

# **Supporting Information for**

# A planar-sheet non-graphitic zero-bandgap sp<sup>2</sup>-carbon phase made by low-temperature reaction of $\gamma$ -graphyne

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This PDF file includes:	Supporting text
	Figures S1 to S27
	Tables S1 to S8
	SI References

### **Contents**

3
ł
1
ł
5
5
5
7
3
3
)
)
1
2
2
3
3
5

# 1. Nomenclature and Abbreviations

Abbreviation	Description
DCM	Dichloromethane
DFT	Density Functional Theory
DMSO	Dimethyl sulfoxide
EI-MS	Electron Ionization Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography–Mass Spectrometry
MD	Molecular Dynamics
MSD	Mass Selective Detector
NMR	Nuclear Magnetic Resonance
Ру	Pyridine
TBAF	Tetra-n-butylammonium Fluoride
TBTEB	1,3,5-Tribromo-2,4,6-triethynylbenzene
TEA	Triethylamine
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TSP	Thermal Separation Probe
UV-Vis	Ultraviolet-Visible

Nomenclature and Abbreviations

### 2. Synthetic Procedures

### 1,3,5-tribromo-2,4,6-triiodobenzene



Periodic acid (41.03 g, 180 mmol) was added in small portions over 15 minutes to concentrated H<sub>2</sub>SO<sub>4</sub> (500 mL) at room temperature. After dissolution of the periodic acid, crushed KI (89.64 g, 540 mmol) was added in small portions at 0°C over 1 hour. To the resulting deep purple solution at 0°C was added 1,3,5-tribromobenzene (18.89 g, 60.0 mmol) in small portions over 25 minutes. After the solution was stirred at room temperature for 5 days, the resulting thick mixture was poured onto ice. The resulting precipitate was filtered and washed with H<sub>2</sub>O ( $5 \times 400$  mL) and then MeOH (5  $\times$  400 mL) to give 1,3,5-tribromo-2,4,6-triiodobenzene (42 g) as a light creamcolored solid. The substance was dissolved in hot pyridine (250 mL) and filtered, after which ethanol (750 mL) was added to the resulting solution at room temperature to yield a solid. The solid was filtered and washed with ethanol ( $3 \times 100$  mL). The solid was dried under high vacuum for 3 days to give 1,3,5-tribromo-2,4,6-triiodobenzene (30 g, 72%) as a pale-yellow solid. The IR spectroscopy signatures (neat) were  $v_{max} = 1488, 1354, 1262, 1227, 1147, 1002, 858, 771, 739,$ 554, 508 cm<sup>-1</sup>. There was no signal for <sup>1</sup>H NMR (500 MHz, DMSO-d6). The <sup>13</sup>C NMR (126 MHz in DMSO-d6) provided  $\delta$  values of 138.61 and 108.23 for the Br substituted carbons and iodinesubstituted carbons, respectively. For EI-MS fragmentation, the m/z were 695.5, 693.5, 691.5, 689.5, 567.6, 566.6, 565.6, 564.6, 439.7, and 437.6.

### <sup>13</sup>C-Labeled ((2,4,6-tribromobenzene-1,3,5-triyl)tris(ethyne-2,1diyl))tris(trimethylsilane)



1,3,5-tribromo-2,4,6-triiodobenzene (139 mg, 0.2 mmol),  $[PdCl_2(PPh_3)_2]$  (42 mg, 0.06 mmol, 30 mol%), CuI (8 mg, 0.04 mmol, 20 mol%), Et<sub>3</sub>N (10 mL), and THF (8 mL) were added to a dry three-necked flask. The flask was sealed and the contents were degassed by three freeze-pump thaw cycles. Trimethylsilylacetylene-<sup>13</sup>C<sub>2</sub> (300 mg, 3 mmol) and Ph<sub>3</sub>P (21 mg, 0.08 mmol, 40 mol%) were added to the mixture. The mixture was stirred at 80°C for 18 h under argon. After the removal of solvent in a rotary evaporator, the residue was further purified by flash chromatography using n-hexane as the eluent to yield labeled ((2,4,6-tribromobenzene-1,3,5-triyl)tris(ethyne-2,1-

diyl))tris(trimethylsilane) as a white solid (25 mg, 0.041 mmol, yield: 21%). IR spectroscopy signature (neat)  $v_{max} = 2958$ , 2924, 2853, 2085, 1338, 1251, 1005, 844, 760, 704, 632 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.29 (d,  $J_{CH} = 2.8$  Hz, 27H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  129.17 (d, J = 18.7 Hz, *C*Br), 127.44 (dd, J = 95.5, 9.9 Hz,  $C_6C \equiv C$ ), 107.00 (dd, J = 141.9, 45.7 Hz, <sup>13</sup>C-enriched C $\equiv C$ Si), 101.66 (dd, J = 141.8, 20.0 Hz, <sup>13</sup>C-enriched C $\in C \equiv C$ ), -0.23 (d, J = 5.3 Hz, Si(CH<sub>3</sub>)<sub>3</sub>).

The substance contains a 2% impurity (determined by <sup>1</sup>H NMR) of 1,4bis(trimethylsilyl)buta-1,3-diyne. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  81.72 (d, J = 13.8 Hz), 80.24 (d, J = 14.4 Hz). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  87.90 (dd, J = 185.6, 33.1 Hz, <sup>13</sup>C-enriched C=CSi), 80.98 (dd, J = 185.6, 14.1 Hz, <sup>13</sup>C-enriched C=CSi), the signal from Si(CH<sub>3</sub>)<sub>3</sub>) is invisible.

### <sup>13</sup>C-Labeled TBTEB



To a solution of labeled ((2,4,6-tribromobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris (trimethylsilane) (25 mg, 0.041 mmol) in THF (5 mL) was added 90 µL TBAF (75% solution in water, 0.247 mmol) and stirred at 0°C for 15 minutes. The solution was then diluted with ethyl acetate, washed with distilled water, and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed on a rotary evaporator. The residue was further purified by flash chromatography using hexanes as the eluent to give labeled 1,3,5-tribromo-2,4,6-triethynylbenzene (TBTEB) as a white solid (11 mg, 0.028 mmol, yield: 67%). 4-bis(trimethylsilyl)buta-1,3-diyne was converted to buta-1,3-diyne during the reaction, which subsequently evaporated. IR spectroscopy signature (neat)  $v_{max} = 3261$ , 2931, 2864, 2043, 1519, 1334, 960, 736, 678, 634 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.76 (dd, J =254.3, 52.7 Hz, 3H, C=CH). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  130.29 (*C*Br), 127.35 (dd, J = 102.5, 13.8 Hz, *C*<sub>6</sub>C=CH), 88.29 (d, J = 185.7 Hz, <sup>13</sup>C-enriched C=*C*H), 80.81 (d, J = 185.7 Hz, <sup>13</sup>Cenriched C<sub>6</sub>C=CH).

### <sup>13</sup>C-Labeled Graphyne

Labeled TBTEB (11 mg, 0.028 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (33 mg, 0.028 mmol), and CuI (0.4 mg, 0.002 mmol) were placed in a Schlenk flask under argon atmosphere and pyridine (5 mL) was added. The tube was sealed and the contents were degassed by three freeze-pump-thaw cycles. The reaction mixture was stirred under an argon atmosphere at 110°C for 3 days, and then *N*,*N*-diethyl-2-phenyldiazene-1-carbothioamide (100 mg) was added and the reaction mixture was stirred for 2 hours at room temperature. The reaction mixture was concentrated by a rotary evaporator. The solid product was washed with toluene, ethyl acetate, water, isopropanol, ethanol, methanol, and acetone (each 40 mL) on the filter (a 0.2  $\mu$ m, TF-200 (PTFE) membrane). Then the residue was dried under a high vacuum for 3 days to give the black solid (7.6 mg).

