Systematic enumeration of crystalline networks with only sp\textsuperscript{2} configuration in cubic lattices

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Systematic enumeration of crystalline networks with some special topological characters is of considerable interest in both mathematics and crystallography. Based on the restriction of lattice in cubic and inequivalent nodes not exceeding three, a simple method is proposed for systematic searching for three-dimensional crystalline networks with only sp\textsuperscript{2}-configuration nodes (C-sp\textsuperscript{2}-TDTCNs). We systematically scan the cubic space groups from No.195 to No.230 and find many C-sp\textsuperscript{2}-TDTCNs including all the previously proposed cubic ones. These C-sp\textsuperscript{2}-TDTCNs are topologically intriguing and can be considered as good templates for searching carbon crystals with novel properties, predicting high pressure phases of element nitrogen and designing three-dimensional hydrocarbon crystals. Structure optimizations are considered by regrading these C-sp\textsuperscript{2}-TDTCNs as carbon crystals and the corresponding energetic stability of these carbon crystals are evaluated, using the the density functional theory (DFT) based first-principle calculations. Our results are of wide interests in mathematics, condensed physics, crystallography and material science.

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INTRODUCTION

Systematic enumeration of crystalline networks with some special topological characters is of considerable interest in both mathematics and crystallography. With particular importance, the three-dimensional (TD) four- and/or three-connected networks relevant to a wide range of systems (especially to the crystal structures, such as zeolitic and the well-known diamond) have been systematically investigated \cite{1, 11}. TD three-connected networks (TDTCNs) have also been considered \cite{2, 4, 6, 8} as topologically intriguing structures in mathematics and are also significant in crystallography. The crystalline ground state of carbon, namely graphite, contains carbon atoms with perfect sp\textsuperscript{2}-configuration (the ground state of the binary compound of boron and nitrogen, hexagonal boron nitride, also prefers such a sp\textsuperscript{2}-configuration). But the graphite structure is not an exact TD network. Many efforts have been paid on predicting carbon crystals with sp\textsuperscript{2}-configuration in exact TD networks with the belief that graphite is not the only way to fill the TD space with only trigonal sp\textsuperscript{2}-like atoms \cite{12, 39}. There are many TDTCNs \cite{2, 4, 6, 8} satisfying such a requirement and some of them have been investigated as carbon crystals \cite{12, 39} showing novel physical properties. The second fact implying the signification of TDTCNs (especially of those with sp\textsuperscript{2}-configuration, sp\textsuperscript{2}-TDTCNs) is about nitrogen. At ambient condition, element nitrogen forms the only gas phase of molecular N\textsubscript{2} with nitrogen-nitrogen triple bond. With the progress in high pressure technology, scientists realized a phase transition from molecular nitrogen (N\textsubscript{2}) to an incompressible single-bonded cubic gauche phase (cg-N) \cite{40, 41}. In such a novel solid phase, nitrogen atoms form nontraditional sp\textsuperscript{2}-hybridization where three electrons bond to three neighbours (fill three sp\textsuperscript{2}-hybridized orbits) forming a distorted sp\textsuperscript{2}-configuration and the lone pair electrons fill the fourth sp\textsuperscript{2}-hybridized orbit. Many followed theoretical predictions \cite{12, 47} also show that high pressure nitrogen prefers the TDTCNs with distorted sp\textsuperscript{2}-configurations. Thirdly, sp\textsuperscript{2}-TDTCNs are also good templates for designing TD hydrocarbon crystals. Many efforts have been paid in this direction \cite{18, 53}. For example, K4-carbon \cite{35, 37} to K4-hydrocarbon \cite{53}, graphene \cite{54} to graphane \cite{48} and graphite to graphane crystals \cite{49}.

