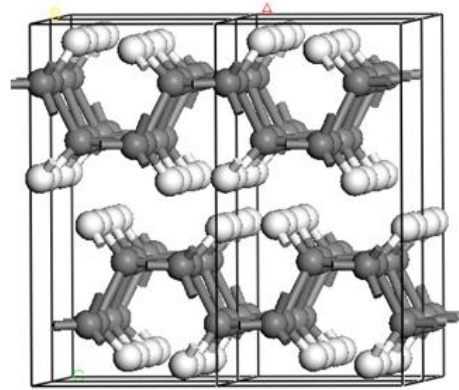
Table S4. The calculated total enthalpy (eV per CH) and density (g/cm<sup>3</sup>) at 200 and 300GPa for graphane I, II, III, and IV, the 3D graphanes (AA and AB stacking type) made up of D, E, F, G and H, respectively.

		200GPa		300GPa	
		Total enthalpy	Density	Total enthalpy	Density
Graphane I		-2.72	3.35	1.09	3.74
Graphane II		-2.74	3.38	1.01	3.79
Graphane III		-3.04	3.49	0.60	3.91
Graphane IV		-3.04	3.51	0.58	3.93
D	-AA-stacking	-2.49	3.34	1.31	3.77
	-AB-stacking	-2.69	3.39	1.06	3.80
E	-AA-stacking	-2.48	3.46	1.19	3.89
	-AB-stacking	-2.48	3.46	1.19	3.89
F	-AA-stacking	-2.75	3.49	0.58 (phase transition to IV)	3.93
	-AB-stacking	-2.18	3.40	1.56	3.80
G	-AA-stacking	-2.68	3.49	0.96	3.92
	-AB-stacking	-2.65	3.48	1.02	3.91
H	-AA-stacking	-2.18	3.31	1.63	3.77
	-AB-stacking	-2.47	3.38	1.31	3.84

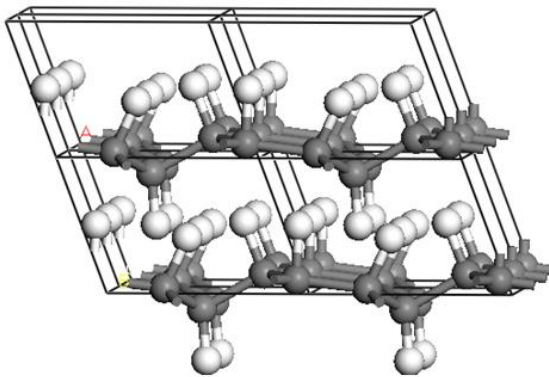
The corresponding structures at 200GPa (not very different to the structures at 300GPa) are shown below:



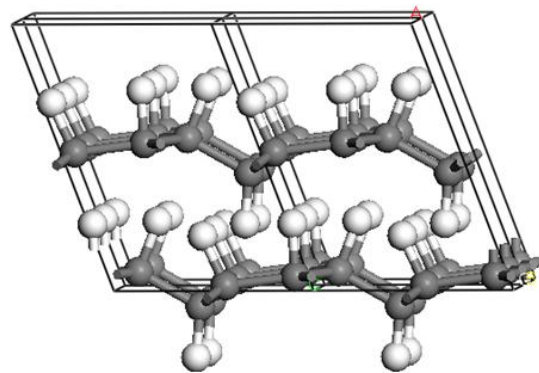
**D -AA- stacking at 200GPa**



**D -AB- stacking at 200GPa**

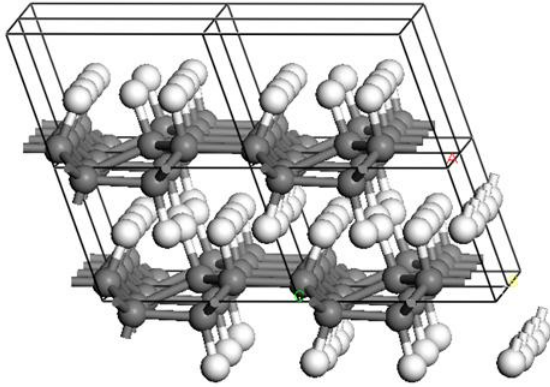


**E -AA- stacking at 200GPa**

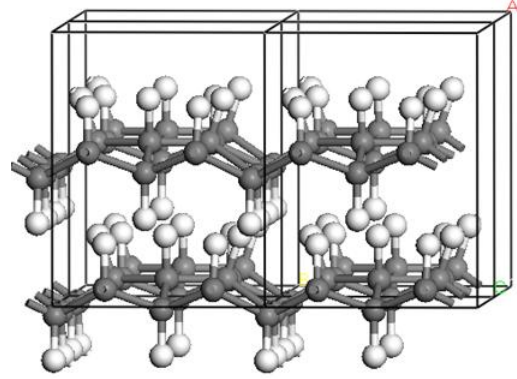


**E -AB- stacking at 200GPa**

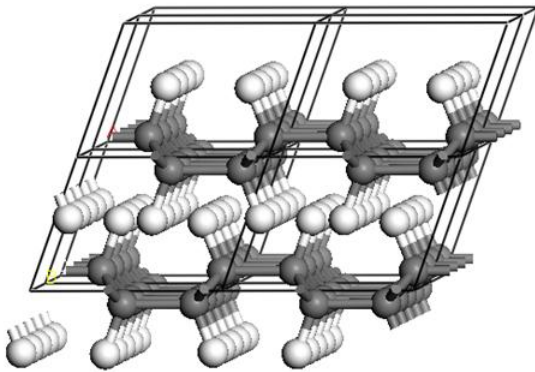




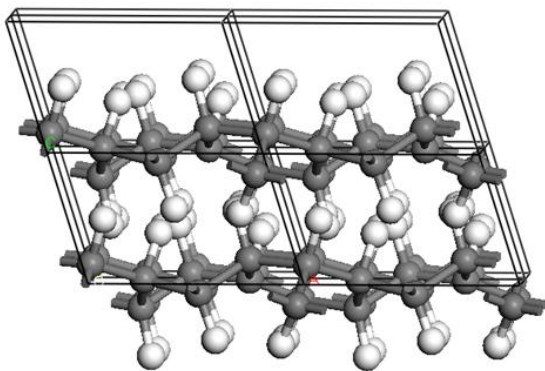
**F -AA- stacking at 200GPa**



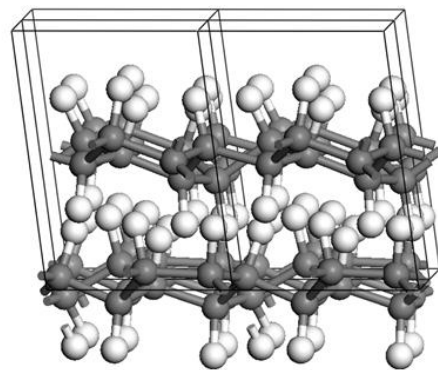
**F -AB- stacking at 200GPa**



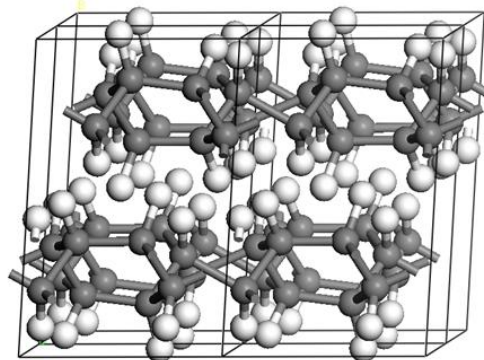
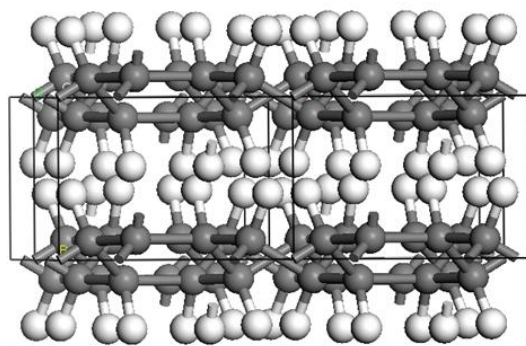
**F -AA- stacking at 300GPa**



**G -AA- stacking at 200GPa**



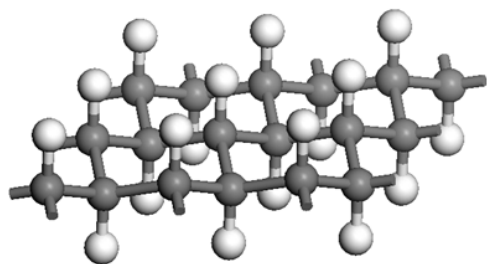
**G -AB- stacking at 200GPa**



Twist-boat-chair -AA- stacking at 200GPa    Twist-boat-chair -AA- stacking at 200GPa

**Figure S9.** 3D graphanes made up of layers D, E, F, G and H. Note that for layer F at 200GPa, the corresponding -AA- stacking at 300GPa is identical to graphane IV at 300GPa.