# **3. Experimental Structural Characterization of Precursors**

<sup>1</sup>H NMR, <sup>13</sup>C NMR, FTIR, and TSP-EI-MS spectra relevant for the synthesis and structure of <sup>13</sup>Clabeled graphyne are in *SI Appendix*, Figs. S1 and S3, *SI Appendix*, Figs. S2 and S4-S9, *SI Appendix*, Figs. S6 and S7, and *SI Appendix*, Figs. S10-S14, respectively.

### 4. Impurities measured by energy-dispersive X-ray spectroscopy for the presently used graphyne

The structure and properties of the presently investigated graphyne do not significantly differ from those we initially reported for graphyne, which is expected since the originally reported synthesis method was used for the present graphyne. For example, the synchrotron-measured diffraction spacings were the same for these samples within the experimental error, when these spacings were measured for graphyne that was in a rotating capillary tube. However, since we did not previously characterize the element content by energy-dispersive X-ray spectroscopy (EDX), we here provide these new results, which are likely more reliable than the previously reported element analysis by X-ray photoelectron spectroscopy (XPS), which are most sensitive to impurities close to the sample surface, because of surface absorption effects.

EDX spectroscopy results for the as-synthesized graphyne powder indicates that it is 66.4 wt% carbon and the previously reported XPS measurements indicate that there is a 1:1 ratio of sp to sp<sup>2</sup> carbons in the graphyne powder (7), which is consistent with  $\gamma$ -graphyne. The average palladium content from EDX spectroscopy does not exceed 1 at% for multiple samples. There is no evidence of silver or gold from the silver paste or gold-coated silicon wafer on which the graphyne powder is mounted. Most likely, the penetration depth of scattered electrons does not exceed the thickness of graphyne particles (~ 20-50 µm). The observed oxygen may be physically absorbed rather than chemisorbed and varies between samples.

# **5. Experimental Characterization of the Structural Transformation and Other Effects of Thermal Annealing**

#### Raman spectra during the structural transition

The synchrotron diffraction peaks of the presently investigated graphyne agree with those observed for the identically synthesized graphyne used for our previous work (7) and are consistent with the theoretically predicted graphyne structures and with previous electron diffraction determined diffraction spacings (7) for (h,k,0) reflections (*SI Appendix*, Table S1). The Raman spectra were collected on a DXR3 Raman Microscope (Thermo-Fisher Scientific Inc.) using a laser excitation wavelength of 532 nm. To avoid exposure of the graphyne sample to oxygen at high temperatures, we used step-by-step annealing in a high vacuum station (0.1 mTorr) to progressively increased temperatures for one hour at each temperature. After each thermal annealing step, the Raman spectrum was collected at room temperature ( $T_{RT}$ ) using as low as possible laser beam power to avoid overheating of the investigated low-density graphyne particle (which was typically ~200x200x50 µm<sup>3</sup>). For the chosen lens magnification of X10 and a 50 µm pinhole aperture, the spectra were collected using a laser beam power of 0.2 mW and a scan time of 5 s for 64 collection scans.

*SI Appendix*, Fig. S16 compares the TGA thermogravimetric mass loss measurements and the DSC heat flow measurements for graphyne, which indicates that much of the calorimetrically-measured exotherm is over before major mass loss occurs by volatilization.

*SI Appendix*, Fig. S17 shows the Raman spectra of a graphyne sample that was heated consecutively to 100, 150, 175, 200, 240, 260, 280, 300, and 320°C for 1 hour and measured at room temperature. As the narrow triple bond transition at 2193 cm<sup>-1</sup> disappears during heating, wide G and D peaks were present that are specific for highly oriented pyrolytic graphite (HOPG) and for carbon structures containing aromatic rings. In a highly crystalline structure of HOPG, here used for wavelength calibration, the optical in-plane stretching vibrations of neighboring carbons (E2g) are concentrated at 1582 cm<sup>-1</sup>. In the graphyne studied here, the G-band of the pristine sample is shifted to lower frequencies than for HOPG, ~1545 cm<sup>-1</sup>. However, heat treatment above the peak of the exothermic reaction temperature (~250°C) shifts the G-band to higher wavenumbers, ~1582 cm<sup>-1</sup> for samples heated to 350°C and ~1595 cm<sup>-1</sup> for a sample heated up to 500°C. The position of triple-bond carbon vibration is independent of the thermal treatment, but the intensity of the peak strongly decays above 175°C (*SI Appendix*, Fig. S17B). *SI Appendix*, Fig. S18 shows the room-temperature FT-IR absorbance plots for a progressively thermally annealed graphyne sample that was exploited for the Tauc absorption plot of Fig. 1D, which yielded the spectroscopic average bandgap plot in the bottom panel of Fig. 1.

The intensity of the G-band peak in *SI Appendix*, Fig. S17B increases by a factor of about three as the annealing temperature increases from the start of the phase transition exotherm to its peak and then decreases to slightly below the pretransition level, while the triple-bond vibration intensity continuously decreases to near zero. This increase in aromatic vibration intensity with decreasing a triple-bond Raman intensity is consistent with our proposed elimination of triple-

bonds by in-plane reaction to form new aromatic rings. However, this behavior of the G-band peak is difficult to fully analyze, since the depth of the penetration of the laser excitation beam will decrease as the transitioning graphyne becomes more absorbing because of the decrease in its bandgap that is shown in the bottom plots of Fig. 1.

# Observing the transformation of <sup>13</sup>C labeled triple bonds in graphyne to exclusively sp<sup>2</sup> carbons by NMR spectroscopy

NMR spectroscopy is a natural choice for investigating structural changes that impact hybridization or interatomic distances. However, initial <sup>13</sup>C solid-state NMR experiments on assynthesized graphyne revealed that the  $T_1$  spin-lattice relaxation time for the core carbons is exceptionally long, consistent with observations in graphitic carbon nanostructures (1, 2). As a result, the sensitivity of the experiments was low, and the obtained spectra were less informative than anticipated.

To address this limitation, we synthesized graphyne selectively labeled with <sup>13</sup>C on all acetylenic bonds (*SI Appendix*, Figs. S1-S7). After labeling these bonds in the precursor monomer with <sup>13</sup>C, graphyne was made from the labeled graphyne precursor (TMS-acetylene-<sup>13</sup>C<sub>2</sub>) using our previously described method (7). A <sup>13</sup>C DP-MAS solid-state NMR spectrum of this labeled graphyne was then acquired (*SI Appendix*, Fig. S8). This spectrum shows two peaks consistent with acetylenic carbons centered at ~90 and 83 ppm. Based on the routine <sup>13</sup>C spectrum of the TBTEB precursor (*SI Appendix*, Fig. S5), the peak at 90 ppm can be assigned to the terminal alkynes, and the peak at 83 ppm to the internal alkynes.

