

Quantum-Chemical Study of the Structure and Properties of Hypothetical Superhard Materials Based on the Cubic Silicon–Carbon Nitrides

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Density functional B3LYP/6-31G(d,p) calculations have been carried out to study the structural peculiarities and physical properties of the series of cubic (defect zinc-blende) silicon–carbon nitrides with composition $\text{Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0, 1, 2, 3$). As model systems, we have considered six clusters with the structure of the adamantane molecule $(\text{CH})_4(\text{CH}_2)_6$ (**I**), hexamethylenetetramine-like molecules $\text{N}_4(\text{CH}_2)_{6-n}(\text{SiH}_2)_n$ (**II–V**) ($n = 0, 2, 4, 6$), and silicon-substituted adamantane molecule $(\text{SiH})_4(\text{SiH}_2)_6$ (**VI**). These 10 heavy-atom clusters have been used to simulate the crystalline fragments of diamond (**I**), cubic (defect zinc-blende) silicon–carbon nitrides (**II–V**), and cubic (zinc-blende) silicon solid (**VI**). It was found that the full B3LYP/6-31G(d,p) geometry optimization of these clusters allow us to reproduce the structures, unit cell parameters, and bulk modulus (hardness) of real crystals (**I** and **VI**) quite well and to predict the structural and mechanical properties of the hypothetical crystalline compounds (**II–V**).

I. Introduction

Since the first prediction of the possible existence of the superhard carbon nitride, $\beta\text{-C}_3\text{N}_4$, by Cohen^{1–3} in 1985–1990, there have been a flurry of experimental studies to synthesize and characterize such covalent solids (films) with the composition C_3N_4 . The number of experimental publications on the extremely hard materials is now too numerous to cite, but a rather complete description on the progress in this field can be visaged from some interesting publications of the last few years.^{4–14} Theoretical publications on the subject have also been made to explain the mechanical properties of some of the synthesized crystalline carbon nitrides, predominantly of the hexagonal $\beta\text{-C}_3\text{N}_4$ and $\alpha\text{-C}_3\text{N}_4$ forms, and to predict the properties of the new hypothetical forms of C/N/Si-containing compounds.^{13–31}

In our original attempt to deposit CN_x films, initiated at the Institute of Atomic and Molecular Sciences in Taipei, Taiwan, in collaboration with K. H. Chen, C. L. Chen, and co-workers,²⁶ it was found that the incorporation of Si atoms, vaporized from the silicon substrates used in the deposition study, resulted in the formation of crystalline SiCN_x films, preferentially with $\sim 1:2$ Si:C ratios. The requirement of Si atoms for formation of good-quality CN_x films was confirmed by the employment of SiH_4 as a precursor, together with CH_4 and NH_3 in the plasma-enhanced deposition.^{27,28}

This observation prompted our interest in the first principle quantum-chemical calculation of the structures and properties of $\text{Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0–3$) clusters beginning in early 1997. As a model system we have chosen the molecular systems reproducing the cubic unit cell structures of diamond and defect zinc-blende crystalline compounds (space group $P4_3/m$): adamantane $(\text{CH})_4(\text{CH}_2)_6$ (**I**), hexamethylenetetramine $\text{N}_4(\text{CH}_2)_6$ (**II**) and its

