Superhard **lon** C_5 and derived carbon nitrides: C_4N and C_2N_2 . Crystal chemistry and first principles DFT studies.

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Abstract

Super-hard C_5 with **lon** topology (**lon**: Lonsdaleite hexagonal diamond) and characterized by the presence of sp^3 and sp^2 –like carbon sites is devised from crystal chemistry and used as template matrix structure for identifying original carbonitrides C_4N and C_2N_2 with **lon** topology except for the equiatomic belonging to a new topology (3,4**L**147). The steric effect of $N(2s^2)$ lone pair is highlighted in C_2N_2 in inducing an original structure of largely separated two-layered stacking of tetrahedra. The investigations based on crystal chemistry were backed by computations within the quantum density functional theory DFT. All systems were found cohesive and both mechanically (elastic constants) and dynamically (phonons band structures) stable. Super hardness characterizes the carbon allotrope C_5 and the nitrides C_4N and C_2N_2 . Metallic-like conductivities and insulating characters were identified.

Keywords

Carbon; carbon nitrides; DFT; Phonons; Hardness; topology.

Introduction

Carbon allotropes, especially those that approach diamond's physical properties (mechanical, electronic, thermodynamic,) benefit from continuous interest within the scientific community (cf. [1] for a mini review). Properties as hardness arising from the threedimensional 3D arrangements of *C4* tetrahedra are possessed by both the prevailing cubic form as well as in the less common hexagonal allotrope 'Lonsdaleite'. Topology-wise [2], the cubic and the hexagonal allotropes are the aristo-types labeled **dia** and **lon**, respectively. Other families of carbon allotropes follow these nomenclatures. Carbon insertions with other carbon hybridizations like sp² and sp¹ into diamond's C(sp³) tetrahedral lattice led to novel allotropes with original physical properties [3].

Expanding to carbon neighbors B and N, boron nitride BN as well as carbon nitrides such as C_3N_4 are superhard, albeit with lower hardness than diamond. They were early synthesized to replace expensive diamond, unstable at elevated temperatures, in mechanical applications (cf. review paper [4]). The research efforts to identify new chemical systems call for structure prediction programs like CALYPSO [5] and USPEX [6] and more recently machine learning crystallography code *CrystalMELA* [7]. Nevertheless, besides the opportunity offered by modern machine learned codes, novel structures with original properties as hardness and electronic structures can be identified from crystal engineering rationale as presented herein. In all cases such predictions need validation through quantitative studies of the energies and the derived physical properties with the help of first principles calculations. Throughout the years the well-established quantum mechanics framework of the density functional theory (DFT) [8,9] has been shown most efficient.

In the present paper, we further develop the topic of novel compounds based on light elements within the B-C-N diagram [4] by focusing on original carbon nitrides. Firstly, we propose a novel cohesive carbon allotrope; hexagonal C_5 through crystal chemistry schematics going from two dimensional 2D carbon to three-dimensional 3D carbon through rationalized C insertion; the 3D allotrope C_5 was found to belong alike Lonsdaleite to **lon** topology (3D **lon**- C_5). A similar protocol was used to derive 3D **lon**- C_6 from 2D carbon, for the sake of comparing the different physical properties between the two allotropes, mainly the mechanical ones in view of the different local structures. C_5 was then used as a template for selective substitutions of carbon for nitrogen leading to the nitride C_4N with **lon** topology on one hand, and to the equiatomic C_2N_2 on the other hand with characteristic layered structure of tetrahedral stacking, found to present a new topology (3,4L147). Particularly, the steric effect of $N(2s^2)$ lone pair in tailoring C_2N_2 into layered-like structure while keeping 3D dimensionality and the elevated hardness are closely examined. The investigations will show that all novel chemical systems (allotropes and phases) are found cohesive and stable both mechanically as well as dynamically and characterized by elevated Vickers hardness with metallic-like behavior for C_6 , C_5 allotropes and C_4N on one hand, and insulating behavior for the equiatomic C_2N_2 , on the other hand.

