Crystalline structures of polymeric hydrocarbon with 3,4-fold helical chains

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Molecular hydrocarbons are well-known to polymerize under pressure to form covalently bonded frameworks. Here we predict by ab initio calculations two distinct three-dimensional hydrocarbon crystalline structures composed of 3-fold and 4-fold helical CH chains in rhombohedral ([R\(\sqrt{3}2\)C]) and tetragonal ([I\(41/a\)]) symmetry, respectively. Both structures with 1:1 stoichiometry are found to be energetically more favorable than solid acetylene and cubane, and even more stable than benzene II solid at high pressure. The calculations on vibrational, electronic, and optical properties reveal that the new chiral hydrocarbons are dynamically stable with large bulk moduli around 200 GPa, and exhibit a transparent insulating behavior with indirect band gaps of 5.9 – 6.7 eV and anisotropic adsorption spectra. Such forms of hydrocarbon, once synthesized, would have wide applications in mechanical, optoelectronic, and biological materials.

The exploration of new technological materials is an enduring topic in high-pressure physics and chemistry, and simple molecular solids are rising as potential precursors due to their high compressibility. It has been shown that many unsaturated hydrocarbons form molecular crystals that polymerize under pressure into extended covalently bonded structures, which can generally be recovered to ambient conditions unlike the cases in N\(_2\), CO\(_2\), and N\(_2\)O where polymeric phases decompose at ambient pressure. Ethylene and acetylene transform to linear polymers at 1–6 GPa through the opening of double and triple bonds. With the aromatic character lost, benzene polymerizes around 23 GPa in the amorphization form at room temperature. A friable and colorless compound has been obtained by heating benzene above 680 K between 7 and 12 GPa, while its structure is unknown so far. It is confirmed in high-pressure studies of both acetylene and benzene that laser irradiation will promote the generation of saturated network polymers with a composition close to (CH)\(_n\).

Nowadays, there is an increasing theoretical attention paid to the nonmolecular hydrocarbon crystalline phases. In addition to the well-known one-dimensional (1D) polyethylene and polyacetylene, many isomeric 2D covalently bonded hydrocarbons called graphane were suggested in the last decade. Wen et al. found from ab initio calculations that benzene phases under pressure transform to ordered CH structures consisting of 1D or 2D arrays of C\(_6\)H\(_6\) rings bridged by sp\(^3\) C-C bonds. This has greatly stimulated the exploration of other possible structures of polymeric hydrocarbon, which could be synthesized by applying high pressure or temperature. Using evolutionary algorithm structure searches, several 3D graphane CH structures with different graphane stackings had been reported. In a recent study, we predicted a diamond-like 3D cubic hydrocarbon crystal, K\(_4\)-CH, through hydrogenating the hypothetical K\(_4\)-carbon. Subsequently, a saturated hexagonal phase of Hex-CH was also proposed from the compressed benzene. It has been established that for the CH system with 1:1 stoichiometry, the fully saturated polymeric CH phases are thermodynamically more stable than any phase retaining discrete molecules.

In this paper, we report by ab initio calculations two novel 3D hydrocarbon framework structures that comprise 3-fold and 4-fold helical CH chains in rhombohedral (R\(3\)) and tetragonal (I\(41/a\)) symmetry, respectively, which are derived from the fully hydrogenation of our recently found all-sp\(^2\) bonded chiral carbene. The structure stability, electronic and optical properties are examined up to 50 GPa. Both chiral crystalline phases are confirmed to be energetically more favorable than solid acetylene and cubane, and significantly stabilized with increasing pressure relative to the benzene II solid. The calculated vibrational and mechanical properties reveal their dynamical stability and large bulk modulus of ~200 GPa. Electronic and optical calculations show the wide-gap insulating behavior typical of saturated hydrocarbon and the unique anisotropic adsorption spectra. Our predictions can be expected to greatly stimulate future experiments to synthesize these new phases.
Results