Predictions of the TDTCNs can be found in many previous works \cite{2, 4, 6, 8} and the predictions of non-graphite TD sp\textsuperscript{2}-hybridized carbon crystals, according to our knowledge, were started in 1983 by Hoffmann (bct4-carbon) \cite{12}. Since 1983, many scientists have reported their predictions on TD sp\textsuperscript{2}-hybridized carbon crystals, such as H6-carbon in 1990 \cite{13}, 6.8\textsuperscript{2}D (polybenzene) and 6.8\textsuperscript{2}P in 1992 \cite{24}, 6.8\textsuperscript{2}G and P56 in 1993 \cite{25}, carbon forms in 1995 \cite{26}, C20-carbon in 1997 \cite{27} and later in 1998 \cite{28}, FCC-(C\textsubscript{28})\textsubscript{2}, FCC-(C\textsubscript{36})\textsubscript{2} and FCC-(C\textsubscript{40})\textsubscript{2} in 1998 \cite{29}, R6-carbon and BCT8-carbon in 1998 \cite{29}, FCC-(C\textsubscript{64})\textsubscript{2} in 2003 \cite{32}, K4-carbon in 2008 \cite{33} and 2009 \cite{36, 37}, C152 and C\textsubscript{200} in 2010 \cite{31}, TD tubular carbons \cite{14, 33, 34, 38, 39} and Schwarztite carbons (P, D, G surface) \cite{15, 21, 22}. By combining graph theory with quantum mechanics, Winkler et al. systematically predicted \cite{39, 51} 14 TD sp\textsuperscript{2}-hybridized carbon crystals with up to six atoms per unit cell. Their
results include previously proposed bct4-carbon[12], H6-carbon[13], R6-carbon[29] and K4-carbon[35–37].

Very recently, with the idea of substitution mentioned by Sheng et al (T-carbon)[55], we have also successfully constructed[56] a simple TD sp²-hybridized carbon crystal (sp²-diamond) with intriguing configuration, which belongs to the same space group of diamond and has only one inequivalent atomic position. However, the number of the TDTCNs is infinite. We can not enumerate all of them without any restrictions. In this paper, we report a partial solution to this problem, based on a restriction of lattice in cubic and inequivalent atomic positions not exceeding three. With such a restriction and the group theory, a systematic (not a global) enumeration of cubic TDTCNs with sp²-like topological configurations (C-sp²-TDTCNs) by designed-computational-program becomes possible. We have systematically scanned all the cubic space groups from No.195 to No.230 and found many C-sp²-TDTCNs including all the previously proposed cubic ones.

METHOD

Before we introduce the method of our systematic enumeration of C-sp²-TDTCNs, four simple but very useful rules are discussed. Rule one, if a C-TDTCN contains only one inequivalent atomic position, the three neighbours for every atoms are themselves; Rule two, if a C-TDTCN contains only two inequivalent atomic positions, its two inequivalent atoms form a chemical bond. Rule three, if a C-TDTCN contains only three inequivalent atomic positions, its three inequivalent atoms form an angle. Rule four, variation of lattice constant for any cubic crystal does not affect its bond angles. Based on these four simple rules, we can systematically search C-sp²-TDTCNs with one, two and three inequivalent atoms by random putting an atom, a bond and an angle, respectively, in a given cubic lattice in a special space group with a defined sp²-criterion. Such an idea enhances the probability of generating C-sp²-TDTCNs in comparison with a totally random method. A simple procedure implementing such an idea is shown in Fig.1. Predictions of C-sp²-TDTCNs containing more than three inequivalent atomic positions or belonging to non-cubic lattice become more complicated (that can also be solved in principle) and are not considered in our present work.

Based on the procedure shown Fig.1, one can systematically search C-sp²-TDTCNs in the following four simple steps. I) Choose a cubic lattice with designated lattice constant and space group and set a sp²-criterion for identifying structures as C-sp²-TDTCNs, namely the cutoff radius (Rcut) for the fourth neighbour, the minima and maxima of bond lengths (Rmin, Rmax) and bond angles (θmin, θmax) in C-sp²-TDTCNs.

II) Randomly input the position or positions for the inequivalent atom or bond or angle in the chosen lattice and operate them by corresponding symmetry operators to construct a testing-crystal. III) Calculate the bond lengths and bond angles for each inequivalent atom and find out the θmin, θmax, Rmin and Rmax in this structure. If θmin<θmin or θmax>θmax give up and go to A to create a new structure. If Rmin<Rmin and Rmax>Rmax give up and go to A to create a new structure. If Rmin<Rmin and Rmax<Rmax, give up and go to A to create a new structure. If Rmin>Rmin and Rmax>Rmax record and enlarge the cell with ratio of Rmax/Rmin. If Rmin>Rmin and Rmax<Rmax give up and go to A to create a new structure. If Rmin>Rmin records and reduce the cell with ratio of Rmin/Rmax. If Rmin>Rmin and Rmax>Rmax record the structure with the initial cell.