Although the apparent population of internal alkynes in this experiment appears larger than the population of terminal alkynes, the ratio between these species requires further investigation. The T<sub>1</sub> spin-lattice relaxation times for crystalline samples can be very long. Thus, even with a long scan delay, detecting certain slow-relaxing populations of spins can be challenging. We used a 180 s pulse delay following the protocol previously used for DP-MAS of <sup>13</sup>C-labeled graphene oxide (2). However, the crystallinity of our graphyne samples is higher than that of typical graphene oxide. Therefore, it is highly likely that the population of the slower relaxing internal alkynes is underestimated in this experiment. Only the <sup>13</sup>C-labeled carbons are detected here. The simple structure of the alkyne region and lack of other prominent NMR peaks indicate that, under our typical conditions of graphyne synthesis, the acetylenic carbons do not undergo significant side reactions (such as spontaneous Masamune-Bergman aromatization).

The sample of selectively labeled graphyne was then heated from ambient temperature to  $325^{\circ}$ C. The heating program had a single 2°C/min ramp from 100°C to the final temperature, consistent with prior DSC experiments. The DP-MAS <sup>13</sup>C solid-state NMR spectrum of the sample after this thermal anneal revealed the complete disappearance of the acetylenic carbons (*SI Appendix*, Fig. S9). The spectrum indicates that these carbons have been transformed into a single type of sp<sup>2</sup> species with a chemical shift of ~130 ppm, most consistent with aromatic carbons. Additionally, a significant decrease in the T<sub>1</sub> relaxation time was observed. This implies that either the material's surface became more accessible to ambient oxygen, the material's crystallinity decreased, or both factors were at play.

A cross-polarization (CP-MAS) NMR experiment indicated no signal enhancement in comparison with the DP-MAS experiment, which means the new  $sp^2$  carbons are not co-localized with any protons. This suggests that the transformation of graphyne did not involve abstraction of adventitious hydrides in the same way as previously described for a small-molecule model (3).

Solid-state NMR of <sup>13</sup>C-labeled graphyne (Section 2 and *SI Appendix*, Fig. S8) was conducted using a Bruker Avance I operating at a <sup>1</sup>H frequency of 800 MHz. <sup>13</sup>C spectra were recorded using a direct polarization (DP) sequence with <sup>1</sup>H decoupling and a repetition delay of 180 seconds under conditions of magic angle spinning at room temperature. The spinning speed was 40 kHz, using a narrow-bore Bruker H/C/N Triple Resonance CPMAS probe operating with 1.3 mm outer diameter rotors. A representative spectrum was recorded using a total of 400 scans.

Solid-state NMR of the thermally treated sample of <sup>13</sup>C-labeled graphyne (heated to  $325^{\circ}$ C, *SI Appendix*, Fig. S9) was conducted using a Bruker AV3-500 operating at a <sup>1</sup>H frequency of 500 MHz. <sup>13</sup>C spectra were recorded using a direct polarization sequence with <sup>1</sup>H decoupling and a repetition delay of 5 seconds under conditions of magic angle spinning at room temperature. The spinning speed was 20 kHz, using a narrow-bore Bruker HX-MAS probe operating with 3.2 mm outer diameter rotors. A representative spectrum was recorded using a total of 10240 scans. The intensity of spectra with repetition delays ranging from 0.5 seconds to 500 seconds was used to calculate the <sup>13</sup>C T<sub>1</sub> relaxation times from the buildup of signal intensities with increasing repetition delays.

### Unusual kinetic aspects of the structural transformation of graphyne

Heat flow measurements were conducted using the temperature-modulated mode of the TA differential scanning calorimeter (DSC) TA Q-2000. The heating rate was  $2^{\circ}$ C/min. The chamber was continuously purged by nitrogen gas. To avoid the chemical interaction of vapor with the graphyne, an ~10 µm diameter hole was punctured in the top lid of the aluminum sample pan.

Unexpected behavior was observed for a graphyne sample heated to a low temperature (150°C) in the exothermic reaction range, annealed at this temperature for one hour, and then cooled down to 40°C before this process was conducted at the same heating rate (2°C/min) to a 25°C higher temperature (*SI Appendix*, Fig. S22). No exotherm occurred during reheating until the annealing temperature was reached or nearly reached and then it briefly occurred and then stopped when the temperature scan was ended because the next higher annealing temperature was reached. This behavior suggests that regions of the reacting graphyne, at the obtained degrees of conversion, transform when their local free energy change reaches essentially zero. *SI Appendix*, Fig. S22 shows the close correlation between these results and the heat flow resulting from heating the graphyne at an uninterrupted heating rate of  $2^{\circ}$ C/min.

### 6. Electrochemical Measurements for Graphyne Annealed One Hour at Progressively Higher Temperatures

This section provides additional information for the electrochemical CV measurements described in the text and in *SI Appendix*, Figs. S20 and S21. These measurements were conducted on a 5layer stack of forest-drawn multiwall carbon nanotube (MWNT) sheets that were spray-coated layer-by-layer with graphyne from a dispersion of graphyne in dimethylformamide. Electrochemical CV measurements were conducted in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile and a high-surface-area Pt counter electrode and an Ag/Ag<sup>+</sup> reference electrode were deployed. These measurements were made for an electrode potential between -1 to 1.5 V vs Ag/Ag<sup>+</sup> and a 50 mV/s scan rate. Separate CV experiments were conducted on a non-annealed MWNT stack and a graphyne/MWNT layer sheet stack containing about 75 wt% of graphyne and about 25 wt% of MWNT.

The pure MWNT sheet stack had no redox peaks and a CV capacitance of 22 F/g. The nonannealed graphyne/MWNT layer sheet stack had a capacitance of 12.2 F/g. Even though ~3% weight loss occurs on heating graphyne to above 305°C (*SI Appendix*, Fig. S16), which was not measured for the graphyne/MWNT sheet stack and accounted for in calculating its gravimetric room temperature CV capacitance, the fully non-Faradaic CV-measured capacitance at room temperature after thermal annealing up to 350°C was 36 F per gram of non-annealed weight. This is very high compared to the CV capacitances of 12.2 F/g and 22 F/g for the non-annealed graphyne/MWNT sheet stack and the non-annealed pure MWNT sheet stack, respectively. Our future work will explore this capacitance advantage of thermally annealed MWNT/graphyne composites by determining the potential scan rate dependence of performance and other key electrochemical aspects.

### 7. MD and DFT Calculation Results

MD and DFT results for formation energies, density, and other properties are presented for pristine graphyne, stacks of pristine graphyne, polyeneized graphyne, ringized graphyne, and stacked sheets of ringized graphyne. Results are also provided for other novel carbons, like biphenylene (4), which is a possible precursor to graphyne (rather than a possible room-pressure reaction product), because of its higher predicted formation enthalpy than graphyne. The calculated space groups, unit cell parameters, and atomic coordinates of the inter-plane-reacted graphyne structures shown in Fig. 3, labeled by the letters given in this figure, are in *SI Appendix*, Table S6. This same information for the in-plane-reacted ringene structures shown in Fig. 4 is in *SI Appendix*, Table S7.

### Graphyne and 3D polyeneized graphyne

As described in the main text, graphyne is theoretically predicted to possibly topochemically react by the inter-sheet reaction of the acetylene groups in graphyne to produce polyacetylene chains. Of the periodic sheet stacking modes illustrated in *SI Appendix*, Fig. S22 (AA, AB1, AB2, and ABC), only the highest energy fully eclipsed AA structure could potentially enable the complete reaction of all triple bonds to form extended polyene chains.

