Two-Dimensional Anisotropic C_{10} Carbon Allotrope with Mechanically Tunable Band Gap

Prashant Vijay Gaikwad*

Department of Physics and Centre for Modeling and Simulation, Savitribai Phule Pune University, Pune 411007, India

ABSTRACT: A high band gap, two-dimensional (2D) twisted octagonal (TO-)C_{10} allotrope of carbon is proposed. This dynamically and mechanically stable structure shows thermal stability up to 500 K and shows one of the largest Young’s modulus of 306.4 GPa nm (close to graphene) among 2D carbon derivatives. TO-C_{10} also possesses one of the highest 2.94 eV (3.97 eV by HSE06) indirect band gap among reported 2D allotropes of carbon. Owing to structural anisotropy with respect to the basal plane and strong directional sp³ bonding, the band gap of the structure is tuned with high strain endurance along with variation in the band gap subject to applied direction of strain. The nature of the band gap also changes between indirect and direct on account of variation in the valence band states, dominantly governed by carbon atoms in the less symmetrically bonded ladder sites. Further, the band gap can be tuned with doping of Si and Ge and also by forming one-directional nanoribbons. Owing to structural inhomogeneity and inherent high band gap, the proposed 2D TO-C_{10} can be a potential candidate for future applications.

INTRODUCTION

Carbon has a large number of allotropes because of small ionic radii, high electronegativity, wide oxidation range, ability to adopt various hybridization states (sp, sp², and sp³), mixed nature of bondings (ionic and covalent), and so forth. The absence of band gap among most of the two-dimensional (2D) allotropes of carbon is governed by energetically favored sp² covalent bonding and limits their applications. Other 2D materials including transition-metal dichalcogenides and black phosphorous have band gap mostly less than 2 eV which results in their inability to respond photons with wavelength less than 620 nm (e.g., blue and UV) in light-emitting diodes and photodetectors.1-3

Engineering of the electronic structure of 2D materials has drawn large interest, for example, opening of band gap of graphene, tuning band gap of bulk Si or Ge from indirect to direct, and so forth.4-8 With the discovery of superconductivity and correlated-insulating behavior shown by twisted bilayer graphene, the emphasis of multidimensional efforts toward the problem has drawn considerable attention despite having large complexities.9-11 Tuning the band gap of graphene is achieved by perturbing through physical potentials via applying electric fields to the bilayer,5,12,13 patterned hydrogen adsorption,5,14 superlattice with different allotropes,5,8 and interaction with the substrate.16,17 The challenges for such processes includes, strong chemical bonding of hydrogen adsorption or substrate interaction changes intrinsic properties of graphene significantly, applying electric field or forming superlattices opens band gap merely by ~0.3–0.7 eV, and so forth. Contrary to opening of band gap, stacking of layers mostly reduces band gap due to interlayer coupling-induced lifting of the degeneracy of states near Fermi.18,19 The usual way of varying the band gap of a structure is by varying composition, doping, or defects, but that may pose experimental challenges of synthesizing the 2D material with maintaining composition and stoichiometry. On similar grounds, the unary composition material has advantage over synthesis but holds limitation of inherent electronic properties of the material. These challenges are overcome by straintronics, wherein systematic application of strain impetus a handle for engineering the band gap of the material.20 2D materials are reported to show interesting properties subject to straintronics. The topologically protected states of graphene near to the Fermi surface are reported to couple with certain phonon modes that lead to phonon softening under biaxial strain.21 Strain is implicated by lattice mismatch with the substrate, thermal expansion, mechanical loading, and so forth.22 Strain can significantly change the lattice structure by distortion; hence, it can vary the electronic structure significantly near to Fermi energy. Usually with application of strain, the deep conduction band states near Fermi comparatively shifts to lower energy than the lowest conduction band states; this causes change in the nature of band gap between direct or indirect.23 In some cases similar to the present case, the variation in the valence band is also authoritatively significant to decide the nature of the band gap.
On the structural front, a large anisotropy of black phosphorous along with one of the highest carrier mobility has led to highly anisotropic electrical, optical, thermal, and mechanical properties. Because of this striking contrast from the traditional, most of the well-documented 2D materials such as graphene, transition-metal dichalcogenides, and so forth have drawn considerable interest in black phosphorous and derivatives.24

The recent report of the 2D pentagonal form allotrope of carbon has shown a large band gap of 2.21 eV (3.25 eV by HSE06) governed by the combination of sp3- and sp3-bonded carbon sites.25 Despite experimentally challenging possibilities due to unusual pentagonal symmetry and mixed hybridization, the scope of experimental realization of 2D carbon allotropes having intrinsic band gap has opened up and hence they have become a great matter of interest for applications. Although most of the experimentally synthesized carbon is in the mixed hybridization form, the recent attempt of achieving high fraction of the sp3-bonded carbon content in the tetrahedral amorphous carbon is reported.26 However, controlling the particular hybridization in a mixed-phase material presents challenges than synthesizing the single phase.

