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First principles search for novel ultrahard high-density carbon allotropes: hexagonal C₆, C₉ and C₁₂

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Abstract

*Hexagonal carbon allotropes C₆, C₉ and C₁₂ with **qtz**, **sta** and **lon** topologies, respectively, were predicted on the basis of crystal chemistry and first principles (DFT) calculations. The new allotropes are mechanically (elastic properties) and dynamically (phonons) stable phases and are characterized by ultra-high Vickers hardness, exceptionally high for **qtz** C₆ and C₁₂, close to the previously studied **qtz** C₃. The electronic band structures of all new allotropes show semi-conducting to insulating behavior. **lon** C₁₂ can be considered as novel “superlonsdaleite”.*

Keywords: Carbon allotropes; DFT; density; hardness; phonons; insulators

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Introduction and context

The search and characterization of original ultra-hard carbon allotropes is an ongoing research field especially with the upstream help of modern materials research software, such as those based on evolutionary crystallography (USPEX) [1], and particle swarm optimization-based crystal structure prediction (CALYPSO) [2]. The identified carbon allotropes are compiled in the SACADA database [3] to help inform researchers of the origin of the allotropes, organized by topological categories identified with the TopCryst program [4], e.g. **dia** for diamond, **lon** for ‘lonsdaleite’ (rare hexagonal form of diamond, here identified as C₁₂). Structures are published in the Cambridge Structural Database (CSD) (see [5] for one of the original carbon allotropes studied here, C₉).

Such structural identifications require further analyses with quantum mechanical calculations to derive quantities that precisely define the desired function, such as the hardness and the mechanical (elastic properties) and dynamic (phonons) stabilities, as well as the electronic band structure. The widely recognized quantum mechanics framework of the Density Functional Theory (DFT) [6,7] is used in DFT-based computations.

The original hexagonal tricarbon C₃ allotrope has recently been claimed from *ab initio* investigations to be superdense and superhard [8], supporting an earlier claim for such properties [9]. Hexagonal C₃ is derived from silica (quartz) and assigned the **qtz** topology (SACADA **qtz** #11). The five-ring carbon topology **unj** (SACADA #29) has also been proposed for hexagonal C₃ [10]. Finally, we have recently investigated the linear C-C-C arrangements known for the isolated molecule in rhombohedral and hexagonal ultra-hard C₃ characterized by mixed sp³-sp² carbon hybridizations [11].

In this challenging context, the aim of this work is to investigate the physical properties (mechanical, dynamical, and electronic) of **qtz** C₃ together with structurally related novel carbon allotropes, namely **qtz** C₆, **qtz** C₁₂, **sta** C₉ and **lon** C₁₂.

Computational framework

The devised structures were subjected to geometry relaxations of the atomic positions and the lattice constants down to the ground state characterized by minimum energy. The iterative computations were performed using the DFT-based plane-wave Vienna Ab initio Simulation Package (VASP) [12,13]. The projector augmented wave (PAW) method was used for the atomic potentials [13]. The exchange X and correlation C effects (XC) were treated within a generalized gradient approximation (GGA) scheme [14]. Test calculations with a hybrid functional HSE06 [15] did not result in significant changes of the GGA results. The relaxation of the atoms to the ground state geometry was performed using a conjugate-gradient algorithm [16]. The Blöchl tetrahedron method [17] with corrections according to the Methfessel and Paxton scheme [18] was applied for geometry optimization and energy calculations, respectively. A special *k*-point sampling [19] was used to

approximate the reciprocal space Brillouin-zone (BZ) integrals. For better reliability, the optimization of the structural parameters was carried out along with successive self-consistent cycles with increasing k-mesh until the forces on the atoms were below 0.02 eV/Å and the stress components below 0.003 eV/Å³.

Mechanical stability was derived from elastic constants calculations [20]. The phonon dispersion band structures were calculated to verify the dynamic stability of the carbon allotropes. The phonon modes were calculated considering the harmonic approximation through finite displacements of the atoms around their equilibrium positions to obtain the forces from the summation over the different configurations. The phonon dispersion curves along the direction of the Brillouin zone were then obtained using the interface code "Phonopy" based on the Python language [21]. The CIF files and the structure sketches including the tetrahedral representations were generated using the VESTA software [22]. The electronic band structures and densities of states were obtained with the full-potential augmented spherical wave ASW method based on DFT using the same GGA scheme as above [23].