According to Ducéré, Lepetit, and Chauvin (5), the AB1 and ABC configurations are the most stable stackings of graphyne. Of these two sheet stackings, only the AB1 configuration would enable topochemical polymerization to form polyacetylene chains. Moreover, this polymerization would be possible for only 2/3 of the triple bonds, since the other triple bonds in a periodic sheet stack are between phenyl rings in the graphyne. More recent work, such as that by Yun *et al.* (6) and Desyatkin *et al.* (7), found that AB2 is the lowest energy stacking configuration of graphyne. This stacking mode would not allow topochemical polymerization of any acetylene groups. Our present DFT calculations (*SI Appendix*, Table S3) predict that the packing energy at 0 K becomes increasingly favorable in the order AA, AB1, AB2, and ABC, although the energy differences between these stackings of graphyne sheets are small.

The only inter-sheet reacted polyeneized structures considered in this study are those that can be topochemically formed by inter-sheet reactions of acetylene groups of graphyne sheets that have either AA or AB1 stacking configurations, since they are the only considered configurations that can result in the topochemical formation of polyene chains without bond breaking in the graphyne. They are the structures called 2-cis, 1-sp polygraphyne; 2-trans, 1-sp polygraphyne; 3-cis polygraphyne; 1-cis, 2-trans polygraphyne; and 3-trans polygraphyne (see Fig. 3). *SI Appendix*, Table S4 provides the density, formation energies, and percentage shrinkage with respect to non-reacted graphyne. Also, our predicted properties of the Hex-C24 phase previously proposed for reacted graphyne (8) are shown in this table, which has sp<sup>3</sup> carbon atoms formed by inter-sheet reaction of phenyl ring carbons in graphyne sheets as well as trans-polyacetylene chains. For the reacted eclipsed graphyne phase, the 1-cis, 2-trans polygraphyne has a similar DFT-calculated enthalpy change on polymerization (-1.163 kJ/g) as the 3-trans polygraphyne (-1.275 kJ/g). However, while further reaction of 3-trans polygraphyne by coupling the phenyl rings by

sp<sup>3</sup> carbon formation is predicted during MD calculations, but not by the likely more reliable DFT calculations, neither calculation predicts this for the other Fig. 3 phases. Importantly, our experimental data indicates that the aromatic rings do not convert to sp<sup>3</sup> rings during graphyne thermal reaction at ambient pressure.

Among the structures with only sp and sp<sup>2</sup> carbon atoms, the 3-trans polygraphyne is the one with the lowest energy by both calculation methods. The structures and their formation energies calculated by ReaxFF agree with DFT calculations in the order of the energy differences between the different polyeneized carbon and that of the non-bonded AB2 graphyne.

### 2D ringized structures

As described in the main text, we have also investigated topochemical routes for in-plane reactions of graphyne's sp-sp<sup>2</sup> carbon atoms to produce purely sp<sup>2</sup> 2D ringized phases. Intra-sheet reaction is predicted to occur via Bergman-like reactions (9, 10), without bond breaking in graphyne, to provide a lower energy structure than graphyne. Other than for the previously investigated biphenylene (4) in *SI Appendix*, Fig. S23 and Table S5, all four of these investigated structures (Fig. 4 and *SI Appendix*, Table S5) that could be formed without bond breaking in graphyne have a lower calculated formation energy than graphyne. Their structures and formation energies that we calculated by ReaxFF agree with our DFT calculations. While other graphene sheet allotropes have been described, such as those of Enyashin and Ivanovskii (11), these structures have either a higher formation energy than graphyne or cannot be formed from graphyne without bond breaking in graphyne. The structure of *SI Appendix*, Fig. S26 is both ringized by in-plane reaction and polyeneized by inter-plane reaction to eliminate all sp bonds.

# Calculation of the temperature-dependent heat capacities of graphyne and 5.6.9 ringene and their use for obtaining the temperature dependence of the enthalpy difference between 5,6,9 ringene and graphyne

As discussed in the main text, the lowest energy ringene phase (5,6,9 ringene) is the only candidate product of graphyne reaction that satisfies all of the experimental observations. Consequently, it is especially important to calculate the heat capacity of this phase and that of the parent graphyne, so that the temperature dependence of the enthalpy difference between 5,6,9 ringene and graphyne can be calculated (from 0 K theoretical enthalpies) for all temperatures at which both graphyne and 5,6,9 ringene are thermally stable.

The heat capacities of non-reacted pristine graphyne in the AB2 stacking configuration (*SI Appendix*, Fig. S27) and 5,6,9 ringene having eclipsed sheets were calculated using the Quantum Espresso (QE) code (12, 13), which performs DFT calculations by employing the plane-wave basis-set and pseudopotentials method. The interactions between electrons and the atomic cores are described by an expansion of the wave function by using plane-wave and norm-conserving pseudopotentials. Norm-conserving pseudopotentials generated using the Troullier-Martins method in conjunction with the Perdew-Burke-Ernzerhof (PBE) functional were used to address both exchange energies and electronic exchange-correlation effects (14, 15, 16). To optimize the crystal structure of our model sheets, the Broyden Fletcher Goldfarb Shanno (BFGS) scheme was used as implemented in QE code (17). We set large cutoff values of 70 Ry and 700 Ry for wave-

functions and charge density, respectively. For electronic self-consistency, a convergence criterion of  $1.0 \times 10^{-5}$  eV was employed. During lattice relaxation, the force acting on each atom was kept below  $1.0 \times 10^{-3}$  eV/Å. The optimization process involved a periodic box (representing a bulk system) with a  $10 \times 10 \times 10$  k-point grid, while electronic property calculations employed a k-point grid of  $20 \times 20 \times 20$ .

Constant-volume heat capacities of periodically stacked sheets of pristine graphyne (in the AB2 stacking configuration of *SI Appendix*, Fig. S22) and eclipsed sheet 5,6,9 ringene (shown in *SI Appendix*, Fig. S27A) were calculated as a function of temperature using the Phonopy package (18) in conjunction with the QE code. Phonopy calculates the phonon spectrum of the investigated material and provides its lattice thermal properties from accurately calculated QE force constants. The second- and third-order interatomic force constants were computed using the supercell finite-displacement approach with step sizes of  $1.0 \times 10^{-2}$  Å. Supercells of 48 atoms (2 sheets) were used to calculate the second-order interatomic force constants. Phonopy provides the temperature-dependent heat capacities of the *SI Appendix*, Fig. S27A structure, where it must be remembered that they are valid only below temperatures where the graphyne transforms and the higher temperatures where the 5,6,9 ringene degrades. *SI Appendix*, Fig. S27B shows that the heat-capacity-based change of the enthalpy of transition is small over relevant temperatures, since the heat capacity difference between the two phases is low when integrated over experimentally relevant temperatures where the graphyne does not transform.

## **Figures and Tables**



**Fig. S1.** <sup>1</sup>H NMR spectrum of unlabeled (*A*) and labeled (*B*) (2,4,6-tribromobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(trimethylsilane) in CDCl<sub>3</sub>. The substance contains a 2% impurity (determined by <sup>1</sup>H NMR) of 1,4-bis(trimethylsilyl)buta-1,3-diyne.



Fig. S2. <sup>13</sup>C NMR spectrum of 1,3,5-tribromo-2,4,6-triiodobenzene in DMSO-d6.



Fig. S3. <sup>1</sup>H NMR spectrum of unlabeled (*A*) and labeled (*B*) TBTEB in CDCl<sub>3</sub>.