1- Computational framework

The identifications of the ground state structures corresponding to the energy minima and the subsequent prediction of their mechanical and dynamical properties were carried out by DFT-based calculations. The Vienna Ab initio Simulation Package (VASP) code [10,11] and the projector augmented wave (PAW) method [11,12] for the atomic potentials were used. DFT exchange-correlation (XC) effects were considered using the generalized gradient functional approximation (GGA) [13]. The relaxation of atoms onto the ground state structures was performed with the conjugate gradient algorithm according to Press et al. [14]. The Blöchl tetrahedron method [15] with corrections according to the Methfessel and Paxton scheme [16] was used for geometry optimization and energy calculations, respectively. Brillouin-zone (BZ) integrals were approximated by a special k-point sampling according to Monkhorst and Pack [17]. Structural parameters were optimized until atomic forces were below 0.02 eV/Å and all stress components were < 0.003 eV/Å³. The calculations were converged at an energy cutoff of 400 eV for the plane-wave basis set in terms of the k-point integration in the reciprocal space from $k_x(6) \times k_y(6) \times k_z(6)$ up to $k_x(12) \times k_y(12) \times k_z(12)$ to obtain a final convergence and relaxation to zero strains for the original stoichiometries presented in this work. In the post-processing of the ground state electronic structures, the charge density projections were operated on the lattice sites.

The mechanical stability criteria were obtained from the calculations of the elastic constants. The treatment of the results was done thanks to ELATE [18] online tool devoted to the analysis of the elastic tensors. The program provides the bulk B and shear G modules along different averaging methods; Voigt's method was used herein [19]. For the calculation of the Vickers hardness a semi-empirical model was used [20]. The dynamic stabilities were

confirmed from the phonon positive magnitudes. The corresponding phonon band structures were obtained from a high resolution of the cubic and hexagonal Brillouin Zones (BZ) according to Togo *et al.* [21]. The electronic band structures were obtained using the allelectron DFT based ASW method [22] and the GGA XC functional [13]. The VESTA (Visualization for Electronic and Structural Analysis) program [23] was used to visualize the crystal structures and charge densities.

2- Crystal chemistry rationale

2a- 2D/3D Carbon systems

Lonsdaleite (space group $P6_3/mmc$ No. 194) is characterized by a single 4-fold atomic position for carbon at 1/3, 2/3, z (Fig. 1a), with z = 0.06275. Such a low magnitude of the coordinate along the hexagonal vertical axis is related to the off-plane carbon atomic arrangement. Indeed, by changing z to 0 a graphitic structure is obtained (Fig. 1b) with noneclipsed (staggered) planes. The space group is kept the same (cf. Table 1). Then, the puckering of the graphitic layers is a key factor in going from 2D to 3D structures. Such transformation: Graphite \rightarrow Diamond is usually induced by high temperature/high pressure (HT/HP) conditions found in the Earth mantle near volcanoes or between tectonic plates with very slow kinetics. Inducing the 2D \rightarrow 3D carbon transformation can be modeled by inserting carbon (white spheres) between layers as shown in Fig. 1c. Geometry relaxation leads anew to a 3D structure with C₆ stoichiometry (Fig. 1d). A relevant feature is the *zigzag* (or shifted) alignment of the C3 entities (brown-white-brown spheres) within the cell that will be opposed to the other C₅ allotrope showing eclipsed-like arrangement (vide infra). The crystal data are presented in Table 1. Focusing on the ground state energies, the cohesive energies were obtained by subtracting the atomic energy of isolated carbon in a box (-6.6 eV) from the total energy, then by averaging as per atom – the same process is done for the other compounds in this paper. The cohesive energies of the three allotropes belonging to P63/mmc, No. 194, the planar 2D-C₄ is found more cohesive than 3D-C₄. This can be expected from the fact that graphitic-like carbon is more stable that 3D diamond-like Lonsdaleite 3D-C₄. Upon inserting extra carbon atoms (white spheres) leading to 3D-C₆ a decrease of the cohesive energy is observed due to expansion of the cell resulting into a rather open structure that will be reflected in the mechanical by a reduced hardness. At this point we mention that C₆ structure was used to model tricarbon C₃ molecule in the solid state [24]. The same stoichiometry C₆ with mixed sp^3-sp^2 in tetragonal system was identified with superhard and semi-conducting properties [25].