Crystal chemistry

C₃ has a structure derived from one of the quartz varieties [10]. The structure belonging to space group *P*₆₂₂, No 180 is shown in Fig. 1a in ball-and-stick and tetrahedral representations with emphasis on the tetrahedral arrangement. These representations are also applied to the other structures.

Table 1 gives literature [8] and currently calculated (in brackets) lattice constants after full unconstrained geometry optimizations. **qtz** C₃ is energetically less cohesive ($E_{\text{coh}}/\text{atom} = -1.37$ eV/at.) than tricarbon formed with linear C—C—C building blocks [11] found with $E_{\text{coh}}/\text{atom} = -1.55$ eV eV/at. Also, as a general trend, all the allotropes examined here are less cohesive than cubic and hexagonal (lonsdaleite) diamond with $E_{\text{coh}}/\text{atom} = -2.46$ eV/atom.

By extending the carbon lattice, we identified a twice as large cell with single sixfold C positions in space group *P*₆₅₂, No 179 for hexagonal C₆. The calculated crystal data are given in Table 1 and the structure is shown in Fig. 1b. In **qtz** topology, C₆ is close to **qtz** C₃, and the atomic averaged volumes are also close, although smaller in novel C₆. We also include results obtained for 5-ring C₆ in **unf** topology such as **unj** C₃ (SACADA #29) [10].

Extending the stoichiometry further, novel C₉ with space group *C*₉ *P*₆₄₂, No 179 with tetrahedral carbon was obtained (Table 1, Fig. 1c) and assigned a new (not SACADA-listed) **sta** topology using TopCryst. The structure was subsequently published in the CCDC crystallography database [5].

For the sake of completeness, in addition to the 6-fold position, space group *P*₆₅₂, No 179 has a 12-fold particular (12c) x, y, z position, which was considered for devising extended C₁₂

stoichiometry. After full geometry relaxation down to the energy minimum, the ground state parameters are given in Table 1, and the structure is shown in Fig. 3e. The tetrahedral arrangement is more regular than in C_3 , C_6 , C_9 and **qtz** C_{12} , and was found to be related to diamond-like. In fact, further analysis of the topology of C_{12} revealed it to be of the **lon** type, i.e., lonsdaleite (hexagonal diamond). Deeper crystallographic characterization led to lonsdaleite's space group $P6_3/mmc$, No 194 for C_{12} characterized by a splitting of the (12c) site into three (4f) sites with parameters given in the last column of Table 1. Consequently, we assign to novel C_{12} the label of “*superlonsdaleite*”. Note that space group No 179 is a subgroup of space group No 194.

Comparing the volumes of the four different carbon stoichiometries can be done by averaging them per atom. Table 1 shows that the volumes of C_3 , C_6 and **qtz** C_{12} are smaller than the values for C_9 and C_{12} , which would lead one to expect higher densities for them, as discussed in the sections on hardness and densities.

Mechanical properties from elastic constants

The analysis of the mechanical behavior was subsequently carried out with the elastic properties by performing finite distortions of the lattice. The system is then fully described by the bulk (B) and the shear (G) moduli obtained by averaging the elastic constants using Voigt's method [20] based on a uniform strain.

The calculated sets of elastic constants C_{ij} (i and j correspond to directions) are given in Table 2. All C_{ij} values are positive. The elastic constants of **lon** C_{12} have the largest magnitudes, close to those of diamond [24]. The structurally related C_3 and C_6 have slightly smaller magnitudes. C_9 has large C_{ij} values, but they remain smaller than all the other carbon allotropes studied.

The bulk B_V and the shear G_V moduli were then obtained from the equations corresponding to the hexagonal system [25]:

$$B_V = 1/9 \{2(C_{11} + C_{12}) + 4C_{13} + C_{33}\}$$

$$G_V = 1/30 \{C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 6(C_{11} - C_{12})\}$$

The last two columns of Table 2 show the obtained B_V and G_V . C_{12} has the largest values, close to the accepted values for diamond, $B_V = 445$ GPa and $G_V = 550$ GPa [26]. The other allotropes also have large bulk and shear moduli values, close to diamond, especially C_3 and C_6 , while C_9 has the smallest values.