FIG. 1: Procedure for systematic searching for C-sp²-TDTCNs
TDTCNs can be found in every space group but some of including all the previously proposed cubic ones (some
off radius of 2.0˚
from No.195 to No.230 based on the requirements of cut-
tion of a structure, which degenerate to the seven ones with relatively
and bond angles. If the reduced structure is still three-connected one
and bond lengths and bond angles. We identify that six of them are the previously proposed
6.8\textsuperscript{2}G (No.230)\textsuperscript{16, 25}, interpenetrated-K4 (No.230, we
revert it as IK4)\textsuperscript{4, 8}, 6.8\textsuperscript{2}P (No.229)\textsuperscript{24}, sp\textsuperscript{2}-diamond
(No.227)\textsuperscript{20}, 6.8\textsuperscript{2}D (No.224)\textsuperscript{24} and K4 (No.214)\textsuperscript{55, 57}
crystals. Their crystalline views (fully optimized carbon crystals with first-principles method with calculation
details provided in the supplementary information) are shown in FigS1. (a), (b), (c), (d), (e) and (f),
respectively, in the supplementary information. We name
these C-sp\textsuperscript{2}-TDTCNs as 230-96h, 230-16b, 229-48k, 227-96g, 224-24i and 214-8a, respectively, according to their
space group numbers and Wyckoff positions. Their corresponding lattice constants and inequivalent atomic
positions are summarized in Table SI in the supplementary information. The seventh one belonging to 206 space
group has not been reported as a carbon crystal before but was proposed as the 3/6/c5 configuration by E. Koch et al in 1995\textsuperscript{6} (The structure of sp\textsuperscript{2}-diamond\textsuperscript{55} was also proposed as 3/6/c3 by E. Koch 1995\textsuperscript{6}). Its perspective views of both crystalline and primitive cells are shown in FigS1 (g) and (h), respectively. From its crystalline view, we can see that it contains eight interconnected benzene rings in its cubic cell similar to that of 229-48k but in different connecting manner. We name it as 206-48e according to its space group number and the fact that it contains one inequivalent atomic position at the Wyckoff position of 48e (0.888, 0.985, 0.155).

In our searching process, only seven C-sp\textsuperscript{2}-TDTCNs containing one inequivalent atomic position were found. Although our searching process is non-global, we still believe that there are only seven C-sp\textsuperscript{2}-TDTCNs with one inequivalent atomic position under the given requirements of cutoff radius, bond lengths and bond angles. We have also found, in some other space group, many C-sp\textsuperscript{2}-TDTCNs with only one inequivalent atomic position which degenerate to the seven ones with relatively higher symmetry. For example, we found four equivalents for 224-24i (6.8\textsuperscript{2}D) in space groups 228 (228-192h), 227 (227-192i), 215 (215-24j) and 201 (201-24h), respectively. More equivalent relations among these C-sp\textsuperscript{2}-TDTCNs with only one inequivalent atomic position are shown in Table SI. Furthermore, these seven inequivalent C-sp\textsuperscript{2}-TDTCNs can also be found in the following two con-atomic positions for these C-sp\textsuperscript{2}-TDTCNs are based on the post-processes of structure optimizations by regarding these C-sp\textsuperscript{2}-TDTCNs as sp\textsuperscript{2}-hybridized carbon crystals. We have considered further energy evaluation for these C-sp\textsuperscript{2}-TDTCNs. In the following, we introduce our results of C-sp\textsuperscript{2}-TDTCNs templates for sp\textsuperscript{2}-like carbon crystals, high pressure crystals of element nitrogen and TD hydrocarbon crystals.

FIG. 2: Some selected crystalline views of new C-sp\textsuperscript{2}-TDTCNs found in present work. Different colors indicate inequivalent atomic positions and D, G, P indicate the surface types.