The sp3-hybridized 3D allotropes of carbon such as diamond show a large band gap. It has been observed recently that surface-bonded hydrogen-induced migration of sp3 hybridization can show interlayer bonding between few-layered (up to 4 layer) graphene assemblies.27 Controlling the reaction dynamics of synthesis of diamond has been well established, and diamond nucleation kinetic barriers for phase transition from graphene are proposed to be lowered because of defects or surface stabilization; hence, such assemblies may provide carbon assemblies with band gap. In this direction, recently, we have proposed free-standing few-layered thermomechanically robust N-terminated assemblies of sp3-bonded carbon phases, providing respective bulk-like electronic, mechanical, and thermal properties.28

It had been believed for a long time that only hexagon is the basic building block, and then pentagon was proposed.25 Recently, a higher co-ordination cluster assembly-based route is reported to be useful to predict 2D structures of ZnO. This fundamental method exploits the higher co-ordination behavior to the most stable clusters from the bottom to top approach and uses them as a building block to predict 2D monolayer structures.29 Using this approach, the thermally and mechanically stable octagonal ZnO monolayer which consists of eight atom units as a building block is proposed.29 Earlier studies have also confirmed the possibility of octagonal geometries in many structures. Because the IV, II–VI, and III–V group elements usually share the structural similarities, it is logical to exploit fundamentally the use of octagonal units as a building block. In the similar line, 2D octagonal carbon is already predicted.30

With the informative platform of straintronics, anisotropic 2D material, octagonal carbon, and our previous work on sp3-bonded carbon phases, the present work is carried out with endeavor of predicting the large band gap 2D allotrope of carbon. It has led to theoretical prediction of the present sp3-bonded 2D carbon allotrope having structural anisotropy with respect to the basal plane. It has been subjected to band gap engineering with the aid of strategic advantages of straintronics, doping, and one-dimensional confinement.

## RESULTS AND DISCUSSION

### Stability and Thermomechanical Properties.

In present work, the twisted octagonal ring of carbon connected by two C atoms (termed as C1 sites) on each side of the basal plane is used to form the 2D structure, which is henceforth referred to as the twisted octagonal carbon (TO-C10) structure. It has two parallel twisted ladders (termed as C2 sites) along the b parameter, connected in the basal plane by alternate vacant sites and C atoms (termed as C3 sites). The unit cell of TO-C10 contains 10 C atoms (2 at C1 sites and 8 at C2 sites), and the unit cell is marked by dashed rectangles as seen in

Table 1. Cohesive Energy (Ec), Band Gap (Eg), Lattice Parameters (a, b, c), Bond Angles (A), and Thickness (h) of TO-C10 and TO-C10bulk Forms

| system      | Ec  (eV) | Eg  (eV) | a  (Å) | b  (Å) | c  (Å) | h  (Å) | A  (deg) |
|-------------|---------|---------|--------|--------|--------|--------|----------|
| TO-C10      | 6.23    | 2.94    | 6.22   | 2.93   | 1.44   | 75.8−131.4 |
| TO-C10bulk | 6.78    | 2.07    | 5.88   | 2.62   | 6.02   | 90.0−145.1 |

Figure 1. xy-plane and z-axis view of geometries of (a) two-layer assembly of TO-C10, (b) vacancy at the basal plane C atom (C1), and (c) vacancy at the ladder C atom (C2) site. Representative C1 and C2 sites are also shown along the xy-plane and z-axis view in (a). The unit cell of TO-C10 is represented by a dotted rectangle.
28 The calculated cohesive energy of sp3-hybridized all allotropes, graphene (7.98 eV/atom), graphite (7.99 eV/atom), diamond (7.85 eV/atom), lonsdaleite (7.83 eV/atom), and so forth, is lower than that of sp2-bonded carbon allotropes, graphene (7.98 eV/atom), graphite (7.99 eV/atom), and so forth.28 The calculated cohesive energy of sp3-hybridized TO-C10 is 6.23 eV/atom and is lower than that of 2D mixed hybridized (sp2 and sp3) penta-graphene (7.08 eV/atom) or significantly lower than that of sp2-hybridized metallic 2D octagonal carbon (7.47 eV/atom). However, the kind of effort vested toward identification of only sp3-hybridized 2D allotropes of carbon is very less. The present work contributes toward the identification of sp3-hybridized 2D carbon allotropes and thus formed the TO-C10 structure which proposes candidacy for the material with anisotropic properties and their applications.