Vickers hardness (H_V) has been predicted using four contemporary theoretical models. The thermodynamic (T) model [27], which is based on thermodynamic properties and crystal structure, shows surprising agreement with available experimental data [28] and is therefore recommended for hardness evaluation of superhard and ultrahard phases [29]. The Lyakhov-Oganov (LO) approach [30] takes into account the topology of the crystal structure, the strength of covalent bonding, the

degree of ionicity and directionality; however, in the case of ultrahard phases of light elements, this model gives underestimated hardness values [28,29]. Two empirical models, Mazhnik-Oganov (MO) [31] and Chen-Niu (CN) [32], use the elastic properties. Fracture toughness (K_{Ic}) has been evaluated within the Mazhnik-Oganov model [31]. The results for the currently proposed hexagonal carbon allotropes and others from the literature are summarized in Tables 3 and 4.

Table 3 gives general information on the crystal structures, densities, hardness and bulk moduli according to the thermodynamic model. Focusing on the density, there is a clear evidence of higher densities for the **qtz** allotropes (C_3 , C_6 and C_{12}) compared to other carbon allotropes. The lowest density is observed for the 5-ring open structure of **unj** C_6 [10,33].

The analysis of all the data (Tables 3 and 4) allows us to conclude that the high density gives rise to high hardness values, which are the highest for the **qtz** allotropes mentioned above; but this does not allow us to say that their hardness is higher than that of diamond. Finally, the bulk moduli are also higher for the **qtz** C_3 , C_6 and C_{12} allotropes, but remain within the limits of diamond/lonsdaleite.

Dynamic properties from the phonons

An important criterion of phase stability is obtained from the phonon's properties. Phonons are quanta of vibrations; their energy is quantized by the Planck constant 'h' which is used in its reduced form \hbar ($\hbar = h/2\pi$), giving the phonons energy: $E = \hbar\omega$ (frequency: ω)

All four carbon allotropes were subjected to phonon studies to determine their respective dynamic properties. Fig. 2 shows the phonon bands. In the horizontal direction, the bands develop along the main lines of the hexagonal Brillouin zone (reciprocal k-space). The vertical direction shows the frequencies ω , which are given in terahertz (THz) units.

There are $3N-3$ optical modes found at higher energy than three acoustic modes, starting from zero energy ($\omega = 0$) at the Γ point, center of the Brillouin zone (BZ), up to a few terahertz. They correspond to the lattice rigid translation modes of the crystal (two transverse and one longitudinal). The remaining bands correspond to the optical modes and culminating at $\omega \sim 40$ THz in C_{12} , a value observed for diamond by Raman spectroscopy [36].

Focusing on C_3 , the phonons have a negative frequency (*) along $\Gamma-A$ i.e., along the vertical direction of the BZ indicating instability towards a transient state, i.e., the structure could be unstable, and a possible phase transition could occur. However, we note that in the "qtz" C_3 paper [9] the authors claimed all positive phonons without showing corresponding band structures. While we do not question their results, we point out that in the same calculation protocols for all four carbon forms, the other carbon stoichiometries show no negative phonons and they are considered to be dynamically stable. We propose that the extension of the carbon stoichiometry in the presently studied series is a stabilizing factor of the carbon structure.

Electronic band structures and density of states

Using the crystal parameters in Table 1, the electronic band structures were obtained using the all-electrons DFT-based augmented spherical method (ASW) [23] and are shown in Figure 3. The bands develop along the main directions of the primitive tetragonal Brillouin zones. As all four systems are characterized with a band gap between the valence band (VB) and the empty conduction band (CB), the energy reference along the vertical energy axis is with the respect to the top of the VB.

The band structures of C_3 and C_6 are different, although they are similar in shape. The lowest CB band is at M in both. For the VB, however, the highest band is found at A point in C_3 , whereas in C_6 the highest valence band is at the Γ point, as is more commonly found. In C_9 the band gap is small ~ 0.5 eV, indicating semiconducting behavior. Finally, the largest band gap is observed for the diamond-like C_{12} with a magnitude close to 4 eV with indirect Γ_{VB} - M_{CB} character.