**Fig. S4**. The <sup>13</sup>C NMR spectrum of unlabeled (*A*) and labeled (*B*) ((2,4,6-tribromobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(trimethylsilane) in CDCl<sub>3</sub>. (*B*) contains a 2% impurity, which was determined by <sup>1</sup>H NMR to be 1,4-bis(trimethylsilyl)buta-1,3-diyne.



Fig. S5. The  ${}^{13}$ C NMR spectrum of unlabeled (A) and labeled (B) TBTEB in CDCl<sub>3</sub>.



**Fig. S6**. The FTIR spectrum of <sup>13</sup>C labeled (2,4,6-tribromobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(trimethylsilane).



Fig. S7. The FTIR spectrum of labeled TBTEB.





**Fig. S8.** Room temperature Direct Polarization Magic-Angle Spinning (DP-MAS) <sup>13</sup>C solid-state NMR spectrum of  $\gamma$ -graphyne selectively labeled with <sup>13</sup>C.



**Fig. S9**. Room temperature Direct Polarization Magic-Angle Spinning (DP-MAS) <sup>13</sup>C solid-state NMR spectrum of the selectively labeled <sup>13</sup>C graphyne after thermal annealing by heating from 100°C to 325°C at 2°C/min.



Fig. S10. Electron ionization mass spectrum of Br-edge graphyne volatiles at 150°C.



Fig. S11. Electron ionization mass spectrum of Br-edge graphyne volatiles at 210°C.



Fig. S12. Electron ionization mass spectrum of Br-edge graphyne volatiles at 250°C.



Fig. S13. Electron ionization mass spectrum of Br-edge graphyne volatiles at 290°C.



Fig. S14. Electron ionization mass spectrum of Br-edge graphyne volatiles at 350°C.



**Fig. S15.** (*A*) EDX spectrum of the graphyne particles pictured in (*B*). Many graphyne platelets are assembled in the lateral plate direction for the pictured graphyne particles, since electron microscopy on dispersed graphyne indicates that the individual platelets have lateral dimensions of below 300 nm. The peaks in (*A*) are labeled according to the most intense line (K or L) of each identified element. Unlabeled peaks are weaker lines of the already identified elements. The small line at 4.5 keV is associated with the thin metallic titanium layer deposited on the surfaces of particles in order to avoid charging. The above EDX and scanning electron microscope (SEM) image were acquired on a Zeiss Sigma 500 VP using a 10 kV accelerating voltage for the SEM image. Graphyne particles were grounded in silver paste on a gold-coated silicon substrate. To avoid overlap between gold and phosphorous EDX peaks, ~10 nm of titanium was deposited to provide a conductive layer to prevent sample charging. The EDX analysis was performed using APEX<sup>TM</sup> software to determine atomic and weight percentages.



**Fig. S16.** Comparison of the temperature dependence of (*A*) thermogravimetric weight loss measurements and heat flow measurements (above capacitive baseline) during the first heating of graphyne from near room temperature to 600°C and (*B*) weight loss measurements during this first heating cycle and on subsequent cooling and cooling-heating cycles between these temperatures. The rate of heating and cooling was 5°C/min, and the DTA analysis was in nitrogen gas. The used TA SDT Q600 thermal analyzer enabled simultaneous measurement of weight change (TGA) and heat flow (DSC). Prior to the above measurements, the graphyne was annealed in air for one hour at 65°C in order to largely remove absorbed solvent. Similar

results were obtained for graphyne that was treated at 65°C for 30 minutes in a high vacuum in order to remove solvents before the measurements.



**Fig. S17.** (*A*) The room temperature Raman spectra (using 532 nm low-intensity excitation) for the initial graphyne (blue curve) and graphyne that was subsequently annealed at progressively higher temperatures for 1 hour in 0.1 mTorr vacuum. All measurements for 10 consecutive annealing temperatures were done for the same local point on a 200x200x50  $\mu$ m<sup>3</sup> particle. For clarity, the spectra for different annealed temperatures are shifted along the y-axis to minimize spectra overlap. (*B*) The dependencies of G-band and triple-bond vibration intensities upon thermal annealing for one hour at each progressively increased temperature. The decrease in G-band Raman intensity for temperatures above 220°C is explained in the next supplemental figure.



**Fig. S18.** Raman spectra collected in air for pristine graphyne using increasing power of the laser beam (532 nm) and fixed exposure time for each next measurement (~11 minutes, corresponding to 128 5-s scans). Each measurement was performed at the same exposure site using an aperture of 50  $\mu$ m and a lens magnification of X10. (*A*) The original raw-data plots without subtraction of the background. The linear

increase of scattering signal towards higher wavenumbers, which is largely due to the background, is caused by the Rayleigh scattering of nanoparticles, which we also observed for nanodiamond and graphdiyne reference powders. The peaked red curve illustrates the radiation intensity-induced change in background scattering. (*B*) The spectra of (*A*) with subtracted background. For clarity, the spectra for different laser powers are shifted along the y-axis. For a laser power of 0.2 mW, the initial spectrum (blue line) did not change by more than  $\pm$  5% during 120 minutes of exposure. However, excitation at 0.5 mW laser power gradually shifts the slope of Raman intensity curve 1 towards curve 2 and reduces the triple-bond peak by 7-10 % after 11 minutes of scan collection. The 1 mW laser beam shifts curve 2 towards curve 3 (green line) and further reduces the triple-bond peak. However, the G and D peaks remain almost constant for 0.2 and 0.5 mW beam powers and start to gradually increase for laser powers from 1 to 2 mW. For  $P_{\text{Laser}} > 1.0$ mW the background decreases, apparently due to volatilization of impurities and the radiation-induced bandgap closure of graphyne (decreasing the laser-beam penetration depth). Correspondingly, the higher beam power reduced the intensities of the G and D peaks.



**Fig. S19.** The room temperature spectra of IR absorbance spectra for graphyne that was annealed in high vacuum (0.1 mTorr) for 1 hour at progressively higher temperatures. The measurement parameters were:  $50x50 \ \mu\text{m}^2$  aperture, 4 cm<sup>-1</sup> resolution, and 10 consecutive scans. The dashed arrow line shows the red shift of the plasmonic edge that is responsible for the derived band gap in Fig. 1A (bottom panel).



**Fig. S20.** Illustrative CV spectra for graphyne that was spray coated on a very low areal density forestdrawn MWNT aerogel sheet as the working electrode and then annealed for one hour in a vacuum at progressively increasing temperature before cyclic voltammetry was conducted at room temperature after each annealing step. The spray coating was by graphyne dispersed in dimethylformamide. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile and a high-surface-area Pt counter electrode and an  $Ag/Ag^+$  reference electrode were deployed. While these CV spectra show that the CV redox peaks increase with thermal annealing until they vanish as the annealing temperature increases, the ratio of redox peak intensity to overall capacitance decreases with increasing temperature thermal annealing. This capacitance increase results from diffraction-indicated sheet wrinkling that originates from strains between reacted and unreacted graphyne sheet regions during the graphyne transformation, which likely increases the available surface area for both non-Faradaic and Faradaic capacitance.



**Fig. S21.** The room temperature electrochemical cyclic voltammetry capacitance, redox peak height (measured at positive potentials), and the ratio of redox peak intensity to the total electrode capacitance for graphyne that has been annealed in vacuum for an hour at progressively higher temperatures, as a function of the maximum annealing temperature. The 12.5% decrease in the redox peak height to capacitance ratio at below 200°C might be due to the removal of volatiles, especially if their removal affects double-layer capacitance more than redox capacitance.