The dynamical stability of the structure is determined and resultant dispersion profile is incorporated in Figure S3. It shows the absence of negative frequencies which reflects the dynamical stability of TO-C10. The thermal stability is investigated by ab initio molecular dynamics (AMD) calculations, wherein the assembly is simulated at 500 K for 8 ps in a time step of 1 fs. Figure 2 shows the variation of potential energy of the system with time up to 8 ps in steps of 1 fs at 1800 K. The inset shows the variation in system temperature with time.

Figure 2. Thermal stability of 2D TO-C10 at 500 K. The inset shows (a) xy-plane and (b) z-axis view of the final structure, while (c) shows the variation in system temperature with time.

potential energy of the system with time, indicating thermodynamical stability of TO-C10. The inset shows geometry of the final structure (a) in xy-plane and (b) along z-axis view. Thus, the obtained final structure is found to be significantly distorted; however, the basic skeleton of the structure remains the same. This distorted structure quickly regains the original state on relaxation and liberates 0.08 eV/atom energy.

Strain-induced mechanical stability of the TO-C10 plane is investigated. Strain energy (ΔE) is defined as the energy difference between the respective unstrained and strained systems. TO-C10 is subjected to uniaxial (along a and b) and biaxial strain within a small limit of ±5%, and the variation in ΔE is mapped to applied strain in order to determine the elastic properties. The parabolic region of ±5% strain is used to extract the elastic constants by fitting second-order partial derivative of strain energy with respect to strain.28 The strain is enforced by changing the respective lattice constant, and then the ions are relaxed with restricting the dimensions of the unit cell. Calculated elastic constants C11, C12, C44, 3C66 Young’s modulus, and Poisson’s ratio (ν) of TO-C10 are 320.7, 293.0, 11.7, 154.5, and 306.5 GPa nm, and 0.04, respectively; the detailed plot (Figure S6) along with relevant discussion can be found in the Supporting Information. Young’s moduli are 320.2 and 292.6 GPa nm along C11 and C44 directions, respectively. The mechanical stability of the structure is established by the virtue of Born–Huang criteria.31 The calculated average Young’s modulus is 306.5 GPa nm and is significantly larger than penta-graphene (265 GPa nm) and comparatively close to that of graphene (338 GPa nm) among 2D carbon allotropes.25,28 Strong sp3-hybridized structures govern the large Young’s modulus and can in principle enhance further by reducing inbuilt strain with appropriate engineering of the structure. In that direction, N is found to be a suitable candidate, and the resultant structure is found to show substantially higher Young’s modulus, and these results will be communicated separately.

Furthermore, to investigate stability with respect to the layered structure, a two-layer assembly of the 2 × 2 × 1 supercell of TO-C10 containing 80 carbon atoms (40 atoms per plane) is relaxed with consideration of van der Waals forces. The resultant structure shows (Figure 1a) two layers separated by a 3.09 Å distance with no significant structural changes in the individual layer.

The stability of the structure with respect to defects is determined by performing calculations using a 2 × 3 × 1 supercell containing 60 carbon atoms. The single vacancy created at the site of terminal C atom (C1) is nonmagnetic and demands a supply of 3.77 eV energy for formation, while it reduces the band gap of the system to 1.66 eV. The basal plane vacancy of the central single C atom (C1) shows 4.0 μB magnetic moment and requires a supply of 12.12 eV energy to form. The vacancy at the C1 site shows spin-resolved band gaps of 1.16 and 2.05 eV and can be further exploited for spintronic applications. Higher defect formation energy again establishes the energetical stability of the TO-C10 structure. The sp3-bonded TO-C10 shows 0.72 eV larger band gap, and it is 0.24 Å thick along the z-direction than the pentagonal structure.25