Conclusions

Novel carbon allotropes C_6 , C_9 and C_{12} have been proposed based on crystal chemistry engineering, supported by quantitative assessments through calculations within quantum mechanical density functional theory (DFT). The novel allotropes with increasingly larger tetrahedral networks belong to different topologies: **qtz** C_6 (quartz derived), **sta** C_9 (novel topology) and **lon** C_{12} (lonsdaleite-like). All phases were found to be energetically cohesive on the one hand, and mechanically (elastic properties) and dynamically (phonons) stable on the other hand. Furthermore, their electronic behavior was found to range from wide band gap insulators to semiconductors. An exceptionally high Vickers hardness was predicted for **qtz** C_6 , close to the previously reported **qtz** C_3 and seemingly slightly higher than that of diamond. **lon** C_{12} can be considered as a novel ‘superlonsdaleite’. The excellent mechanical properties of novel carbon allotropes allow them to be considered as potential ultra-hard materials [37], however, experimental routes to their synthesis should be explored.

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Table 1 Crystal structure parameters of hexagonal carbon allotropes.

	a (Å)	c (Å)	V_{cell} (Å ³)	V_{atom} (Å ³)	Position
qtz C ₃ ^{#180} [8] *	2.6010 (2.5975)	2.7866 (2.7925)	16.326 (16.316)	5.44	C(3c) $\frac{1}{2}, 0, 0$
qtz C ₆ ^{#179}	2.5975	5.5858	32.63	5.43	C(6a) 0.498, 0, 0
sta C ₉ ^{#181}	2.5889	8.6153	50.57	5.64	C ₁ (3a) 0, 0, 0 C ₂ (6f) 0, 0, 0.2227
qtz C ₁₂ ^{#181}	5.1949	2.7953	65.27	5.44	C ₁ (6g) 0.25, 0, 0 C ₂ (6i) 0.25, 0.5, 0
lon C ₁₂ ^{#179}	2.5046	12.498	67.97	5.66	C(12c) $\frac{2}{3}, \frac{1}{3}, 0.0210$
lon C ₁₂ ^{#194}	2.5046	12.498	67.97	5.66	3 × C(4f) $\frac{2}{3}, \frac{1}{3}, z$ $z_1 = 0.0210$ $z_2 = 0.1457$ $z_3 = 0.8124$

* The values in brackets have been calculated in the present work.

Table 2 Elastic constants C_{ij} and Voigt values of bulk (B_V) and shear (G_V) moduli of hexagonal carbon allotropes (all values are in GPa).

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B_V	G_V
qtz C_3 ^{#180}	1196	78	64	1162	559	439	558
qtz C_6 ^{#179}	1186	88	64	1162	549	441	550
sta C_9 ^{#181}	1031	170	62	1081	430	415	448
qtz C_{12} ^{#181}	1158	86	54	1147	536	428	540
lon C_{12} ^{#179}	1211	107	11	1338	552	446	573
lon C_{12} ^{#194}	1211	107	11	1338	552	446	573

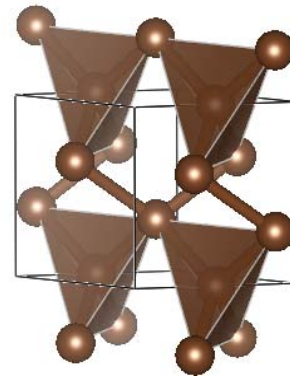
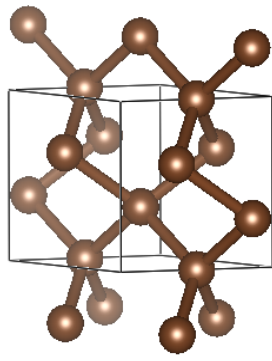
Table 3 Vickers hardness (H_V) and bulk moduli (B_0) of hexagonal carbon allotropes calculated in the framework of the thermodynamic model of hardness [27] (pw = present work).

	Space group	$a = b$ (Å)	c (Å)	ρ (g/cm ³)	H_V (GPa)	B_0 (GPa)
qtz C ₃ #180 [9]	$P6_222$	2.605	2.801	3.635	101 ^{<i>pw</i>}	458 ^{<i>pw</i>}
qtz C ₃ #180 [8]	$P6_222$	2.613	2.811	3.600	100 ^{<i>pw</i>}	454 ^{<i>pw</i>}
qtz C ₃ #180 [<i>pw</i>]	$P6_222$	2.6010	2.7866	3.665	101	462
unj C ₆ #178 [33]	$P6_122$	3.5626	3.3673	3.233	90 ^{<i>pw</i>}	407 ^{<i>pw</i>}
qtz C ₆ #179	$P6_522$	2.5975	5.58585	3.666	102	462
sta C ₉ #181	$P6_422$	2.5889	8.6153	3.590	99	452
lon C ₁₂ #179	$P6_522$	2.5046	12.498	3.525	98	444
qtz C ₁₂ #181	$P6_422$	5.1942	2.7925	3.668	102	462
lon C ₁₂ #179	$P6_522$	2.5046	12.498	3.525	98	444
lon C ₁₂ #194	$P6_3/mmc$	2.5046	12.498	3.525	98	444
Lonsdaleite	$P6_3/mmc$	2.5221 ^[34]	4.1186 ^[34]	3.5164	97	443
Diamond	$Fd-3m$	3.56661 ^[35]		3.5169	98	445 ^[26]