RESULTS AND DISCUSSION

In our present work we systematically enumerate the C-sp\textsuperscript{2}-TDTCNs by the method as discussed above. We name all the C-sp\textsuperscript{2}-TDTCNs with their space group number and their corresponding Wyckoff positions. For example, the previously proposed 6.8\textsuperscript{2}D\textsuperscript{24}, C20-carbon\textsuperscript{27, 28} and P192\textsuperscript{17} (P8\textsuperscript{19}), containing one, two and three inequivalent atoms, are named as 224-24i, 225-96k-96k-32f and 225-96k-96k-32f, respectively. With such a nomenclature, we can know the fundamental information of a structure, which are useful for identifying if it has been proposed previously and excluding repeating structures. Based on such a nomenclature, some C-sp\textsuperscript{2}-TDTCNs possess the same name due to their commonness in both space group and Wyckoff positions. We provide their structural characters to distinguish them. We have systematically scanned all the cubic space groups from No.195 to No.230 based on the requirements of cutoff radius of 2.0 Å, bond angles distributing in 109\textdegree-135\textdegree and bond lengths within the range from 1.3 Å to 1.7 Å and found many structurally intriguing C-sp\textsuperscript{2}-TDTCNs including all the previously proposed cubic ones (some of them are selected to show in Fig2). Especially, C-sp\textsuperscript{2}-TDTCNs can be found in every space group but some of them degenerate to the ones with relatively higher symmetry.

The summarized lattice constants and inequivalent
TABLE I: The nominations, characters or previous names (Ch/Pn), lattice constant (LC: Å), inequivalent positions (POS), and cohesive energy (Ecoh: eV/atom) of C-sp\(^2\)-TDTCNs with two inequivalent atomic positions

| C-sp\(^2\)-TDTCNs | Ch/Pn | LC   | POS1                        | POS2                        | Ecoh  |
|-------------------|-------|------|-----------------------------|-----------------------------|-------|
| 239-96h-48g       | New   | 10.341 | (-0.144, -0.326, 0.776)    | (-0.301, -0.875, 0.551)    | -6.824|
| 229-96l-96l       | New   | 12.534 | (-0.389, 0.231, -0.311)    | (0.054, -0.222, -0.629)    | -7.278|
| 227-192i-192i     | D96-D8| 18.048 | (0.339, -0.716, -0.606)    | (0.811, -0.412, -0.334)    | -7.443|
| 227-96g-32e       | D32-D8| 11.203 | (0.834, -0.166, 0.506)     | (0.387, 0.613, 0.613)      | -7.191|
| 227-192i-96g      | D72-D9| 15.605 | (0.130, 0.431, -0.749)     | (-0.281, 0.925, -0.781)    | -7.253|
| 226-192j-64g      | New   | 13.227 | (0.399, -0.447, -0.796)    | (0.621, -0.621, -0.379)    | -7.191|
| 225-48h-32f       | C20   | 9.146  | (-0.139, -0.139, 0.139)    | (0.000, -0.198, 0.198)     | -6.878|
| 225-48g-32f       | New   | 9.572  | (0.250, 0.430, -0.250)     | (0.850, 0.650, -0.650)     | -6.819|
| 225-192l-96k      | D32-D8| 11.203 | (0.834, -0.166, 0.506)     | (0.387, 0.613, 0.613)      | -7.191|
| 225-192l-96j      | New   | 15.605 | (0.130, 0.431, -0.749)     | (-0.281, 0.925, -0.781)    | -7.253|
| 224-48l-48l       | D96-D8| 9.168  | (0.728, 0.837, 0.947)      | (0.328, 0.642, 0.642)      | -7.121|
| 224-12g-8e        | New   | 5.342  | (0.000, 0.000, 0.362)      | (0.358, 0.642, 0.642)      | -7.219|
| 221-24m-24l       | P48-P9| 9.168  | (0.083, 0.353, 0.353)      | (0.500, 0.838, 0.278)      | -7.124|
| 221-48n-24l       | P72-P8| 9.464  | (0.840, 0.371, 0.734)      | (0.072, 0.500, 0.726)      | -7.525|
| 221-48n-24k       | P72-P8| 9.462  | (0.339, 0.234, 0.129)      | (0.000, 0.572, 0.774)      | -7.521|
| 220-24d-16c       | New   | 6.808  | (0.234, -0.500, 0.250)     | (-0.412, -0.412, 0.588)    | -7.118|
| 217-12e-8c        | Cage-N10 | 4.979 | (0.648, 0.000, 0.000)      | (0.324, -0.324, -0.324)    | -6.249|
| 215-46g-4e        | New   | 4.904  | (0.500, 0.500, 0.140)      | (0.693, 0.307, 0.307)      | -6.365|
| 215-24j-24j       | New   | 8.723  | (0.076, 0.458, 0.347)      | (0.677, 0.789, 0.561)      | -7.188|
| 214-48l-48i       | G48-G7| 10.532 | (0.347, -0.640, 0.196)     | (0.007, -0.669, 0.492)     | -7.039|
| 212-24e-8c        | New   | 7.705  | (0.803, 0.473, 0.305)      | (0.715, 0.715, 0.715)      | -6.972|
| 205-24d-16c       | New   | 6.391  | (0.410, 0.390, 0.672)      | (0.258, 0.242, 0.758)      | -6.967|
| 204-48h-24g       | G36-G7| 9.365  | (-0.133, -0.342, 0.274)    | (0.285, 0.000, 0.572)      | -6.721|
| 200-12j-8f        | New   | 5.451  | (0.241, 0.369, 0.000)      | (0.223, 0.777, 0.777)      | -7.067|
| 195-6g-4e         | New   | 4.1303 | (0.000, 0.500, 0.322)      | (0.241, 0.759, 0.759)      | -6.366|