Inspired by the stability, a bulk structure is formed using TO-C10. It is a bi-tetrahedral structure, and more details of the structure can be found in the Supporting Information (Figures S1, S2, and Table S1). The thermal stability of TO-C10 bulk is investigated by AMD calculations. Figure 3 shows the variation of potential energy with time up to 8 ps in steps of 1 fs at 1800 K. The inset shows significantly distorted final structure along (a) xy view and (b) z-axis view; however, the basic skeleton of the structure remains similar. It suggests that TO-C10 bulk is thermally stable up to 1800 K. The electronic structure of TO-C10 bulk (Figures 4b and 5c) shows that it has a direct band gap of 2.07 eV. The higher band gap of TO-C10 than its bulk form can be ascribed to the larger structural flexibility and quantum confinement effect. However, the high flexibility is unlikely to be the dominant factor given the less E<sub>f</sub> (Table 1) of the 2D form than TO-C10 bulk. The lower limit of bond angles of TO-
C$_{10}^{\text{bulk}}$ is shifted to 90° by virtue of the bi-tetrahedral structure which comparatively reduces strain and increases energetically stability than 2D TO-C$_{10}$. The formation energy of TO-C$_{10}$ with respect to the bulk counterpart ($E_{\text{c diff}}$) is 0.55 eV/atom and is slightly a higher side for exfoliation. Also, TO-C$_{10}^{\text{bulk}}$ has chemical bonding and considerable atomic rearrangements along the c axis; hence, chemical exfoliation may be experimentally difficult.

It has been reported recently that Young's modulus can show the trend of variation with the density of the 2D material. However, we argue that the correlation of the mechanical property is highly dependent on hybridization of states in the material and only 2D materials of carbon with particular hybridization, either sp$^3$ or sp$^2$, can show such individual trends because of variation in the strength of bonding.

**Electronic Structure**. The electronic structure is investigated using band structure and site-projected partial DOS (l-DOS). Figure 4a and Figure 5a shows the l-DOS and band structure plots of pristine TO-C$_{10}^{\text{pristine}}$, respectively. It clearly shows qualitatively similar band structures. The states at the valence band are sp$^3$-hybridized states, while contribution of s states of carbon is comparatively larger at the conduction band. The relative contribution of s states of carbon increases for deep-level states as well as moving higher in energy than the Fermi energy. This is similar to other sp$^3$-hybridized phases of carbon, for example, diamond, lonsdaleite, and so forth.$^{28}$ The principle difference is in reduction of the forbidden region from 4.11 eV (for diamond) to the present case 2.94 eV.$^{28}$ This reduction of ~1 eV in the forbidden region can be ascribed to the bonding in deformed tetrahedral geometry of the TO-C$_{10}$ structure, wherein the bond angles and lengths are varied from 109.5°, 1.54 Å from the perfect tetrahedral structure, to that as shown in Table 1. The atoms in the ladder region of TO-C$_{10}$ (C$^2$ sites) have maximum deformation relative to the tetrahedral structure, and hence their states appear in the forbidden region causing reduction in the band gap. This generates strain and decreases the structural and thermal stability of the system. Figure 6 shows the band-decomposed partial charge density of Fermi ± 2 states of the TO-C$_{10}$ structure. The Fermi and Fermi − 1 valence states show charge delocalization around C$^2$ sites (in the ladder region) along the b parameter, whereas, the absence of charge at C$^1$ sites can be clearly observed. This supports the conclusions of l-DOS analysis of C$^2$ sites being responsible for reduction in the band gap. Figure 5a depicts the band structure of TO-C$_{10}$, while (b) shows the same using a more accurate HSE06 functional. The landscape of electronic states gets clearer with the use of band structure analysis along with respective l-DOS plots. The band structure plots shows a maximum of the valence band in the M−Γ path and gives rise to indirect band gap. On application of strain along the b parameter, the conduction band states near Fermi remains similar but the C$^2$ atom-derived states undergoes major transition and changes nature of the band gap from indirect to direct as shown in subsequent section. All the bands along the path of symmetry points X−M in the Brillouin zone are doubly degenerate because of two-fold symmetry rotation operation. Similar features are observed previously for penta-graphene, penta-CN$_2$, and so forth materials.$^{25,32}$ Because of

![Figure 3. Thermal stability of TO-C$_{10}^{\text{bulk}}$ at 1800 K. The inset shows (a) xy-plane and (b) z-axis view of the final structure and (c) variation in the system temperature.](image)

![Figure 4. Site-projected partial density of states (DOS) plots of (a) TO-C$_{10}$ and (b) TO-C$_{10}^{\text{bulk}}$, and with single atom vacancy defect at (c) C$^1$ and (d) C$^2$ sites. Fermi energy is adjusted to 0 for respective plots.](image)
inherent rotational two-fold symmetry, 2D, doped, and bulk form structures show doubly degenerate bands along the X–M path. The nearly flat valence band during the Γ to X path suggests the degeneracy of these states. This degeneracy increases with applied strain along parameter b as a consequence of and bringing more symmetry in the structure as discussed in the next section.