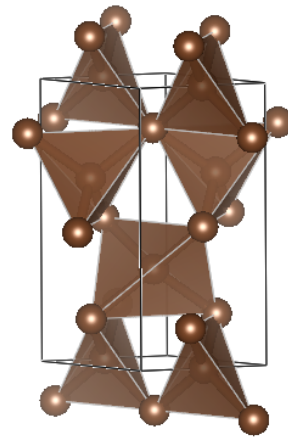
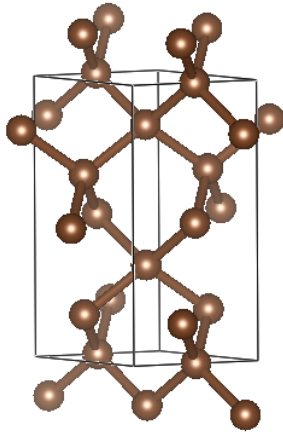
Table 4 Mechanical properties of hexagonal carbon allotropes: Vickers hardness (H_V), bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν) and fracture toughness (K_{Ic})

	H_V				B		G_V	E^*	ν^*	K_{Ic}
	T	LO	MO	CN	B_0	B_V				
	GPa									
qtz C ₃ ^{#180} [9]	101 ^{pw}	89 ^{pw}	–	–	458 ^{pw}	433	–	–	–	–
qtz C ₃ ^{#180} [8]	100 ^{pw}	89 ^{pw}	99 ^{pw}	98 ^{pw}	454 ^{pw}	416	521	1103	0.06 ^{pw}	5.9 ^{pw}
qtz C ₃ ^{#180} [pw]	101	90	106	104	462	439	558	1176	0.054	6.4
unj C ₆ ^{#178} [33]	90 ^{pw}	82 ^{pw}	–	–	407 ^{pw}	–	–	–	–	–
qtz C ₆ ^{#179}	102	90	105	101	462	441	550	1165	0.060	6.4
sta C ₉ ^{#181}	99	88	83	75	452	416	448	989	0.104	5.5
qtz C ₁₂ ^{#181}	102	90	103	101	462	428	540	1140	0.056	6.2
lon C ₁₂ ^{#179}	98	90	109	107	444	446	573	1204	0.050	6.6
lon C ₁₂ ^{#194}	98	90	109	107	444	446	573	1204	0.050	6.6
Lonsdaleite	97	90	99	94	443	432	521	1115	0.070	6.2
Diamond	98	90	100	93	445 ^[26]		530 ^[26]	1138	0.074	6.4

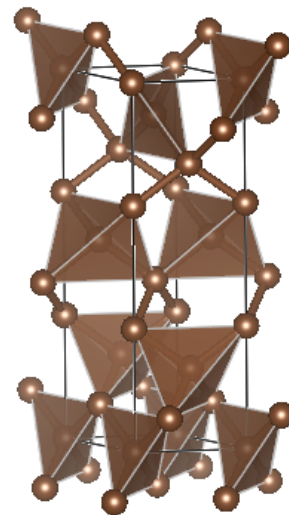
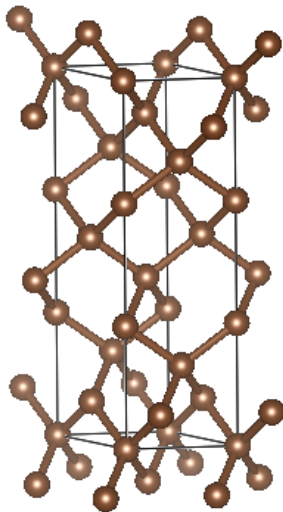
* E and ν values calculated using isotropic approximation



(a)



(b)



(c)