Alternative 2D-C₄ layered structure devised with eclipsed-like planes facing each other, i.e. oppositely to Fig. 1a, is shown in Fig. 2a. The space group is *P6cc*, No. 184, i.e., a lower symmetry than above studied allotropes, but the cohesive energy is close to 2D-C₄ above. The four carbon atoms in (4b) 1/3, 2/3, ³/₄ Wyckoff position are distributed with 2 C at $z= \frac{1}{4}$ and 2 C at $z=\frac{3}{4}$, leading to two horizontal planes. Inserting an extra carbon at $z=\frac{1}{2}$ (white sphere) leads to C₅ stoichiometry with a configuration shown in Fig. 2b. Such a strained structure was geometry relaxed following the protocol described in Section 1. The resulting calculations led to the 3D structure shown in Fig. 2c. Crystal symmetry search led to assign the space group *P*-6*m*2 No. 187 with two 2-fold carbon positions and one Wyckoff position at the cell center. The crystal data are given in Table 1, last columns. The representation in Fig. 2d shows two cells along the *c* hexagonal axis exhibiting two successive *C3* (brown-white-brown carbons) linear entities aligned along *c*, oppositely to the *zigzag* arrangement in C₆.

With three different carbon sites, such a structure will be used as a template to examine the effect of different nitrogen substitutions for carbon leading to a two carbonitrides as shown below. Regarding the cohesive energies whilst it decreases with respect to 2D-C₄, the relevant result is the strong decrease of the volume of C₅ signaling condensation. Such result lets expect a dense carbon allotrope with large hardness, i.e., strong incompressibility. Lastly, the topological analysis using TopCryst program [2] showed **lon** topology, like Lonsdaleite as above mentioned C₆.

To summarize on the two carbon allotropes: Starting from staggered 2D planes on one hand, and from eclipsed-like 2D planes facing each other, on the other hand, threedimensional 3D carbon allotropes were produced, and geometry optimized to their ground states, namely hexagonal C_6 and C_5 respectively. Energy-wise, while the 2D starting structures were found with slightly larger cohesive 2D-C₄ in space group *P*6₃/*mmc*, No. 194 (alike graphite) than 2D -C₄ in space group *P*6*mm*, No. 184, 3D C₆ was identified with much lower cohesion than C_5 (Table 1, last line). Crystallographically, the starting carbon planes different stacking of the 2D structures have been shown to have consequences on the 3D carbon structures involving vertically aligned *C3* motifs (eclipsed) in C₅ (Fig. 3a) versus *zigzag* -like (non-eclipsed or staggered) *C3* arrangement in C₆. Oppositely to the energy trends of the 2D pristine C₄ starting templates, 3D C₅ is found much largely cohesive than 3D- C_6 as shown in Table 1. Their different stackings of *C3* units along the hexagonal direction will have drastic effects on the mechanical properties, specifically regarding the hardness.

2b- Binary phases

C₅ was subsequently used as a template to devise binary C-N chemical systems by introducing nitrogen substitutionally. Namely, the following binary systems were obtained: C₄N and C₂N₂. Table 2 presents the calculated lattice parameters, and the structures are shown in Figure 3 in ball-and-stick and polyhedral representations. These binary systems were obtained following a protocol that we now detail: The replacement of central carbon (white sphere in Fig. 2c) by nitrogen leads to carbon rich nitride C₄N which shows a structure like pristine C₅ with small differences as for the slightly smaller volume and the lower cohesive energy. The shortest interatomic distance is observed for C-N with 1.35 Å but the C-C distances remain within range of C_5 . Then, increasing the amounts of nitrogen leading to C_3N_2 and C₂N₃ stoichiometries led to little cohesive systems after full geometry relaxations. Also, dynamic instabilities (negative phonon acoustic modes, cf. section 4-2) were also observed. Therefore, C₃N₂ and C₂N₃ were discarded from further analyses. However, by removing body center nitrogen, i.e., at N(1f) position from C₄N and letting C2 (2i) position be occupied by nitrogen thus leading to the C₂N₂ equiatomic nitride, a cohesive system (-1.66 eV/atom) was obtained with fully relaxed structure parameters given in the 2nd column of Table 2. The structure shown in Fig. 3c exhibits the peculiar feature of two puckered C-N layers forming corner sharing C2N2 tetrahedra within the layer, as illustrated in the tetrahedral representation. The C-N distance is now larger than in C₄N, i.e., d(C-N) = 1.46 Å and the interlayer distance is large as inferred from d(N-N) > 3 Å. Such features need further assessments that we approach with the charge densities and the electron localization projections in next Section 3.

3- Projections of the charge densities and the electron localization: where are the electrons?