The l-DOS plots of C1 and C2 site vacancy defects are as shown in Figure 4c,d, respectively. In the case of C1 site vacancy, each of the first neighbor atoms possesses sp3-hybridized unsaturated states in the forbidden region which gives rise to 4 μB of magnetic moment. In the case of C2 vacancy, owing to peculiar geometry of the structure, the first nearest-neighbor atom forms the double bond in the basal plane and does not possess dangling bonds as shown in Figure 1c. Hence, such vacancy does not contribute to the magnetic moment and causes relatively higher stability. The two C atoms in the ladder region forms the 4-coordinated single bonds, while the C atoms in the basal plane form the double bond. However, the 4-coordinated nearest-neighbor C atoms of this double bond spatially separate pз states of double-bonded C atoms and hinder their electron localization (π bonds) and give rise to a finite band gap of 1.66 eV as shown in Figure 4d. The thermomechanically stable structure of TO-C10 shows an indirect band gap of 2.94 eV, and this makes TO-C10 to be a large band gap and a large Young’s modulus 2D allotrope of carbon.

Strain-Induced Electronic Properties. Strain-induced variation in the mechanical and electronic properties of TO-C10 is exploited because of inherent structural anisotropy with respect to the basal plane. Figure 7 shows the variation in the strain energy and band gap with applied uniaxial strain along lattice parameter a (ΔEa, Ea) and b (ΔEb, Eb), respectively. Significant lattice parameter-dependent variation can be seen in strain energy; however, variation in the band gap is more prominent. The band gap decreases with increase in lattice strain along the a parameter, while it increases with compression of the lattice parameter till −6% (3.03 eV) and then decreases with further compression. On the contrary, applying uniaxial strain along the b parameter results in first increase in the band gap from 2.84 to 3.04 eV (at 4% strain) and then decreases gradually. On compression of lattice parameter b, the band gap decreases. The nearly linear behavior of decrease in the band gap with application of strain, along the b parameter larger than 4% and along the a parameter.
parameter larger than $-6\%$, can be clearly seen and can be probed for the applications. A similar feature is seen from $-6$ to $11\%$ of applied strain along the $a$ parameter, but the variation in the band gap is small. The band gap vanishes at $+25$ and $-18\%$ of applied uniaxial strain along the $a$ parameter and at $-12$ and $+20\%$ of applied strain along the $b$ parameter. The opposite trend of band gap variation for both the lattice parameters at lower values of strain is because of the peculiar geometrical flexibility of the TO-C$_{10}$ structure. Stretching (compression) of lattice parameter $b$ ($a$) leads to relaxing of bond lengths in the direction of tetragonal symmetry bonding and hence increases the band gap. However, this increase in the band gap due to relaxation of one lattice parameter generates strain in the other in-plane lattice parameter. The strain enforced along lattice parameter $a$ can endure larger values due to higher capability of stretching of bond lengths of C$^1$ carbon (basal plane carbon) atoms. Higher ability to elongate more in the zigzag direction is known in graphene or like materials because of the ability to suppress bond elongation by adjusting bond angles. Despite having a zigzag nature, the strain enforced along the $b$ parameter endures less stretching because of bonds of C$^2$ (terminal carbon along $z$-axis) atoms with the basal plane C$^1$ site atoms. This behavior is the artifact of the large deviation of asymmetric bond angles of C$^2$ carbon atoms than the diamond-like sp$^3$ hybridized structure, and it results in decreased band gap than diamond (4.11 eV)$^{28}$ as evident by l-DOS and partial charge density analysis.