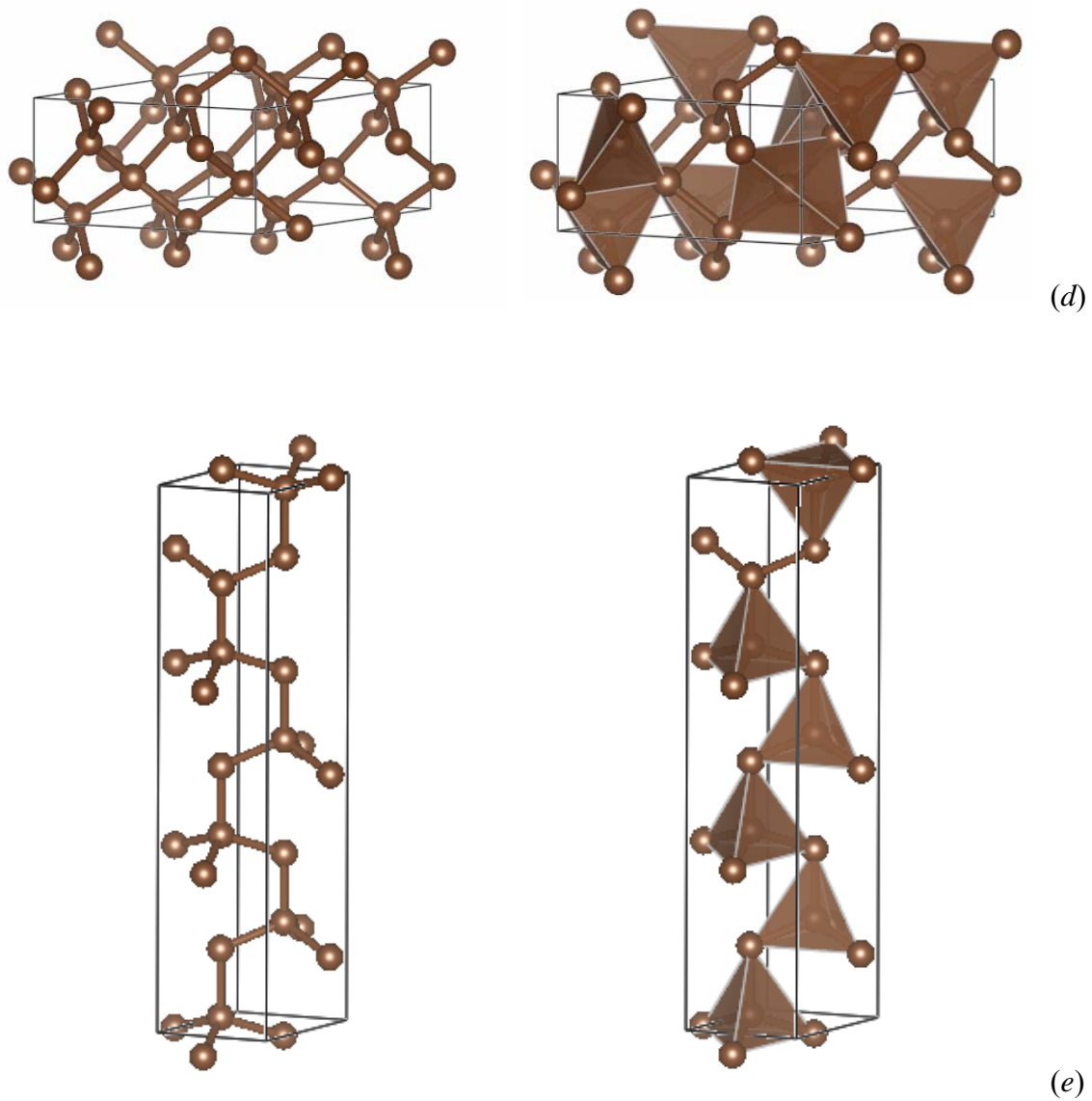
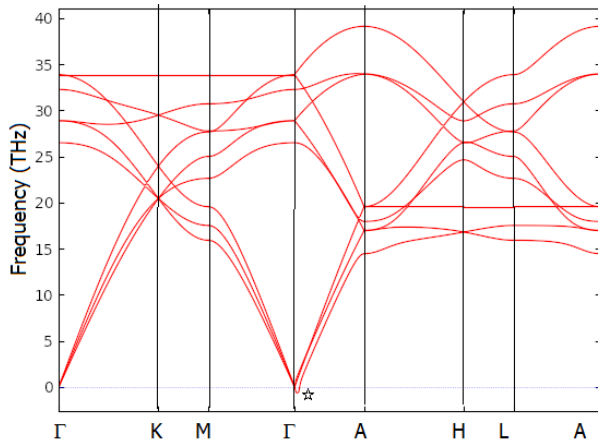
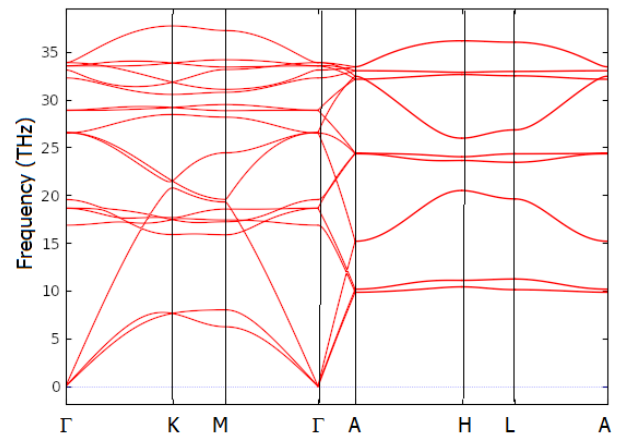