**Fig. S22.** Measurements for characterizing the kinetics of graphyne transformation. Using a  $2^{\circ}$ C/min. heating rate and a very fast cooling rate, the DSC-measured heat flow was measured for 9.80 mg of graphyne powder that was heated to a temperature that is soon after the beginning of the graphyne transformation, annealed at this temperature for one hour, and then cooled back to  $40^{\circ}$ C. Afterwards, the same cycle of heating and cooling was conducted numerous times for this graphyne sample using a progressively 25°C higher annealing temperature than for the last one-hour annealing temperature. The blue-dashed line is for a single uninterrupted full-range scanning measurement using the same heating rate of  $2^{\circ}$ C/min.







**Fig. S24**. Orthogonal to sheet plane views of AA, AB1, AB2, and ABC stacking arrangements for graphyne. Only the AA and AB1 packing modes are consistent with the interplanar reaction of triple bonds to form polyacetylene chains in reacted graphyne.



**Fig. S25.** Upper (top) and lateral views (bottom) of the ReaxFF-MD optimized atomic geometries of the predicted 2D carbon products from in-plane Bergman-like reactions. These structures are for (A) 5,6,9 ringene, (B) 4-9 ringene, (C) 4-9 double ringene, (D) 4-8 ringene, and (E) biphenylene. The so-called biphenylene (E) has been previously investigated.



**Fig. S26.** Two possible transformations that convert an eclipsed AA stacking mode of graphyne to all-sp<sup>2</sup> carbon phases by a sequence of in-plane reaction and cross-plane reaction, without breaking any bond in the original graphyne. The polyene chains in (A) and (B) are cis and trans, respectively. Only one-fifth of the acetylenic carbons react inter-layer by forming polyacetylene chains and the rest react intra-layer by forming new rings.



**Fig. S27.** The theoretically calculated temperature dependence of heat capacitances for (*A*) 5,6,9 ringene (black curve) and unreacted graphyne (gray curve) and (*B*) the corresponding effect of these heat capacities on the enthalpy change of reaction for temperatures in the above curves where graphyne does not react and the especially high temperatures where the reacted graphyne volatilizes. (*A*) The Quantum Expresso calculated constant-volume heat capacities of periodically stacked sheets of graphyne (gray curve) and 5,6,9 ringene (black curve) as a function of temperature when ignoring higher temperature graphyne sample reaction, as well as reacted graphyne volatilization at extreme temperatures. In fact, much of the entire sample will evaporate in a vacuum by  $600^{\circ}$ C. (*B*) The thereby calculated temperature dependence of enthalpy change between the above parent and product states, which are valid only below the above indicated temperatures. Although the 0 K calculated enthalpy difference (-2.17 kJ/g) was for a Quantum Expresso calculation, ReaxFF potential and VASP calculations (-1.84 and -2.21 kJ/g, respectively) provided similar results.

**Table S1.** Comparison of synchrotron-diffraction interplanar spacings (d) for previously investigated and presently investigated unreacted graphyne with the d spacings derived for the previously determined (8) electron-diffraction-derived hexagonal unit cell and the theoretically calculated unit cell. Because of long-range disorder in inter-layer stacking, only (h,k,0) and (0,0,1) reflections are observed, and the chosen c-axis axial lengths are the measured and calculated intersheet spacings. Since reliable inter-sheet spacings were not determined by electron diffraction-derived hexagonal unit cell hexagonal unit cell has a = 6.88 Å. Also, while the theoretically calculated inter-planar spacing slightly varies depending upon the assumed 3D structure, only its approximate value (3.4 Å) is reported. The theoretically calculated a-axis length is about 6.88 Å. X-ray diffraction peaks are sometimes not observed because of unfavorable orientation for the investigated powder samples.

h,k,l	d <sub>x-ray</sub> (Å), previous	d <sub>x-ray</sub> (Å), present	d <sub>electron</sub> (Å), previous	Theory (Å) at 0K
1,0,0	6.02		5.96	5.96
0,0,1	3.48	3.41		3.4
1,1,0	3.44		3.44	3.44
2,0,0	3.01	3.07	2.98	2.98
1,2,0	2.64	2.63		

**Table S2.** Atomic and weight percent composition from *SI Appendix*, Fig. S15. The palladium content of graphyne measured in several samples is less than one atomic percent.

Element	С	Br	Pd	0	Р	Ν	Si	Cu	Ι
Atomic %	85.7	3.0	0.9	6.4	5.8	2.9	0.1	< 0.1	< 0.1
Weight %	66.4	15.5	6.4	5.8	2.9	2.9	0.1	< 0.1	< 0.1

**Table S3**. The density and formation energies calculated by DFT for the investigated stacking modes of graphyne.

Stacking structure	Density [g/cm <sup>3</sup> ]	Energy [eV/atom]	Difference from the most favorable energy structure
AA	1.636	-7.4354	+9.9 meV/atom (79 J/g)
AB1	1.743	-7.4447	+0.5 meV/atom (4 J/g)
AB2	1.753	-7.4453	0 meV/atom (0 J/g)
ABC	1.749	-7.4462	-0.9 meV/atom (-7 J/g)

**Table S4**. The density, formation energy, and energy differences with respect to the non-bonded AB2 stacking of graphyne structures and the relative percentage of shrinking along all directions for 2-cis, 1-sp polygraphyne; 2-trans, 1-sp polygraphyne; 3-cis polygraphyne; 1-cis, 2-trans polygraphyne; and 3-trans polygraphyne, as well as for Hex-C24. Values obtained from MD ReaxFF potential energy minimizations are in black and those from DFT calculations, which are likely more reliable, are in blue.

Structure	Density [g/cm <sup>3</sup> ]	Energy [eV/atom]	Energy [10 <sup>1</sup> kJ/g]	Ebonded – Enon- bonded [eV/atom] (kJ/g)	(LBONDED – LNON-BONDED)/LNON- BONDED along X (Y) [Z] direction
Non-bonded	1.799	-6.903	-5.545	0	0
AB2	1.753	-7.445	-5.971	0	
2-cis, 1-sp	2.400	-7.049	-5.663	-0.146 (-1.173)	-0.2% (-2.34%) [-24.1%]
polygraphyne	2.423	-7.477	-5.997	-0.032 (-0.257)	-1.23% (-3.33%) [-24.2%]
2-trans, 1-sp	2.419	-7.072	-5.681	-0.168 (-1.350)	-0.52% (-6.28%) [-22.3%]
polygraphyne	2.417	-7.518	-6.030	-0.073 (-0.585)	-0.92% (-5.41%) [-22.6%]
3-cis polygraphyne	2.439	-7.144	-5.739	-0.241 (-1.940)	-1.40% (-1.38%) [-26.1%]
1-cis, 2-trans	2.550	-7.207	-5.789	-0.304 (-2.442)	-6.24% (-4.11%) [-23.5%]
polygraphyne	2.559	-7.591	-6.088	-0.145 (-1.163)	-5.78% (-4.34%) [-24.0%]
3-trans	2.544	-7.231	-5.809	-0.328 (-2.635)	-5.70% (-6.78%) [-21.6%]
polygraphyne	2.616	-7.604	-6.099	-0.159 (-1.275)	-6.44% (-5.85%) [-23.4%]
Hex-C24	2.766	-7.353	-5.907	-0.450 (-3.615)	-0.97% (-1.15%) [-35.2%]
	2.771	-7.871	-6.313	-0.426 (-3.417)	-0.08% (+0.06%) [-36.8%]

**Table S5.** The formation energies and relative percentages of shrinking along sheet directions for pristine graphyne and four possible intra-sheet reaction products calculated using the MD ReaxFF potential (in black) and DFT calculations (in blue). The energy differences were calculated with respect to a pristine layer of graphyne. The A-D structures are labeled in Fig. 4 and *SI Appendix*, Fig. S23 and the biphenylene structure is also shown in *SI Appendix*, Fig. S23. The below X and Y directions are for the orthogonal cells shown in Fig. 4, where the pictured orthogonal cells have DFT-calculated a-axis and b-axis sheet-plane values at 0°K of 6.882 and 11.921 Å for graphyne, 5.914 and 11.465 Å for 5,6,9 ringene, and 6.119 and 11.039 Å for 4-9 double ringene. Since 4-8 ringene cannot be described by an orthorhombic cell, it is not in the cell length change comparison. The calculated hexagonal unit cell parameter for graphyne is 6.882 Å.