Although the band gap diminishes at larger values of strains, the occurrence of mechanical failure because of Kohn anomaly-induced phonon instability at lower values of strain is well known.$^{21,33}$ In the present case, soft phonons appear at an applied uniaxial strain of $+18\%$ along $a$ and $-10$ and $+14\%$ along the $b$ parameter. For the biaxial strain, the soft phonons appear at $+13\%$ of applied strain. The negative strain is not sustained by TO-C$_{10}$ when subjected along the $a$ parameter and equibiaxis and applying as small as $-3\%$ strain leads to phonon instability caused by the acoustic mode of vibrations along the out-of-plane direction. It is clear that apart from along the $b$ parameter, applying negative strain (contraction) is dynamically not favored by TO-C$_{10}$. Also, applying negative strain is experimentally not a feasible idea because it may lead to wrinkles and other physical deformations in 2D materials; hence, positive strain is focused in further studies. The negative strain and biaxial strain are plotted in Figures S7 and S8, the details of which can be found in the Supporting Information. Respective band structures and phonon dispersion curves at 17 and 18% subjected to $a$ and 13 and 14% subjected to strain along $b$ parameters are shown in Figure 8. It shows the soft phonons at the $\gamma$ point on application of 18% strain along the $a$ parameter, whereas the applied strain of 14% along the $b$ parameter leads to soft phonons at the $K$ point, which is similar to that of graphene.$^{21}$ Applying strain along the $b$ parameter more than 4% and compression of the $a$ parameter more than 6% leads to change in the nature of band gap from indirect to direct. This is because of shifting of $p$ states of C$^2$ atoms at a higher level in the valence band with respective strains. Interestingly, the variation in the band gap of the structure on enforcement of strain is observed to induce large variation in the valence band, whereas the variation in the conduction band is comparatively less. Application of large uniaxial strain along the $b$ parameter and biaxial strain leads to symmetry-driven increase in the degeneracy of states near Fermi energy conduction and valence bands. The detailed analysis has shown that the large variation in the band gap and other electronic properties are primarily governed by strain-driven variation in the bonding of C$^2$ atoms. This can be primarily indulged by application of biaxial strain and uniaxial strain along the $b$ parameter. The important bond lengths are C$^1$ with C$^3$ atoms ($b_{2}^{c_1-c_3}$) and two types of bond lengths for C$^2$ with C$^3$ atoms, that is, in the $x$-$y$ plane ($b_{2}^{c_2-c_3}$) and along the $z$ axis ($b_{3}^{c_1-c_3}$). On application of 17% strain along the $a$ parameter, these bond lengths are 1.80, 1.59, and 1.58 Å, whereas on application of strain of $-7\%$ along the $a$ parameter (1.51, 1.58, and 1.58 Å) or greater than 5% along the $b$ parameter (1.58, 1.66, and 1.55 Å), the bonding shows comparatively more symmetric bond lengths ($b_{2}^{c_2-c_3}$, $b_{2}^{c_2-c_3}$, and $b_{3}^{c_1-c_3}$), respectively. However, this leads to a large variation in the bond angles from 74 to 133° and that causes the instability in the system.

Figure 8. Effect of strain on the electronic [(a) through (d)] and phonon [(e) through (h)] band structure of TO-C$_{10}$ at 17 and 18% along the $a$ parameter and 13 and 14% of applied uniaxial strain along the $b$ parameter, respectively.
The observed variation in the conduction band with applied uniaxial strain is exploited further for electron affinity (EA) properties by addition of a single electron to the strained TO-C\textsubscript{10} which is reflected by varying EA. The EA of the system is defined as the difference of total energy of the system without and with addition of a single electron. The TO-C\textsubscript{10} structure shows EA to be of value $-0.27$ eV. This value of EA on application of uniaxial strain in the range of $-9$ to $+18\%$ is found to vary from $0.37$ to $-0.42$ eV in the case of strain along the $a$ parameter and $0.66$ to $-0.32$ eV in the case of strain along the $b$ parameter, respectively. These observations in EA can be of potential interest in the field of field emission and other electronic applications. It is incorporated in Figure S9 along with details, which can be found in the Supporting Information. Because the prime interest of the present work is on electronic band gap engineering, more attention is paid on the electronic structure further by doping and size confinement.

**One-Dimensional Confinement and Doping.** The variation of band gap subject to structural confinement along one dimension is known for carbon 2D allotropes and is always been a matter of interest for applications. Figure 9 shows laterally 1 (a,b) and 2 (d,e) unit cell wide 1D structures of TO-C\textsubscript{10} which are shown along the $xy$-plane and $z$-axis views, respectively. The structural relaxation in the case of 1 unit cell wide system leads to only corner sharing C\textsuperscript{1} atoms in the basal plane to be of four-coordinated, while rest of the atom forms linear double bonds with the nearest neighbors. The bond length of the double-bonded atom shortens to 1.3 Å and in the case of four coordinated sites (C\textsuperscript{1} atoms), it is 1.47 Å which is considerably shorter 1.57–1.59 Å than that of the pristine structure. Double bonds of the structure diminishes the band gap as shown in 1-DOS plots in Figure 9c,f. In the case of the 2 unit cell wide system, the TO-C\textsubscript{10} geometry tries to retain but undergoes stretching of bond lengths. The doubly bonded carbon atoms at the edge (bond lengths $\approx 1.33$ Å) shortens the 2 unit cell wide region (bond lengths $\approx 1.47$ Å), and this results in stretching of bond lengths (bond lengths $\approx 1.81$ Å) in the 1 unit cell wide central region of the geometry. The basal plane atoms along confined dimension form the double bonds; however, the near-neighbor singly bonded C atoms hinder the $\pi$ bondings of these double bonds and open up the forbidden region by $0.87$ eV as shown in Figure 9f. Both of the confined systems are nonmagnetic, and their electronic and structural properties are greatly influenced by the confinement effect.