When we consider the situation of C-sp\(^2\)-TDTCNs containing two inequivalent atomic positions, we have found 25 inequivalent C-sp\(^2\)-TDTCNs. The perspective crystalline views of these 25 inequivalent C-sp\(^2\)-TDTCNs are shown in FigS2 in the supplementary information and their corresponding lattice constants and inequivalent atomic positions are summarized in Table I. Most of the 25 C-sp\(^2\)-TDTCNs are new except that the C20-carbon (225-48h-32f) has been proposed as a carbon crystal\(^{27, 28}\) and the cage-N10 (217-12e-8c) has been proposed \(^{47}\) as a high pressure nitrogen phase. Some of them can be regarded as new Schwarzite surfaces (indicated in Table I), such as 227-192i-192i (D\(_{96}\)-D\(_{8}\)) surface with 96 atomic positions in its primitive cell and octagon rings, D96-D8), 221-24m-24l (P surface with 48 atomic positions in its primitive cell and nonagon rings, P48-P9) and 204-48h-24g (G surface with 36 atomic positions in its primitive cell and heptagon rings, G36-G7). These C-sp\(^2\)-TDTCNs distribute in space groups of 230, 229, 227, 226, 225, 224, 221, 220, 217, 215, 214, 212, 205, 204, 200, and 195. Some of them can also be found in other space groups or in the following condition of C-sp\(^2\)-TDTCNs containing three atomic positions (see the equivalent relations in Table II and III in the supplementary information). In addition, we have also found some C-sp\(^2\)-TDTCNs with two inequivalent atomic positions degenerating to those with only one inequivalent atomic position. Such as the one named as 228-96g-96g is equivalent to 224-24i (6.8\(^2\)D). More examples can be found in Table II in the supplementary information.

C-sp\(^2\)-TDTCNs with three inequivalent positions

There are more C-sp\(^2\)-TDTCNs containing three inequivalent atomic positions and the increase of the inequivalent atomic positions enlarges the state space and reduces the probability of meeting the special C-sp\(^2\)-TDTCNs in our searching process. Fortunately, we have found 48 of them including some Schwarzite type surface structures (indicated in Table II), such as the G type...
| C-sp²-TDTCNs | Ch/Pn | LC | POS1     | POS2     | POS2     | Ecoh  |
|--------------|-------|----|----------|----------|----------|-------|
| 230-96h-96h-96h | G144-G8 | 15.944 | (-0.054,-0.491,0.569) | (-0.152,-0.559,0.661) | (-0.099,-0.488,0.644) | -7.531 |
| 229-96l-48k-16f | New | 11.844 | (0.229,0.638,0.059) | (0.413,0.263,-0.263) | (0.317,0.317,0.317) | -7.125 |
| 229-48j-48k | New | 11.739 | (0.241,0.156,0.000) | (0.327,-0.187,-0.187) | (0.281,-0.111,-0.111) | -7.013 |
| 229-96l-48k-48k | P192-P8 | 14.901 | (0.278,-0.047,0.390) | (0.289,-0.173,0.289) | (0.324,-0.091,0.324) | -7.627 |

TABLE II: Nominations, characters or previous names (Ch/Pn), Lattice constant (LCÅ), Inequivalent positions (POS), Cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with three inequivalent atomic positions