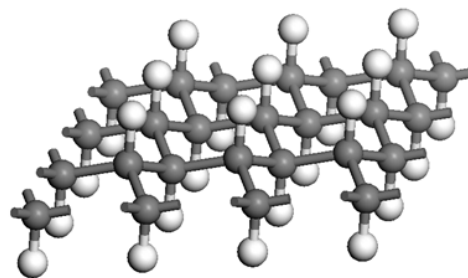
## 9. A study of “releasing” pressure on some 3D graphanes.



2D layer cut from graphane I

$$E_{\text{tot}} = -11.49 \text{ eV per CH}$$

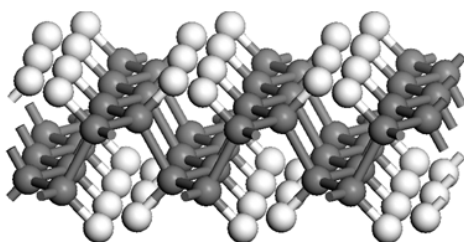
$$\text{C-C} = 1.357 \text{ \AA}; \text{C-H} = 1.012 \text{ \AA}$$



2D layer cut from graphane II

$$E_{\text{tot}} = -11.62 \text{ eV per CH}$$

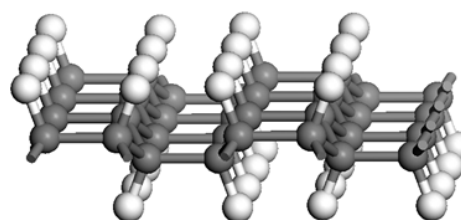
$$\text{C-C} = 1.364 \text{ \AA}; \text{C-H} = 1.018 \text{ \AA}$$