Apart from strain-dependent variation, the band gap of TO-C\textsubscript{10} can be further tuned by doping. We have investigated several materials with substitutional doping, and among them, doping of Si and Ge at the basal plane C\textsuperscript{1} site has shown dynamical stability. The respective structures (Figure S1) along with phonon dispersion graphs (Figure S3) can be found in the Supporting Information. On account of larger ionic radii, the lattice parameter $a$ (x-direction) increases, while respective angles ($A$) and stability of 2D assembly decrease with increase in the dopant atomic number. This decrease in the stability of the structure is reflected by respective cohesive energies ($E_{\text{cSi}} = 5.78$ eV and $E_{\text{cGe}} = 5.39$ eV), wherein higher $E_s$ of Si suggests that it is energetically more favorable than doping of Ge. The site-projected DOS plots of Si and Ge doping are incorporated in Figure S5 and can be found in the Supporting Information along with relevant details. On doping of Si, the structure shows a band gap of 2.26 eV. This decrease in the band gap is principally due to appearance of hybridized $p$ states of Si with carbon at the top of the valence band. These $p$ states of Si are highly directional and on bond formation with C atoms, these states undergo deformed orientation than the pristine as reflected by the change in the structural parameters. The entire landscape of the electronic structure is seen to be more discrete on account of the dominant confinement effect. The thermal stability is also reduced on Si doping in TO-C\textsubscript{10} to 400 K. The variation in potential energy with time is plotted in Figure S4, and it can be found along with respective details in the Supporting Information. On doping of Ge, the band gap is reduced to 0.65 eV, and states around the Fermi level are dominantly governed by s and p states of the dopant. The bonding in the case of Ge-doped TO-C\textsubscript{10} is different as reflected by increased contribution from s states of Ge (Figure S5), and it does not show thermal stability even at room temperature.
CONCLUSIONS

In conclusion, a new 2D TO-C_{10} carbon allotrope [space group Pban (50)] is proposed. It is dynamically and mechanically stable with thermal stability up to 500 K. Owing to only sp^{3}-hybridized strong bonding, it shows one of the largest indirect 2.93 eV (3.97 eV by HSE06) band gaps among the 2D allotropes of carbon reported till date. TO-C_{10} has directional Young’s modulus because of structural anisotropy with respect to the basal plane, and it is of the value 320.2 GPa nm along C_{11} and 292.6 GPa nm along C_{22} directions. The average Young’s modulus is 306.5 GPa nm, and to the best of our knowledge, it is one of the highest reported Young’s modulus among 2D carbon allotropes, close to that of graphene. The stability with respect to defects is investigated, and higher defect formation energy and structural integrity with respect to stacking of layers establishes again the stability of the structure. The proposed bulk structure of TO-C_{10} contains bi-tetrahedral geometry, and it is thermally stable up to 1800 K. It is a nonmagnetic material with a band gap of 2.07 eV.