230-96h-96h-96h (G144-G8) and P type 229-96l-48k-48k (P192-P8, proposed before[17, 19]). Most of them are never mentioned in literatures. Their corresponding lattice constants and inequivalent positions are summarized in Table II and their corresponding perspective crystalline views can be found in the supplementary Fig S3 and Fig S4. Some of them are identified to be the previously proposed FCC-(C₃₆)₂²³ (227-96g-96g-96g),
FCC-(C_{40})_{2}^{28} (227-192i-96g-32e), FCC-(C_{28})_{2}^{23} (203-96g-96g-32e) and P56-P7^{16} (195-12j-12j-6g). We notice that many new surface structures, such as 227-192i-192i-96g (D120-D7), 227-192i-192i-192i (D144-D8), 224-48l-48l-24l (D144-D8), 221-24l-24l-8g (P56-P8), 221-48n-48n-24k (P120-P8), 217-48h-48h-48h (G72-G8), and 201-24h-24h-8e (D56-D7) have not been proposed previously. Some new structures belonging to the same name (see 217-48h-48h-48h, 215-24j-24j and 206-48e-48e-48e) and we provide additional signs reflecting their structural characters for distinguishing them. For example, 6*A7^{6} means the structure with characteristic hexagons connecting six heptagons at its six armchair edges and 6*Z6^{6} indicates characteristic hexagons connecting six hexagons at its six zigzag vertexes.

From table II, we can see that these C-sp^{2}-TDTCNs distribute in space groups of 230, 229, 228, 227, 226, 225, 224, 223, 221, 217, 217, 216, 215, 214, 212, 207, 206, 204, 203, 201, 200, 197 and 195. This does not mean that C-sp^{2}-TDTCNs can not be found in other space groups. For example, we found 227-96g-96g-32e in No.210 as 210-96h-96h-32e with relatively lower symmetry. In addition, we have also found some C-sp^{2}-TDTCNs with three inequivalent atomic positions degenerating to those with one or two inequivalent atomic positions. Such as 213-8c-4a-4b to 230-16b (IK4) and 220-48e-48e-48e to 230-96h-32e (IK4). More examples can be found in Table SIII in the supplementary information.

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SUPPLEMENTARY INFORMATION for "Systematic enumeration of crystalline networks with only sp^2 configuration in cubic lattices"

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We optimized these C-sp^2-TDTCNs through regarding them as carbon crystals. Both the lattice constant and atomic positions of these C-sp^2-TDTCNs were fully optimized until the residual forces on each carbon atom to be less than 0.02 eV/Å. All the calculations of structure optimizations and energetic stability evaluations were performed using the density functional theory based VASP code [1] with the projected augmented wave (PAW) potential [2]. The exchange and correlation are approximated by general gradient approximation (GGA) developed by Perdew et al. [3]. The wave functions for all systems are expanded by plane-wave functions with cutoff energy of 500 eV. The Brillouin zone sample meshes based on the Monkhorst-Pack scheme are set to be denser enough (less than 0.25 1/Å) to ensure the accuracy of our calculations.

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TABLE I: The nominations, relations, lattice constant (LC: Å), inequivalent positions (POS), and cohesive energy (Ecoh: eV/atom) of C-sp²-TDTCNs with only one inequivalent atomic position