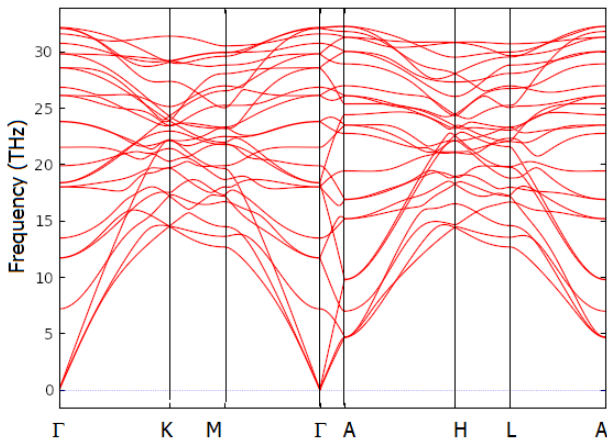
Figure 1. Sketches of the crystal structures of hexagonal carbon allotropes (with polyhedral representation): (a) **qtz** C_3 [9]; (b) **qtz** C_6 ; (c) **sta** C_9 ; (d) **qtz** C_{12} ; (e) **lon** C_{12} .



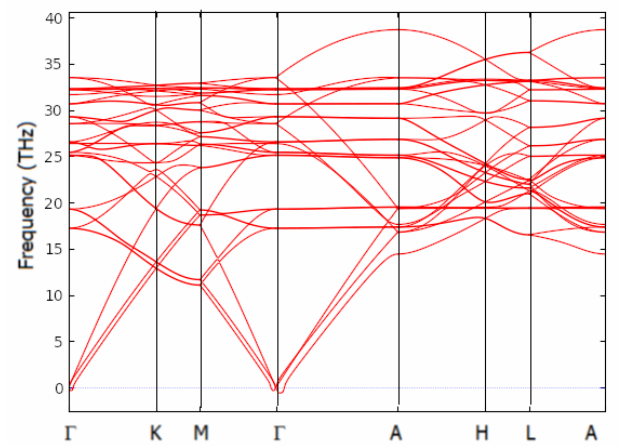
(a)



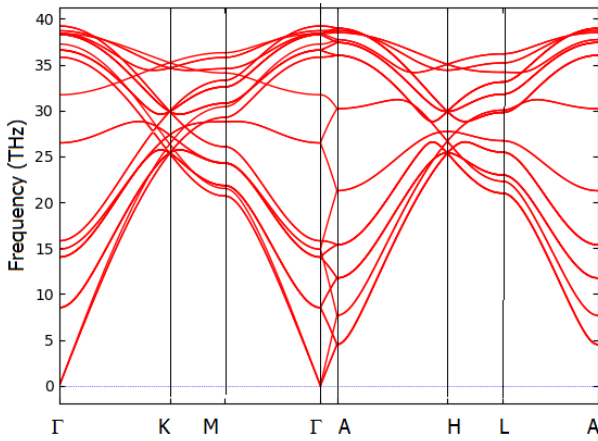
(b)



(c)



(d)



(e)

Figure 2. Phonon band structures of hexagonal carbon allotropes: (a) **qtz** C₃ (#180); (b) **qtz** C₆ (#179); (c) **sta** C₉ (#181); (d) **qtz** C₁₂ (#181); (e) **lon** C₁₂ (#194).