Our newly identified chiral crystalline forms of hydrocarbon are depicted in Fig. 1. The 4-fold chiral structure [Fig. 1(a)] is body-centered tetragonal in \( \text{P}_{4}2_1/\text{a} \) symmetry, and the optimized lattice parameters are \( a = 6.106 \, \text{Å} \) and \( c = 4.146 \, \text{Å} \), with C and H atoms occupying 16f (0.2189, 0.1188, 0.8213) and 16f (0.0707, 0.1018, 0.6617) Wyckoff positions, respectively. This form has eight CH units in the primitive cell and we refer to it as the \( T_8\)-CH. The 3-fold chiral structure in \( \text{R}_3 \) symmetry, hereafter named as \( R_6\)-CH, has a rhombohedral lattice and six CH units per primitive cell. In hexagonal representation [Fig. 1(b)], its equilibrium lattice parameters are estimated to be \( a = 7.392 \, \text{Å} \) and \( c = 3.671 \, \text{Å} \) with 18f (0.4202, 0.0351, 0.0448) C and 18f (0.1816, 0.5314, 0.4693) H positions. As shown in Fig. 1, for both \( T_8\)-CH and \( R_6\)-CH structure, the helical CH chains are formed along the c axis, and each chain is connected to neighboring chains of opposite chirality (left-handed indicated by S and right-handed R) by C-C covalent bonds. The intrachain and interchain C-C bond lengths are respectively 1.559 and 1.564 Å in \( T_8\)-CH, 1.561 and 1.543 Å in \( R_6\)-CH, which are all close to 1.530 Å in diamond\(^9\). Hence, the two chiral hydrocarbons here can be considered as diamond-like CH phases similar to the previously proposed \( K_8\)-CH\(^9\) and Hex-CH\(^9\); they all adopt a fully 3D framework with saturated nature of sp\(^3\) carbon.

Figure 2(a) shows the calculated total energy versus volume curves of various hydrocarbon phases with CH stoichiometry of 1:1. We can see that the \( T_8\)-CH structure is as stable as \( K_8\)-CH, with energy about 0.47 and 1.16 eV/CH lower than solid cubane\(^{23,24}\) and acetylene\(^9\), respectively. Compared with \( T_8\)-CH, the \( R_6\)-CH structure has lower energy (close to Hex-CH), being even more stable than the benzene II\(^{26}\) crystal and its hypothetical layered polymer reported by Wen et al.\(^8\). It is noticeable that the equilibrium volumes of \( K_8\)-CH, Hex-CH, \( T_8\)-CH, and \( R_6\)-CH are in the range 9.6–9.9 Å\(^3/\text{CH}\), much smaller than 14.1–20.5 Å\(^3/\text{CH}\) of benzene II and solid cubane and acetylene (see Table I). These results suggest great potential for synthesizing the low-energy CH structures through compression of metastable molecular phases of hydrocarbon. Furthermore, we find that among all CH systems considered here the most stable phase is the layered graphane\(^8\)\( ^{19}\) crystal in an AA stacking (0.04 eV/CH lower in energy than graphene III). The less favorable energetic state of diamond-like CH phases compared to that of benzene II is presented in Fig. 2(b) in a wide pressure range 0–50 GPa. It is found consistent with previous calculations\(^{15}\) that instead of graphane I, graphane III becomes the most stable phase under pressures above 12 GPa. For diamond-like CH phases, an increasing stabilization with pressure can be seen relative to benzene II and solid cubane, benzene II polymer, and graphane I and III. The inset shows the data for solid acetylene. (b) Enthalpy difference with respect to benzene II for the various CH phases as a function of pressure.

Moreover, the hexagonal phases of \( R_6\)-CH and Hex-CH are more favorable than \( T_8\)-CH or \( K_8\)-CH in enthalpy by about 0.15 eV/CH in the whole pressure range. Meanwhile, \( R_6\)-CH is found to be preferable to Hex-CH above 25 GPa, and to compete with graphane I above 50 GPa. In view of the above enthalpy results, the experimental syntheses of diamond-like CH phases are thermodynamically possible.

We have fitted the energy versus volume data to the Murnaghan equation of state\(^{27}\) to obtain the bulk moduli (\( B_0\)) of different hydrocarbons, as listed in Table I. The predicted \( B_0\) of diamond-like CH phases are significantly higher than those of molecular hydrocarbons, with \( T_8\)-CH and \( R_6\)-CH having the values of 201.7 and 185.2 GPa, respectively. Note that for benzene II we calculate the bulk modulus to be \( B_0 = 9.8 \, \text{GPa} \), which is close to the reported experimental value of \(~5.5 \, \text{GPa}\).\(^{38}\)

Phonon calculations give a criterion for the structure stability of a crystal. Therefore, we calculated phonon dispersion curves for the \( T_8\)-CH and \( R_6\)-CH phases at 0 GPa, as presented in Fig. 3(a) and 3(b). The absence of imaginary frequency modes indicates that these two chiral structures are dynamically stable. High frequency C-H stretching phonon modes emerge around 3047 and 2992 cm\(^{-1}\) for \( T_8\)-CH and \( R_6\)-CH, respectively, which can be compared with the observed broad infrared peaks at 2950 and 2920 cm\(^{-1}\) (assigned to the C-H stretching modes involving sp\(^3\) carbon atoms) for amorphous samples recovered from compressed acetylene\(^8\)\(^,\)\(^9\).