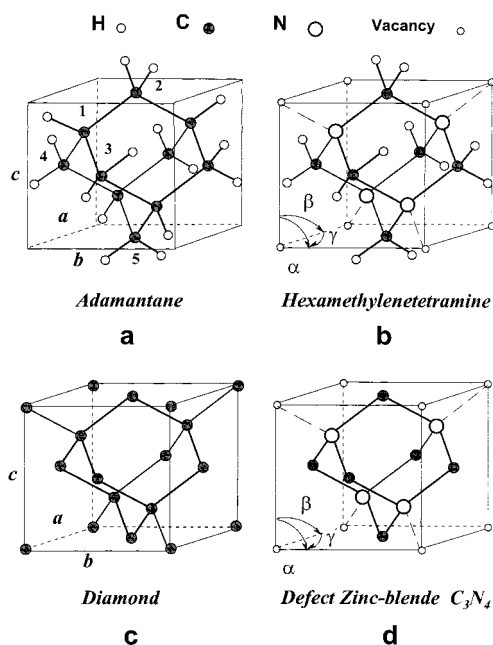


Figure 1. Model molecular systems, (a) adamantane $(\text{CH})_4(\text{CH}_2)_6$ and (b) hexamethylenetetramine $\text{N}_4(\text{CH}_2)_6$, reproducing the cubic unit cells of such crystalline solids as (c) diamond and (d) defect zinc-blend carbon nitrides $\text{dz-C}_3\text{N}_4$. a , b , c and α , β , γ are the unit-cell parameters.

derivatives $\text{N}_4(\text{CH}_2)_{6-n}(\text{SiH}_2)_n$ (**III–V**) (where $n = 2, 4, 6$ is the number of carbon atoms replaced by silicon atoms), and silicon-substituted adamantane $(\text{SiH})_4(\text{SiH}_2)_6$ (**VI**) (in which every carbon atom is replaced by a silicon atom). The correspondence between the structures of the model molecular systems (adamantane and hexamethylenetetramine) and the cubic unit cell of the crystalline solids (diamond and defect zinc-blende carbon nitrides with composition C_3N_4) is illustrated in Figure 1a–d. The structure of the hypothetical defect zinc-blende carbon nitride (we will denote structures of such kind as $\text{dz-C}_3\text{N}_4$) can be described as being derived from the diamond

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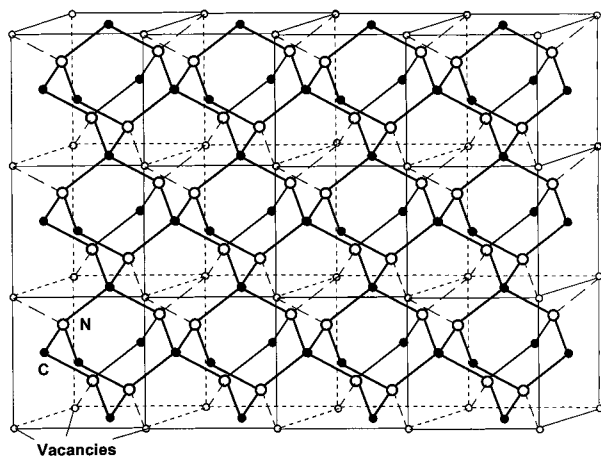


Figure 2. Fragment of a three-dimensional network of the cubic (defect zinc-blende) crystal structure of the carbon nitrides $\text{dz-C}_3\text{N}_4$ constructed from the simple hexamethylenetetramine model systems (Figure 1b and 1d).

structure by the replacing some of the carbon atoms with nitrogen atoms so that each C atom is bound to four N neighbors by covalent sp^3 bonds and each N atoms is bound to only three C atoms (one C site is vacant) with the C–N–C bond angle close to the tetrahedral (sp^3) angle of 109.5° rather than the trigonal (sp^2) angle of 120° . The three-dimensional network of the cubic (defect zinc-blende) crystal structure of the carbon nitrides $\text{dz-C}_3\text{N}_4$ constructed from the simple hexamethylenetetramine model systems (Figure 1b and 1d) is illustrated in Figure 2.

Note that prior to the completion of this work, Wang et al.³¹ published a theoretical paper on the structural and mechanical properties of silicon–carbon–nitrides of the same composition but having hexagonal $\beta\text{-Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0-3$) crystal packing. These systems are based on the well-known hexagonal $\beta\text{-Si}_3\text{N}_4$ structure, which belongs to space group $P6_3/m$. The authors have used the full-potential LAPW (linearized augmented plane wave) method,^{32,33} based on the local density (LDA) approximation for the exchange–correlation potential³⁴ and Kerker-type pseudopotentials.³⁵ From these calculations it was found that the systematic substitutions of the Si atoms by the C atoms in silicon nitrides of the $\beta\text{-Si}_3\text{N}_4$ form result in an increase of the bulk modulus up to 444 GPa.³¹