Structure	Energy [eV/atom]	Energy [kJ/g]	Energy difference [eV/atom] (kJ/g)	(LBONDED – LNON-BONDED)/LNON- BONDED along X (Y) direction
Pristine	-6.850	-5.503	0	0

	-7.398	-5.933	0	0
А	-7.079	-5.687	-0.229 (-1.837)	-16.3% (-5.88%)
	-7.674	-6.154	-0.276 (-2.214)	-14.1% (-3.82%)
В	-7.003	-5.626	-0.153 (-1.227)	-12.5% (-14.3%)
	-7.561	-6.064	-0.163 (-1.307)	-10.1% (-11.1%)
С	-7.007	-5.629	-0.157 (-1.259)	-14.1% (-9.75%)
	-7.557	-6.061	-0.159 (-1.275)	-11.1% (-7.39%)
D	-6.885 -7.443	-5.531 -5.969	-0.035 (-0.281) -0.045 (-0.361)	
Biphenylene	-6.717	-5.396	+0.133 (+1.067)	-3.02% (-2.97%)
	-7.393	-5.929	+0.005 (+0.040)	-1.61% (-1.61%)

**Table S6.** The calculated space groups, unit cell parameters, and fractional atomic coordinates of the inter-plane-reacted graphyne structures shown in Fig. 3, labeled by the alphabetic capital letters in this figure. After the space group and unit cell dimensions for each structure, the labels of different independent carbons and their fractional coordinates in the x, y, and z directions are given. Carbons arising from phenyl rings in the original graphyne are specially designated by the term phenyl.

Structur	·e	Spac grou	e p	a (Å)		<b>b</b> (Å)		<b>c</b> (Å)	α (°)	β (°)	γ (°)
B. 2-cis, 1 polygraphy	-sp yne	Bmm	ıb	11.512	8	6.7913		5.0538	90.000	90.000	90.000
C1 (sp <sup>2</sup> )	0.7	71340	0.4	47030	0	.34875	(	C2 (phenyl)	0.89228	0.14784	0.78323
C3 (phenyl)	1.(	00000	-0.	.45420	0	0.24590		C4 (sp)	0.50000	-0.33975	0.22996

Structure	Space group	<b>a</b> (Å)	<b>b</b> (Å)	<b>c</b> (Å)	a (°)	β (°)	γ (°)
C. 2-trans, 1- sp polygraphyne	Bmmb	6.8124	11.2657	5.1611	90.000	90.000	90.000

C1 (sp <sup>2</sup> )	0.21512	0.02663	0.13927	C2 (phenyl)	0.89772	-0.14031	0.84419
C3 (phenyl)	0.29532	-0.25000	0.34147	C4 (sp)	0.41069	0.25000	0.15772

Structur	·e	Spac grou	ce Ip	a (Å	)	<b>b</b> (Å)		<b>c</b> (Å)		a (°)	β (°)	γ (°)
D. 3-cis polygraphy	yne	P6 <sub>3</sub> /m	cm	6.822	21	6.822	1	4.7200		90.000	90.000	120.000
C1 (phenyl)	0.0	00000	0.2	21088	0.	49841	C	C2 (sp <sup>2</sup> )	0	0.00000	0.41920	0.40116

Structur	e	Spac grou	e p	a (Å)	I	<b>b</b> (Å)		<b>c</b> (Å)		a (°)	β (°)	γ (°)
E. 1-cis, 2 trans polygraphy	2- /ne	Pbca	l	12.956	1	11.3934	4	5.0687		90.000	90.000	90.000
C1 (phenyl)	0.8	82799	0.	14276	0	.10037	(p	C2 bhenyl)		0.93464	0.14197	0.12582
$C3 (sp^2)$	0.′	77114	0.	03532	0	.01553	C	$4(sp^2)$		0.73056	0.96344	0.21512
C5 (sp <sup>2</sup> )	0.9	98924	0.	02662	0	.12477	(p	C6 bhenyl)		0.67425	0.85536	0.13224
C7 (phenyl)	0.′	72793	0.	75050	0	.11316	(p	C8 bhenyl)	(	0.00968	0.74903	0.86804
C9 (sp <sup>2</sup> )	0.8	84315	0.	74931	0	.11425	Cl	$10 (sp^2)$		0.89458	0.74994	0.86455
C11 (phenyl)	0.9	93611	0.	14336	0	.62496	Cl	12 (sp <sup>2</sup> )		0.98888	0.02652	0.62487

Structur	e	Spac grou	e p	<b>a</b> (Å)		<b>b</b> (Å)		<b>c</b> (Å)	a (°)	β (°)	γ (°)
F. 3-tran polygraphy	s yne	Fddo	1	12.865	6	22.2830	)	2.5535	90.000	90.000	90.000
C1 (phenyl)	0.9	94604	0.	55457	0	.55193	(	C2 (sp <sup>2</sup> )	0.88800	0.11210	0.11861
C3 (phenyl)	0.8	35870	0.	25000	0	.75000	(	C4 (sp <sup>2</sup> )	0.97433	0.25000	0.75000

**Table S7.** The calculated space groups, unit cell parameters, and fractional atomic coordinates of the in-plane-reacted ringene structures shown in Fig. 4 and *SI Appendix*, Fig. S23. These structures are for effectively infinitely separated sheets, since eclipsed sheets are periodically translated from each other by 40 Å in the c-axis direction. After the space group and unit cell dimensions for each structure, the labels of different independent carbons and their fractional coordinates in the x, y, and z directions are given. Since all carbons become part of sp<sup>2</sup> carbon rings, those arising from phenyl rings in the original graphyne are specially designated by the term phenyl.