3-1 Charge density projections.

For an illustration of the peculiar characteristics brought by nitrogen into the carbon lattice, the analysis is extended to a qualitative illustration of the charge densities. The difference of Pauling electronegativities (χ): χ C= 2.55 versus χ N = 3.04 let expect charge transfer from C to N. The other relevant point is the hybridization characters of carbon in C₅ and C₆, i.e., sp³ and sp². Figure 4 illustrates with yellow volumes the charge density. In Fig. 4a C₆ shows continuous charge density with characteristic C(sp³) and shifted *C3* vertical alignment with central C(sp²). Similar features of charge densities are observed in Fig. 4b for C₅ where the alignment of *C3* is not shifted but aligned with the nearest neighbor in the second cell as shown in the double cell of Fig. 3a RHS.

Significant charge density changes occur upon substituting central carbon for nitrogen, illustrated in Fig. 4c, with the large charge density localized on N, explained by its larger electronegativity versus C as mentioned above. This is also observed in Fig. 4d exhibiting the charge density on N pointing to the empty structure space along *c* hexagonal (vertical) direction. The labeling as carbonitrides of both C_4N and C_2N_2 is justified chemistry-wise.

3-2 Electron localization projections.

We further elaborate on the electron distribution in the equiatomic C_2N_2 especially as regarding the role played by the nitrogen lone pair in the interlayer space. For this purpose, we used the scheme of the electron localization function (ELF) devised by Becke and Edgecomb [26] as initially proposed within Hartree–Fock calculations. It was later adapted to DFT methods by Savin et al. [27] as based on the kinetic energy in which the Pauli Exclusion Principle is included. ELF is defined as a normalized function with $0 \le ELF \le 1$. For ELF = 0 very low electron localization (blue zones) and ELF = 1 for strong localization (red zones corresponding to large grey volume. A free electron–gas like behavior corresponds to ELF $\sim \frac{1}{2}$ with green zones (cf. ruler in Fig. 5). Figure 5 shows the corresponding 3D ELF of C_2N_2 with gray volumes on the left-hand side (LHS) and the 2D ELF slice on the right-hand side (RHS) with colors defined in the vertical ruler. The large gray volumes (LHS) of strong electron localization represent the nonbonding nitrogen lone pair (LP) pointing towards the interlayer space and less towards carbon where the C-N bonding occurs. RHS projection illustrates further the ELF with the large red area due to N(LP) covering almost all the empty space between the layers and leaving little zero localization (blue zones); it can be proposed that these features maintain the structure stability and let expect exceptional mechanical properties. The yellow areas qualifying medium localization is found between C and N, whence the bonding between them.

4- Physics of C₅ and the binary carbonitrides C₄N and C₂N₂.

4-1 Mechanical properties from the elastic constants

An analysis of the mechanical behavior was carried out with the calculation of the elastic properties through inducing finite distortions of the lattice. The system is then fully described by the calculated sets of elastic constants C_{ij} (i and j correspond to directions). Table 2 reports the elastic constants of C_5 , the binary carbonitrides C_4N and C_2N_2 as well as hexagonal C_6 presented in Section 2a (Table 1) for the sake of comparison. All C_{ij} values are positive, signaling mechanically stable phases. C_5 has systematically larger C_{ij} magnitudes versus C_6 that can be inferred from the two different structures involving vertically aligned *C3* motifs (eclipsed) in C_5 (Fig. 3a) versus *zigzag* (non-eclipsed) *C3* arrangement in C_6 (*vide supra*). The carbonitrides derived from C_5 also exhibit similarly large C_{ij} magnitudes especially C_4N whereas C_2N_2 shows smaller magnitudes. However, the large C_{33} magnitude close to 500 GPa in such layered-like system can be highlighted and correlated to the repulsive action of the two nitrogen LP's facing each other, as discussed above with the ELF.