| C-TDTCNs     | Relation     | LC        | POS         | Ecoh  |
|--------------|--------------|-----------|-------------|-------|
| 230-96h      | 6.8²G        | 9.587     | (0.117, 0.548, 0.424) | -7.391 |
| 230-16b      | IK4-carbon   | 4.426     | (-0.125,-0.375, 0.375) | -6.346 |
| 229-48k      | 6.8²P        | 7.843     | (0.689, 0.689, 0.913) | -7.364 |
| 227-96g      | sp²-diamond  | 9.667     | (-0.049, 0.549,-0.726) | -7.179 |
| 224-24i      | 6.8²D        | 6.095     | (0.250, 0.087, 0.589) | -7.585 |
| 214-8a       | K4-carbon    | 4.126     | (-0.125,-0.375, 0.375) | -6.529 |
| 206-48e      | 3/6/c5       | 7.505     | (0.345,-0.111, 0.015) | -6.798 |
| 228-192h     | 6.8²D        | 12.191    | (0.207, 0.043, 0.875) | -7.585 |
| 227-192i     | 6.8²D        | 12.191    | (0.625, 0.793, 0.543) | -7.585 |
| 223-48i      | 6.8²P        | 7.843     | (0.311, 0.087, 0.689) | -7.364 |
| 222-48i      | 6.8²P        | 7.843     | (0.311, 0.087, 0.689) | -7.364 |
| 220-16c      | IK4-carbon   | 4.426     | (-0.125,-0.375, 0.375) | -6.346 |
| 215-24j      | 6.8²D        | 6.095     | (0.250, 0.087, 0.589) | -7.585 |
| 213-8c       | K4-carbon    | 4.126     | (-0.125,-0.375, 0.375) | -6.529 |
| 212-8c       | K4-carbon    | 4.126     | (0.375, 0.375, 0.375) | -6.529 |
| 211-48j      | 6.8²P        | 7.843     | (0.689, 0.689, 0.913) | -7.364 |
| 210-96h      | sp²-diamond  | 9.667     | (-0.049, 0.549,-0.726) | -7.179 |
| 206-16c      | IK4-carbon   | 4.426     | (-0.125,-0.375, 0.375) | -6.346 |
| 204-48h      | 6.8²P        | 7.843     | (0.689, 0.689, 0.913) | -7.364 |
| 203-96g      | sp²-diamond  | 9.667     | (-0.049, 0.549,-0.726) | -7.179 |
| 201-24h      | 6.8²D        | 6.095     | (0.250, 0.087, 0.589) | -7.585 |
| 199-8a       | K4-carbon    | 4.126     | (-0.125,-0.375, 0.375) | -6.529 |
TABLE II: The nominations, relations, lattice constant (LC: Å), inequivalent positions (POS), and cohesive energy (Ecoh: eV/atom) of C-sp^2-TDTCNs with two inequivalent atomic positions