The states of TO-C_{10} governed by comparatively less symmetric C_{2} site atoms (ladder region) than the ideal structure (diamond), are at the top of the valence band and decreases the band gap of the structure with having an indirect nature because of appearance of maximum of the valence band in between the M and Γ path. These delocalized states are principally responsible for the strain-engineered mechanical and electronic structure properties. The two-fold symmetry of the structure governs the doubly degenerate states along the X−M path for 2D and 3D TO-C_{10} structures. Also, it causes large degeneracy of states around Fermi energy from the Γ to X path on the application of a larger value of strain along the a parameter and biaxial strain. Application of larger than +4% (−6%) positive (negative) strain along the a (b) parameter changes the valence states significantly because of structural deformation toward a relatively more symmetric structure and also converts to direct nature of the band gap because of the shifting of valence states at the Γ point. Similarly for biaxial strain, the changeover to direct nature of the band gap appears after +8% of applied strain. The appearance of soft phonons because of Kohn anomaly and hence degrading dynamical instability is observed at 18, 14, and 12% of applied uniaxial strain along a, b, and applied biaxial strain, respectively. The interaction of phonon acoustic modes of out-of-plane vibrations with these ladder region carbon atom states principally causes the dynamical instability. The structure is dynamically not susceptible to the application of negative strain (compression) subjected to the a parameter and biaxial strain, but the zigzag nature of the material along the b parameter leads to ability to endure negative strain in the same direction up to −10%. Application of uniaxial strain is also found to influence EA of the TO-C_{10}, and it can be tuned from 0.66 to −0.42 eV.

The one-dimensional confined ribbons of TO-C_{10} shows increase in the band gap with lateral size. For one unit wide layer, the band gap diminishes because of double bonds of C atoms at edges, while for the double unit cell wide layer, the 0.87 eV band gap appears because of hindering of π electrons of doubly bonded C atoms by near-neighbor singly bonded sp^{3}-hybridized C atoms. The discrete nature of the states reflects the large confinement effect; however, the bulk stabilization as reflected by geometry is starting to appear even as small as a two unit cell wide ribbon. The band gap of the system is also tuned with the dynamically stable substitutional doping of Si and Ge at C sites. The Si doping shows thermal stability up to 400 K, while Ge doping does not show thermal stability even at room temperature. The 2.26 eV direct band gap appears on doping of Si and reduces significantly to 0.65 eV on doping of Ge at the expense of reduced stability. The directional p states of Si, and s and p states of Ge, principally govern the states around Fermi energy and cause observed decrease in band gap because of inherent strain in the structure induced by their larger atomic radii.

Owing to strong sp^{3}-hybridized bonding and anisotropic structure, TO-C_{10} shows versatile directional variation in the strain-induced mechanical and electronic properties and hence is proposed to be the potential candidate for future applications.

COMPUTATIONAL METHODOLOGY

Density functional theory-based spin-polarized electronic structure calculations, are performed using the accurate plane-augmented wave method as implemented in the Vienna ab initio simulation package (VASP). The Perdew, Burke, and Ernzerhof exchange-correlation energy functional within GGA is employed. The plane wave basis cutoff value of 400 eV is used. The cutoff values for total energy and convergence of forces on a single atom of 10^{-6} eV and 0.01 (eV/Å), respectively are used. To avoid interaction between images, a vacuum of 20 Å is maintained along the z-direction. The 7 × 11 × 1 k mesh generated by the Monkhorst−Pack scheme is used for unit cell calculations and then scaled appropriately. A 2 × 3 × 1 supercell containing 60 carbon atoms is used to investigate dynamical stability by performing phonon calculations using VASP, within the framework of density functional perturbation theory, and using the PHONOPY code interface. AMD calculations are performed to investigate thermal stability of the structure using VASP. For that, the Nosé−Hoover thermostat is used and canonical ensemble calculations at single k point are performed on the 3 × 3 × 1 supercell (containing 90 carbon atoms) in the case of the 2D structure, while the 2 × 2 × 2 supercell (containing 80 carbon atoms) is used in the case of bulk TO-C_{10} (TO-C_{10}bulk) systems. Mechanical stability is investigated by the finite distortion method, the details of which can be found elsewhere.

The cohesive energy (E_{c}) of the system is defined as follows: E_{c} = E_{C} - E_{C}/n, where the total energy of the system containing n number of C atoms is denoted by E_{C} and E_{C} is the energy of the isolated single carbon atom. The single vacancy defect formation energy is defined as follows: E_{VPE} = E_{C} + E_{C_{1}} - E_{C'}, where E_{C_{1}} is the energy of the system with vacancy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00108.

Structural information and stability analysis of TO-C_{10}, its bulk form and 2D form doped with Si and Ge, thermal stability of the Si-doped system, l-DOS plots of doped systems, quadratic fitting of strain energy with respect to applied uniaxial strain, phonon dispersion.
plots with respect to applied negative strain and biaxial strain and their respective band structure plots, and variation in EA with respect to applied strain (PDF)

### AUTHOR INFORMATION

Corresponding Author
*E-mail: prashanth@physics.unipune.ac.in, prashantvg03@gmail.com*

**ORCID**
Prashant Vijay Gaikwad: 0000-0002-0446-9426

**Notes**
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