2D layer cut from graphane III

$$E_{\text{tot}} = -10.72 \text{ eV per CH}$$

$$\text{C-C} = 1.378 \text{ \AA}; \text{C-H} = 1.015 \text{ \AA}$$

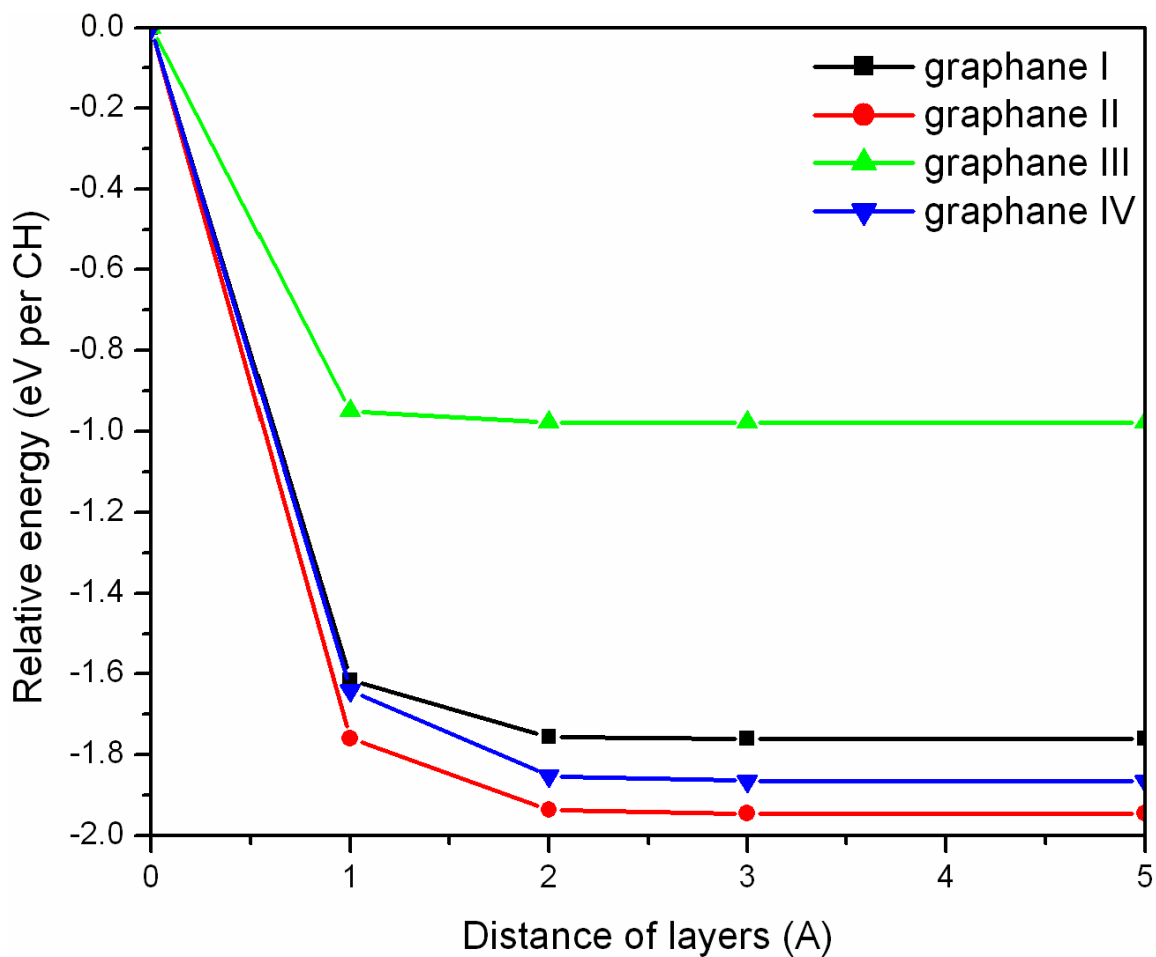


2D layer cut from graphane IV

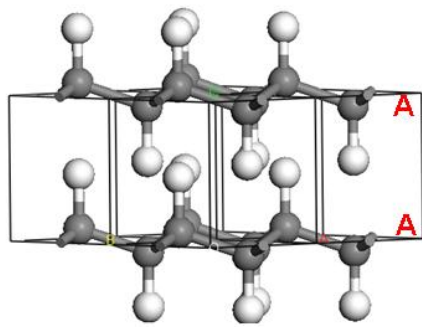
$$E_{\text{tot}} = -11.58 \text{ eV per CH}$$

$$\text{C-C} = 1.375 \text{ \AA}; \text{C-H} = 1.008 \text{ \AA}$$

**Figure S10.** 2D layers cut from stacking graphanes at 300 GPa. The geometries of these layers are fixed. A single point calculation is performed. The total energy (eV per CH) and C-C and C-H distances are shown. The 2D layer in graphane III has the highest energy among these layers.

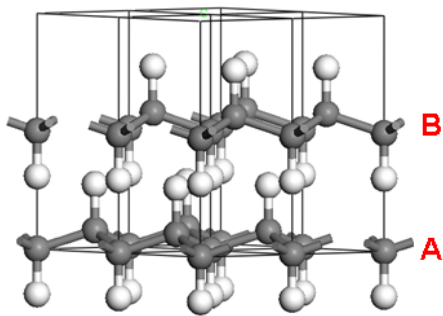
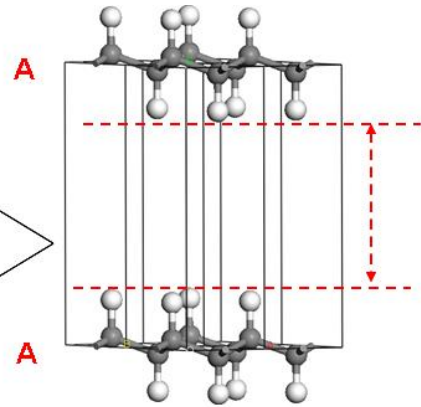


**Figure S11.** Potential energy for one-dimensional “dilation” of three-dimensional graphane structures along c axis. The ab planes in these graphanes are fixed. That means that C-C and C-H distances are fixed, just the inter-layer distance is varied. The optimized stacked graphane structures at 300GPa are taken as the corresponding references. The process also can be thought of as releasing pressure only along c axis, as shown in **Figure S12**.