Structure	Space group	<b>a</b> (Å)	<b>b</b> (Å)	<b>c</b> (Å)	α (°)	β (°)	γ (°)
A. 5,6,9 ringene	P2/m	5.914	11.465	40.000	90.000	90.000	89.194
C1 (sp <sup>2</sup> )	0.69814	0.25964	0.50000	C2 (sp <sup>2</sup> )	0.37261	0.85869	0.50000
C3 (phenyl)	0.71046	0.46955	0.50000	C4 (phenyl	) 0.32886	0.40326	0.50000
C5 (phenyl)	0.21591	0.05490	0.50000	C6 (phenyl	) 0.97615	0.87136	0.50000
C7 (phenyl)	0.82573	0.06703	0.50000	C8 (phenyl	) 0.43495	0.63058	0.50000
C9 (sp <sup>2</sup> )	0.95815	0.25081	0.50000	C10 (sp <sup>2</sup> )	0.90963	0.64861	0.50000
C11 (sp <sup>2</sup> )	0.54797	0.93862	0.50000	C12 (sp <sup>2</sup> )	0.05690	0.55158	0.50000

Structure	Space group	a (Å)	<b>b</b> (Å)	<b>c</b> (Å)	a (°)	β (°)	γ (°)
B. 4-9 ringene	P1	12.379	10.600	40.000	87.922	84.286	90.290
C1 (sp <sup>2</sup> )	0.33082	0.25374	0.49803	C2 (sp <sup>2</sup> )	0.88768	0.28280	0.50681
C3 (sp <sup>2</sup> )	0.12252	0.77602	0.49608	C4 (sp <sup>2</sup> )	0.52157	0.75307	0.50505
C5 (sp <sup>2</sup> )	0.44258	0.25499	0.49851	C6 (sp <sup>2</sup> )	0.81127	0.18169	0.49830
C7 (sp <sup>2</sup> )	0.23190	0.75111	0.49942	C8 (sp <sup>2</sup> )	0.63255	0.73214	0.50818
C9 (phenyl)	0.37677	0.45738	0.50477	C10 (phenyl	l) 0.87899	0.51815	0.52535
C11 (phenyl)	0.17353	0.39702	0.50195	C12 (phenyl	0.73027	0.39424	0.52324
C13 (phenyl)	0.08788	0.04081	0.49067	C14 (phenyl	0.60402	0.95560	0.49684
C15 (phenyl)	0.39833	0.92208	0.49737	C16 (phenyl	0.96326	0.88278	0.47751
C17 (phenyl)	0.48555	0.13135	0.49598	C18 (phenyl	0.88392	0.08653	0.48573
C19 (phenyl)	0.24791	0.61520	0.50247	C20 (phenyl	0.68658	0.61941	0.51937
C21 (sp <sup>2</sup> )	0.00077	0.24443	0.49968	C22 (sp <sup>2</sup> )	0.68967	0.18367	0.50161

C23 (sp <sup>2</sup> )	0.41444	0.70254	0.50514	C24 (sp <sup>2</sup> )	0.88344	0.70184	0.51296
C25 (phenyl)	0.15680	0.53791	0.50180	C26 (phenyl)	0.65201	0.49299	0.52243
C27 (phenyl)	0.99340	0.11614	0.49020	C28 (phenyl)	0.59829	0.09090	0.49629
C29 (sp <sup>2</sup> )	0.11291	0.27510	0.50008	C30 (sp <sup>2</sup> )	0.65832	0.30110	0.51356
C31 (phenyl)	0.35751	0.58498	0.50551	C32 (phenyl)	0.79864	0.61766	0.52466
C33 (phenyl)	0.38476	0.05128	0.49493	C34 (phenyl)	0.87284	0.96798	0.47482
C35 (sp <sup>2</sup> )	0.33815	0.80451	0.50042	C36 (sp <sup>2</sup> )	0.88179	0.79011	0.48865
C37 (phenyl)	0.28633	0.37390	0.50171	C38 (phenyl)	0.84372	0.39486	0.52059
C39 (phenyl)	0.06834	0.89934	0.48773	C40 (phenyl)	0.50823	0.88616	0.49911
C41 (sp <sup>2</sup> )	0.28529	0.13400	0.49571	C42 (sp <sup>2</sup> )	0.79115	0.87069	0.48466
C43 (sp <sup>2</sup> )	0.07142	0.63443	0.50208	C44 (sp <sup>2</sup> )	0.57412	0.39790	0.51367
C45 (sp <sup>2</sup> )	0.17164	0.13839	0.49577	C46 (sp <sup>2</sup> )	0.68664	0.85775	0.49818
C47 (sp <sup>2</sup> )	0.47322	0.38122	0.50465	C48 (sp <sup>2</sup> )	0.96775	0.61123	0.51503

Structure	Space group	a (Å)	b (Å	.)	<b>c</b> (Å)	α (°)	β (°)	γ (°)
C. 4-9 double ringene	Pm	6.119	11.03	39	40.000	90.000	90.000	90.000
C1 (sp <sup>2</sup> )	0.91265	0.36570	0.50000		C2 (sp <sup>2</sup> )	0.05071	0.71631	0.50000
C3 (sp <sup>2</sup> )	0.03163	0.25813	0.50000		C4 (sp <sup>2</sup> )	0.27169	0.69828	0.50000
C5 (phenyl)	0.73191	0.54257	0.50000	C	6 (phenyl)	0.44037	0.36911	0.50000
C7 (phenyl)	0.19330	0.94004	0.50000	C	8 (phenyl)	0.80695	0.91504	0.50000
C9 (phenyl)	0.95657	0.12915	0.50000	C	10 (phenyl)	0.36084	0.58201	0.50000
C11 (sp <sup>2</sup> )	0.35060	0.14029	0.50000		C12 (sp <sup>2</sup> )	0.50384	0.74478	0.50000
C13 (phenyl)	0.28805	0.46705	0.50000	C	14 (phenyl)	0.15203	0.06480	0.50000
C15 (sp <sup>2</sup> )	0.29551	0.26086	0.50000	C	16 (phenyl)	0.57088	0.62250	0.50000
C17 (phenyl)	0.76841	0.04854	0.50000		C18 (sp <sup>2</sup> )	0.59295	0.85653	0.50000
C19 (phenyl)	0.68107	0.41054	0.50000	C	20 (phenyl)	0.00902	0.85414	0.50000
C21 (sp <sup>2</sup> )	0.53115	0.06126	0.50000		C22 (sp <sup>2</sup> )	0.05929	0.47182	0.50000
C23 (sp <sup>2</sup> )	0.43163	0.94457	0.50000		C24 (sp <sup>2</sup> )	0.95087	0.58630	0.50000

Structure	Space group	a (Å)	<b>b</b> (Å)	<b>c</b> (Å)	α (°)	β (°)	γ (°)
D. 4-8 ringene	P2/m	6.307	10.786	40.000	90.000	90.000	95.520
C1 (sp <sup>2</sup> )	0.72023	0.30795	0.50000	C2 (sp <sup>2</sup> )	0.06720	0.70639	0.50000
C3 (phenyl)	0.73492	0.54688	0.50000	C4 (phenyl)	) 0.42877	0.37889	0.50000
C5 (phenyl)	0.20375	0.94894	0.50000	C6 (phenyl)	) 0.82006	0.91469	0.50000
C7 (phenyl)	0.98182	0.14501	0.50000	C8 (phenyl)	) 0.35665	0.57371	0.50000
C9 (sp <sup>2</sup> )	0.40118	0.14268	0.50000	C10 (sp <sup>2</sup> )	0.50872	0.74164	0.50000
C11 (sp <sup>2</sup> )	0.55835	0.05702	0.50000	C12 (sp <sup>2</sup> )	0.04480	0.43483	0.50000

**Table S8.** The DFT calculated electronic bandgaps for the ringene structures shown in Fig. 4 and *SI Appendix*, Fig. S23.

Structure	Bandgap [eV]	Band character
A. 5,6,9 ringene	0	
B. 4-9 ringene	0.1009	Direct
C. 4-9 double ringene	0.2324	Direct
D. 4-8 ringene	0.1748	Indirect

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