The C_{ij} magnitudes are translated into mechanical properties trough deriving the bulk (B_V) and shear (G_V) moduli were obtained by Voigt's averaging [18] of the elastic constants using ELATE software [19]. The last two columns of Table 2 show the bulk and the shear moduli with values that follow the trends observed for C_{ij}. From the bulk and shear moduli, the ratio G_V/B_V called the Pugh ratio [28] allows distinguishing ductile behavior $(G_V/B_V < 1)$ from brittle behavior $(G_V/B_V > 1)$. The Pugh ratios of the different chemical systems are given in Table 3 in the last but one column. With $G_V/B_V(C_6) = 0.87$ a ductile behavior can be assigned to C₆ due to its structural characteristics of *C3 zigzag* stacking along the hexagonal c axis. Oppositely $G_V/B_V(C_5) = 1.03$ larger than 1 and the derived nitrides with similar Pugh

ratios can be considered as brittle. Using the Pugh ratios, we then calculated the Vickers hardness *Hv* with Tian et al. model of microscopic theory of hardness [20]:

$$Hv = 0.92 (G_V/B_V)^{1.137} G_V^{0.708}$$

The last column of Table 3 shows the calculated values of H_V . Expectedly, $H_V(C_6) = 49$ GPa is calculated much lower than $H_V(C_5) = 70$ GPa qualified consequently as super-hard but $H_V(C_4N) = 72$ GPa is slightly larger due to the smaller volume and the short C-N connections. Lastly, $H_V(C_2N_2) = 62$ GPa is a large magnitude despite the layered-like structure. It can be assumed that the high hardness arises from the strong bonding within the thick layers of *C2N2* tetrahedra.

4.2 - Dynamic properties from the phonons

A relevant criterion of phase dynamic stability is obtained from the properties of the phonons, defined as quanta of vibrations. Their energy is quantized with the Planck constant 'h' used in its reduced form, i.e., \hbar with $\hbar = h/2\pi$, resulting into by $E = \hbar\omega$ where ω is the frequency. Figure 6 depicts in four panels the phonons band structures of the two allotropes C_6 and C_5 and the latter's derived nitrides C_4N and C_2N_2 . The bands develop along the major lines of the hexagonal Brillouin Zone (horizontal x-axis). The frequency along the y-axis is expressed in units of Terahertz (THz, with 1 THz = 33 cm^{-1}). There are 3N-3 optical modes found at higher energy than three acoustic modes that start from zero energy ($\omega = 0$) at the Γ point (center of the Brillouin Zone), 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 optic modes. All phonon frequencies are found positive letting confirm the dynamic stability of the announced allotropes and the two nitrides. The highest frequencies in all panels are close to 40 THz, equivalent to 1650 cm⁻¹. This magnitude is exactly within the range of C=C vibrations with a strong signal, i.e., 1625-1680 cm⁻¹ in the molecular state as listed in the web-available "RAMAN Band Correlation Table". The second highest vibration is found with bands around 50 THz in C₄N, arising from the shorter C-N distance of 1.35 Å versus inter-carbon separation in C₅ with of 1.46 -1.54 Å (Table 1). Lastly, in Fig. 6c the flat band along Γ -A at E = 0 THz, i.e., along the vertical k_z BZ direction of reciprocal space, is a signature of no dispersion of bands along the empty structural gap characterizing C_2N_2 .

4-3 Electronic band structures

Figure 7 shows in four panels the band structures of the two allotropes and the two nitrides in the hexagonal Brillouin Zone. The zero energy along the y-axis is considered with respect to the Fermi level E_F crossed by finite bands in C₆, C₅ and C₄N, i.e., with no separation between the valence band VB and the conduction band CB at E_F . These three systems are then considered as metallic as resulting from the presence of C(sp²) with dispersed π -like electrons.

An exception can be observed for the equiatomic C_2N_2 where direct band gap of ~5 eV between A_{VB} and A_{CB} and the top of the valence band VB. Here the energy reference E_V is considered with respect to the top of VB. Such a result can be explained by the localization of charge density around N pointing through the LP towards the interlayer space.