Figure 1 | Schematic representation of the chiral crystalline structures of \( T_8\)-CH (a) and \( R_6\)-CH (b). Carbon atoms are shown as large olive spheres, and hydrogen atoms are shown as small red spheres. R and S refer to right- and left-handed helical CH chains, respectively.
In addition, we also checked the phonon dispersion for both chiral phases under pressure confirming their dynamical stability up to at least 50 GPa.

The electronic band structure calculations within the hybrid functional method have demonstrated the insulating nature of the two chiral saturated CH phases. The valence band maximums of $T_8$-CH [Fig. 3(c)] and $R_6$-CH [Fig. 3(d)] are at the C and A points in the Brillouin zone while the conduction band minimums are along the Z-X direction and at the M point, giving indirect band gaps of 6.67 and 5.88 eV at 0 GPa, respectively. Hence, both chiral phases are predicted to be optically transparent as previously proposed.

We have further explored the electronic properties at increasing pressures. The calculated band gaps as a function of pressure for $K_4$-CH, Hex-CH, $T_8$-CH, and $R_6$-CH are shown in Fig. 4(a). According to the results, $T_8$-CH remains dielectric at pressures up to at least 50 GPa. The band gap has only a weak dependence on pressure and decreases from 6.67 to 6.42 eV as pressure increases from 0 to 50 GPa. For $R_6$-CH, the band gap decreases more rapidly with increasing pressure and reaches 88% of the original band gap at 50 GPa, indicating a stronger pressure dependence similar to those for $K_4$-CH and Hex-CH.

We now move on to discuss the optical properties of the $T_8$-CH and $R_6$-CH phases in terms of the calculated frequency dependent imaginary part of the dielectric matrix. By comparing the optical spectra at 0 GPa obtained with light polarized either along the c axis or in the ab plane [Fig. 4(b) and 4(c)], we find that the spectra differ in

| Structure | Space group | a (Å) | b (Å) | c (Å) | $V_0$ (Å³/CH) | $d_{C-C}$ (Å) | $E_{\text{tot}}$ (eV/CH) | $B_0$ (GPa) | $E_g$ (eV) |
|-----------|-------------|------|------|------|---------------|----------------|---------------------|-------------|---------|
| $K_4$-CH  | $I_2\overline{1}3$ | 4.252 |      |      | 9.62          | 1.565          | 0.43               | 198.4       | 6.07    |
| Hex-CH    | $R3m$      | 5.974 | 5.764|      | 9.92          | 1.542, 1.575   | 0.27               | 175.2       | 6.54    |
| $T_8$-CH  | $I4_1/a$   | 6.106 | 4.146|      | 9.67          | 1.559, 1.564   | 0.43               | 201.7       | 6.67    |
| $R_6$-CH  | $R_3$      | 7.392 | 3.671|      | 9.66          | 1.543, 1.561   | 0.30               | 185.2       | 5.88    |
| Benzene II| $P2_1/c$   | 5.382, 5.338 | 7.457 | 16.96 | 1.387         | 0.32            | 9.8                 | 5.14        |
| Solid cubane | $R_3$ | 5.918 | 10.991 | 14.07 | 1.557         | 0.90            | 18.9                | 6.60        |
| Solid acetylene | $Cmca$ | 4.978, 5.713 | 5.742 | 20.49 | 1.208         | 1.59            | 9.1                 | 5.43        |
| Benzene II polymer | $P2_1/c$ | 4.449, 3.713 | 8.667 | 12.53 | 1.517-1.551   | 0.34            | 31.3                | 5.05        |
| Graphane III | $Cmca$ | 2.515, 9.502 | 3.745 | 11.51 | 1.524, 1.522  | 0.04            | 30.6                | 4.76        |
| Graphane I   | $P3m1$   | 2.506 | 4.503 | 12.41 | 1.515         | 0.00            | 19.7                | 4.87        |