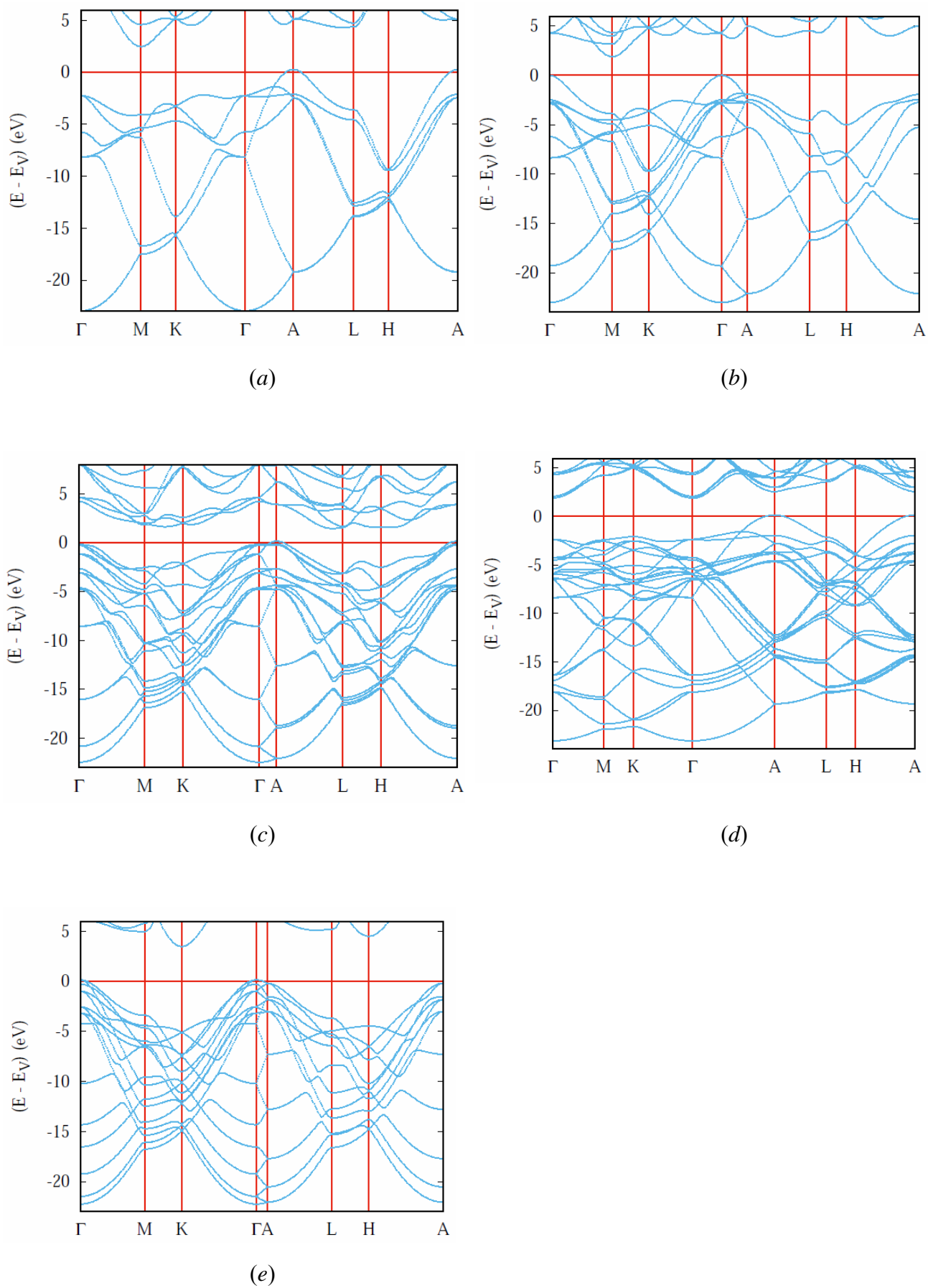


Figure 3. Electronic band structures of hexagonal carbon allotropes: (a) **qtz** C₃ (#180); (b) **qtz** C₆ (#179); (c) **sta** C₉ (#181); (d) **qtz** C₁₂ (#181); (e) **lon** C₁₂ (#194).