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TABLES

	3D-C ₄ <i>P</i> 6 ₃ / <i>mmc</i>	2D-C ₄ <i>P</i> 6 ₃ / <i>mmc</i>	3D-C ₆ P6 ₃ /mmc	2D-C ₄ <i>P6mm</i>	3D C ₅ <i>P</i> -6 <i>m</i> 2		
	No. 194	No. 194	No. 194	No. 184	No. 187		
<i>a</i> , Å	2.505	2.460	2.484	2.461	2.487		
<i>c</i> , Å	4.169	6.732	6.953	6.698	5.581		
$V_{cell},{ m \AA}^3$	22.66	35.29	37.14	37.14	29.88		
Shortest dist.	d(C-C) =1.54	d(C-C) =1.42	d(C1-C2) =1.45	d(C-C) =1.42	d(C-C') =1.46		
/Å			d(C1-C1) =1.55		d(C-C) =1.54		
Atomic	C(4f) 1/3,2/3,0.06275	C(4f)1/3,2/3,0.0	C1(4f) 2/3,1/3,0.9579	C(4b) 1/3,2/3, 3/4	C1 (2h) 1/3 2/3 0.861		
position			C2(2d) 2/3,1/3, ¹ / ₄		C2 (2i) 2/3 1/3 0.762		
					C'(1f) 2/3 1/3 1/2		
E(Total)eV	-36.28	-36.90	-48.88	-36.72	-42.49		
E _{coh} /at. eV	-2.47	-2.63	-1.54	-2.58	-1.89		

Table 1 Crystal structure parameters of carbon allotropes.

<i>P</i> -6 <i>m</i> 2 No 187	C_4N	C_2N_2
Topology	lon	3,4 L 147
<i>a</i> , Å	2.521	2.377
<i>c</i> , Å	5.388	6.382
V_{cell} , Å ³	29.66	31.25
	d(C1-N)=1.35	d(C-N)=1.46
Shortest d-d- Å	d(C2-C2)=1.52	d(C-C)=1.63
	d(C1-C2)=1.57	d(N-N)=3.73
Atomic	C1 (2h) 1/3 1/3 0.751	C (2h) 1/3 2/3 0.872
position	C2 1f) 2/3 1/3 ¹ ⁄2	N (2i) 2/3 1/3 0.792
E(Total) eV	-41.99	-33.42
E _{coh} /at. eV	-1.74	-1.66

Table 2. Crystal structure parameters of novel binary phases.

Atomic energies (atoms in a large box): E(C) = -6.6 eV, E(N) = -6.8 eV.

Table 3. Elastic constants C_{ij} , bulk B_{Voigt} , shear G_{Voigt} modules, and Vickers hardness $H_{Vickers}$ are in GPa (Giga Pascals) unit.

	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	$\mathbf{B}_{\mathrm{Voigt}}$	G_{Voigt}	G_V / B_V	H _{Vickers}
C ₆	641	139	100	1525	251	306	387	337	0.87	49
C ₅	920	95	46	1453	412	333	407	423	1.04	70
C ₄ N	851	108	159	1707	372	356	409	435	1.06	72
C_2N_2	1056	140	52	498	458	268	344	356	1.03	62

FIGURES



Figure 1. Schematic transformation from 3D C₄ Lonsdaleite (a) to layered 2D C₄ (b), then in (c) the subsequent insertion of carbon (white spheres), and d) the fully geometry optimized 3D C₆ structure. Space group $P6_3/mmc$, No. 194 (see text).



Figure 2: Schematic transformation from layered 2D C₄ (a) and the change of stoichiometry to C₅ (b) by inserting C at $z=\frac{1}{2}$ (white sphere); c) the fully geometry optimized 3D C₅, with d) shwoing a double cell along c-hexagonal direction to highlight the alignment of *C3* (brown-white-brown spheres) motifs along the hexagonal vertical axis. Space group *P*-6*m*2, No. 187 (see text).



b)



Figure 3: Crystal structure in ball-and-stick and tetrahedral representations of a) C_5 (the white sphere illustrates the additional carbon as shown in Fig. 1), b) C_4N , c) C_2N_2 . Brown, and grey spheres represent C and N respectively. Hexagonal c-axis is along the paper sheet.



Figure 4: Charge density projections (yellow volumes) of a) C_6 , b) C_5 , b) C_4N , c) C_2N_2



Figure 5. Electron Localization function ELF in equiatomic C_2N_2 nitride highlighting the large steric effect of non-bonding $N(2s^2)$ -like lone pair (LP) on inducing the bilayer structure. ELF projections are shown in 3D grey volumes and 2D plane LHS (left hand side) and a plane slice along hexagonal direction RHS (right hand side). The ruler represents the ranges of ELF magnitudes from 0 to 1 with corresponding colors (cf. text).



Figure 6: Phonons band structures of a) C_6 , b) C_5 , c) C_4N , d) C_2N_2



Figure 7: Phonons band structures of a) C_6 , b) C_5 , c) C_4N , d) C_2N_2