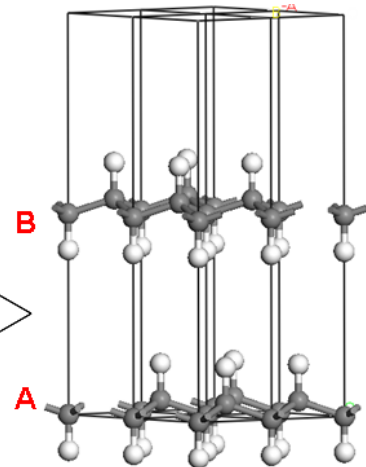
Graphane I at 300 GPa

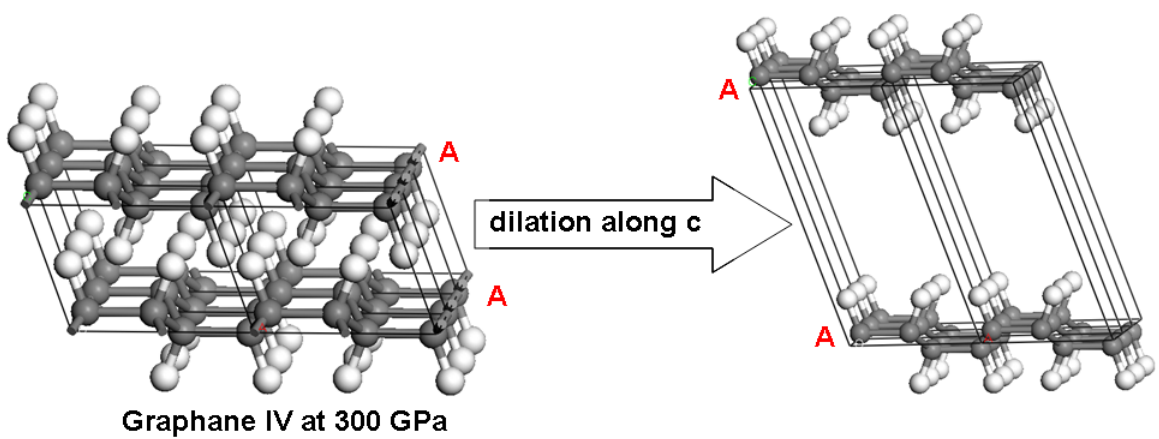
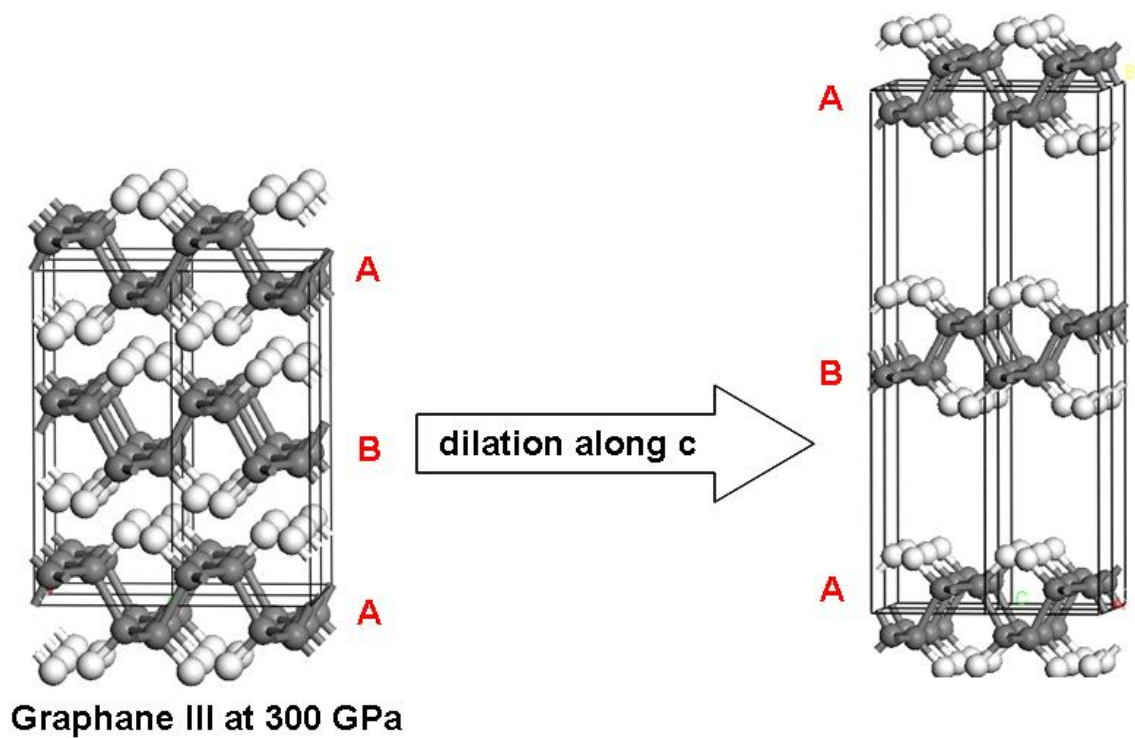
dilation along c



Graphane II at 300 GPa

dilation along c





**Figure S12.** Dilating the three-dimensional graphane structures, so as to convert them into two-dimensional sheets.