| C-TDTCNs | Relation | LC  | POS1                         | POS2                         | Ecoh  |
|----------|----------|-----|------------------------------|------------------------------|-------|
| 228-192h-192h | 6.8^2P | 15.685 | (0.043, 0.155, 0.845) | (0.043, 0.155, 0.655) | -7.364 |
| 228-96g-96g | 6.8^2D | 12.191 | (0.467,-0.375, 0.783) | (0.462, 0.712, 0.375) | -7.585 |
| 226-192j-192j | 6.8^2P | 15.685 | (0.155, 0.957, 0.845) | (0.207, 0.905, 0.905) | -7.364 |
| 221-24m-24m | 6.8^2P | 7.843 | (0.311, 0.087, 0.689) | (0.413, 0.189, 0.811) | -7.364 |
| 220-48c-48c | 6.8^2G | 9.587 | (-0.798,-0.363,-0.674) | (-0.617,-0.547,-0.076) | -7.391 |
| 219-96h-96h | 6.8^2D | 12.191 | (0.125, 0.043, 0.793) | (0.043, 0.125, 0.793) | -7.585 |
| 219-48g-32e | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 218-24i-24i | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 218-12f-8e | 6.8^2P | 7.843 | (0.155, 0.957, 0.845) | (0.207, 0.905, 0.905) | -7.364 |
| 217-24g-24g | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 217-48h-48h sp^2-diamond | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 216-96h-96h | 6.8^2D | 12.191 | (0.125, 0.043, 0.793) | (0.043, 0.125, 0.793) | -7.585 |
| 216-48g-32e | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 215-48i-48i | 6.8^2G | 9.587 | (0.452, 0.424, 0.617) | (0.576, 0.383, 0.548) | -7.391 |
| 214-48h-48h sp^2-diamond | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 213-96g-32e | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 212-48g-32e | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 211-24h-24h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 210-48h-48h sp^2-diamond | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 209-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 208-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 207-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 206-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 205-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 204-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 203-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 202-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 201-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 200-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| 199-48h-48h | 6.8^2P | 7.843 | (0.087,-0.311, 0.311) | (-0.087,-0.311, 0.311) | -7.364 |
| C-TDTCNs   | Relation | LC    | POS1   | POS2   | POS3   | Ecoh   |
|-----------|----------|-------|--------|--------|--------|--------|
| 228-192h-192h-192h | 224-24h-24k-24k | 20.233 | (-0.343, 0.845, 0.577) | (0.440, 0.784, 0.940) | (0.501, 0.750, 0.910) | -7.545 |
| 226-192j-192j-192j | 221-48n-24l | 18.927 | (0.420, 0.315, 0.867) | (0.464, 0.250, 0.863) | (0.367, 0.314, 0.920) | -7.525 |
| 220-48e-48e-48e | 230-96b-48g | 10.340 | (-0.144,-0.326, 0.776) | (-0.301,-0.875, 0.551) | (0.394,-0.526, 0.576) | -6.824 |
| 216-48h-16e-16e | C20 | 9.125 | (0.547, 0.453, 0.272) | (0.373, 0.127, 0.627) | (0.010, 0.390, 0.390) | -6.878 |
| 213-8c-4a-4b | IK4-carbon | 4.426 | (-0.125,-0.375, 0.375) | (0.375, 0.375, 0.375) | (0.125,-0.625, 0.625) | -6.346 |
| 212-8c-4a-4b | IK4-carbon | 4.426 | (0.125,-0.625, 0.625) | (-0.125,-0.375, 0.375) | (0.125,-0.625, 0.625) | -6.346 |
| 210-96h-96h-96h-32e | 227-96g-96g-32e | 12.652 | (0.169,-0.533, 0.830) | (0.068,-0.288, 0.788) | (0.171,-0.171, 0.671) | -7.207 |
| 210-96h-96h-96h-32e | 227-96g-96g-96g | 17.491 | (-0.105, 0.605, 0.801) | (-0.244, 0.858, 0.858) | (-0.123, 0.778, 0.778) | -7.125 |
| 209-96j-96j-96j-32f | 225-96k-96k-32f | 15.146 | (0.596,-0.839,-0.728) | (0.455,-0.307,-0.307) | (0.404,-0.161,-0.272) | -7.219 |
| 207-24k-24k-24k | 221-48n-24k | 9.462 | (0.340, 0.234, 0.129) | (0.000, 0.572, 0.774) | (0.660, 0.766, 0.871) | -7.521 |
| 205-24k-24k-24k | 221-48n-24k | 9.462 | (0.340, 0.234, 0.129) | (0.000, 0.572, 0.774) | (0.660, 0.766, 0.871) | -7.521 |
| 203-96g-96g-32e | 227-96g-96g-32e | 12.652 | (0.169, 0.967, 0.330) | (0.213, 0.713, 0.932) | (0.171, 0.829, 0.671) | -7.207 |
| 203-96g-96g-96g | 227-96g-96g-96g | 17.491 | (-0.105, 0.605, 0.801) | (-0.244, 0.858, 0.858) | (-0.123, 0.778, 0.778) | -7.125 |
| 202-96j-96j-96j | 225-192i-96k | 15.146 | (0.596,-0.839,-0.728) | (0.455,-0.307,-0.307) | (0.404,-0.161,-0.272) | -7.219 |
| 202-96i-96i-32f | 225-96k-96k-32f | 13.221 | (0.319,-0.319, 0.449) | (0.377, 0.623, 0.744) | (0.337,-0.163, 0.337) | -7.076 |
| 201-24h-24h-24h | 204-48h-24g | 9.365 | (0.500, 0.928, 0.785) | (0.726, 0.867, 0.658) | (0.367, 0.842, 0.774) | -7.517 |
| 197-24f-24f-24f | 204-48h-24g | 9.365 | (0.500, 0.928, 0.785) | (0.367, 0.842, 0.774) | (0.342, 0.726, 0.867) | -7.517 |
| 195-12j-4e-4e | 200-12j-8f | 5.412 | (0.499, 0.271,-0.891) | (0.718, 0.718,-0.282) | (0.285,-0.285,-0.715) | -7.067 |
FIG. 1: Crystalline views of the seven inequivalent C-sp$^2$-TDTCNs. (a), (b), (c), (d), (e) and (f) are 230-96h (6.8$^2$G), 230-16b (IK4), 229-48k (6.8$^2$P), 227-96g (sp$^2$-diamond), 224-24i (6.8$^2$D) and 214-8a (K4), respectively. (g) and (h) are the crystalline views of 206-48e (3/6/c5) in crystal cell and primitive cell, respectively.
FIG. 2: Crystalline views of the 25 inequivalent C-sp$^2$-TDTCNs with three inequivalent positions, where different atomic positions are shown in different colors.
FIG. 3: Crystalline views of the 24 inequivalent C-sp\textsuperscript{2}-TDTCNs (No.230-221) with three inequivalent positions, where different atomic positions are shown in different colors.
FIG. 4: Crystalline views of the 24 inequivalent C-sp²-TDTCNs (No. 216-195) with three inequivalent positions, where different atomic positions are shown in different colors.