Figure 3 | Calculated phonon and electronic band structures at 0 GPa. (a) and (b) phonon band structures for $T_8$-CH and $R_6$-CH. The high frequency C-H stretching modes are given in text. (c) and (d) electronic band structures for $T_8$-CH and $R_6$-CH.
shape and intensity, suggesting anisotropic features for both chiral phases. The application of pressure on the two structures induces an opposite optical response. By increasing pressure the C-C bond length is shortened, the band gap decreases and the whole optical spectrum is almost rigidly shifted toward higher energy. The calculated static dielectric constants for the two chiral phases increase slowly with pressure, with the $ab$- ($c$-) components going from 4.045 (4.071) and 3.846 (3.797) at 0 GPa to 4.174 (4.227) and 4.082 (3.934) at 30 GPa for $T_8$-CH and $R_6$-CH, respectively.

To provide more information and characters for possible experimental observation, we have also simulated the x-ray diffraction (XRD) spectra of the various CH phases at 0 GPa. Monochromatic radiation with a wavelength 1.540 56 Å is used, and the results are shown in Fig. 5. Unlike $K_4$-CH where the main peak (110) at $2\theta = 29.69^\circ$ is observed, three sharp XRD peaks of (101) at 25.95°, (200) at 29.23°, and (211) at 39.48° with strong intensities are seen for $T_8$-CH. Furthermore, we also find significant difference between the two hexagonal phases, with the most prominent peak observed to be (101) at 23.08° for Hex-CH and (110) at 24.06° for $R_6$-CH, although both phases share the same peak (201) with close positions. Compared with these diamond-like CH phases, the layered ones have specific XRD peaks at relatively small $2\theta$ values of 19.70° for graphene I, 18.46° for graphene III, and 20.65° for benzene II polymer, which originate from a large interlayer distance in layered crystal structure. We believe that the above comparison between the chiral hydrocarbons found here and other CH structures may be helpful for identifying them in experiments.

**Discussion**

In summary, we have predicted by *ab initio* calculations two new 3D hydrocarbon framework structures composed of 3-fold and 4-fold helical CH chains in $R_3$ and $A_4/a$ symmetry, respectively. These saturated crystalline phases are dynamically stable and have large bulk moduli of ~200 GPa. We confirm their increasing stabilization with pressure relative to the molecular solids such as acetylene, cubane, and benzene with 1:1 stoichiometry in the pressure range 0–50 GPa. Calculations on the electronic and optical properties

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**Figure 4** | (a) Calculated electronic band gaps as a function of pressure for $K_4$-CH, Hex-CH, $T_8$-CH, and $R_6$-CH. (b) and (c) Absorption spectra along the c axis and in the $ab$ plane for $T_8$-CH and $R_6$-CH at 0, 30, and 50 GPa, respectively.

**Figure 5** | Simulated XRD patterns for $K_4$-CH, Hex-CH, $T_8$-CH, $R_6$-CH, graphene I and III, benzene II polymer, and benzene II at 0 GPa. The x-ray wavelength is 1.540 56 Å.
show that both chiral hydrocarbons exhibit a wide-gap insulating behavior and anisotropic adsorption spectra. The simulated XRD patterns show the distinct structural feature with respect to the layered CH phases. The present results will stimulate future experiments on the high-pressure polymerization of molecular hydrocarbons to synthesize the amazing chiral CH phases, which may have wide applications in mechanical, optoelectronic, and biological materials.

Methods

The calculations were performed using the density functional theory within the local density approximation (LDA)36–38 as implemented in the Vienna ab-initio simulation package (VASP)31. We adopted the projector augmented wave (PAW) method32 to describe the electron-ion interaction. The plane wave cutoff energy was set to 800 eV. Brillouin zone integration was carried out at Monkhorst-Pack39 k-point meshes with a grid spacing of 2π × 0.02 Å⁻¹. The geometries were optimized by a conjugate gradient algorithm until the Hellmann-Feynman forces on the ions are less than 10⁻⁵ eV/Å. Phonon calculations were based on the supercell approach40 using the PHONOPY code35. The HSE06 hybrid functional method36 was employed to calculate the electronic and optical properties. The frequency dependent dielectric matrix was obtained by neglecting local field effects25.

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Author contributions

C.S.L., H.D.L. and J.T.W. designed the study and wrote the paper; C.S.L. carried out ab initio simulations. All authors discussed the results and contributed to the manuscript.

Additional information

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