II. Computational Methods

The structural parameters of the series of cubic (diamond and defect zinc-blende) clusters $(\text{CH})_4(\text{CH}_2)_6$ (I), $\text{N}_4(\text{CH}_2)_{6-n}(\text{SiH}_2)_n$ (II–V) ($n = 0, 2, 4, 6$), and $(\text{SiH})_4(\text{SiH}_2)_6$ (VI) have been optimized at the density functional level using Becke's three-parameter nonlocal exchange functional³⁶ with the correlation functional of Lee, Yang, and Parr³⁷ (B3LYP approach). We have used the 6-31G(d,p) basis set including p and d polarization functions for hydrogens and heavy atoms, respectively.³⁸ The same (B3LYP/6-31G(d,p)) method was used for calculation of the vibrational frequencies (force constants) and charge distribution at the optimized (lowest-energy) geometry. The bulk modulus (hardness) of the compounds under consideration has been estimated using the empirical expression proposed by Cohen^{1,13}

$$B = \frac{\langle N_C \rangle}{4} \frac{1971 - 220\lambda}{d^{3.5}} \quad (1)$$

where $\langle N_C \rangle$ and d are the average coordination number and bond

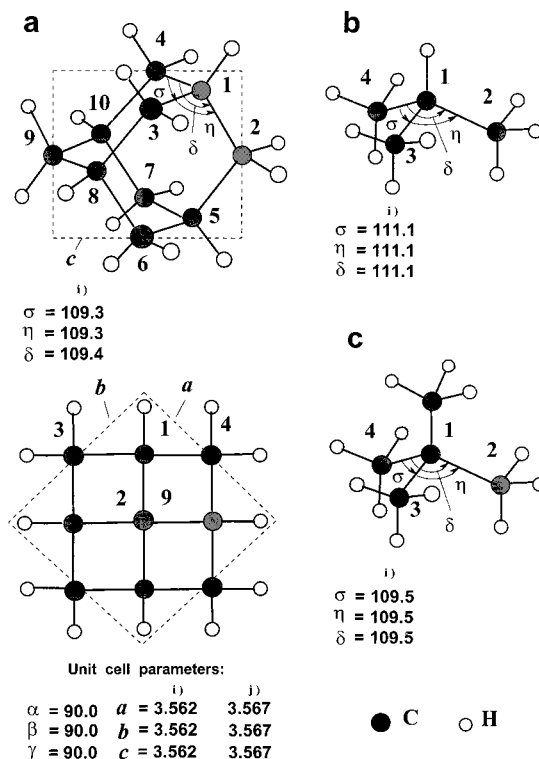


Figure 3. B3LYP/6-31G(d,p) optimized structures of the adamantane $(\text{CH})_4(\text{CH}_2)_6$ (model a), isobutane $\text{HC}(\text{CH}_3)_3$ (model b), and neopentane $\text{C}(\text{CH}_3)_4$ (model c) molecules used to represent crystalline fragments of diamond (compound I). (i) Calculated values of geometrical parameters (lengths in Å, angles in degrees, see Figure 1 and text), this work. (j) Experimental values: refs 20 and 43 (and references therein).

length (in Angstroms) for the compound under consideration, respectively; λ is an empirical parameter which is introduced to account for the effects of ionicity of the chemical bonds of the compounds. The bulk modulus B is in gigapascals (GPa). All the calculations have been performed by using the GAUSSIAN-94 package.³⁹

III. Results and Discussion

Molecular Structures. Since the main structural characteristics (bond lengths and bond angles) of crystalline compounds like diamond and silicon solid are close to that for $\text{C}(\text{CH}_3)_4$ and $\text{Si}(\text{SiH}_3)_4$ molecules, respectively, it seems reasonable to assume that the similar small molecular systems could be used as models for the quantum-chemical studies of the structures of silicon–carbon nitrides. From this point of view, a rather interesting quantum-chemical investigation was undertaken earlier by Julian and Gibbs.⁴⁰ The authors have examined both the results of experimental studies and molecular orbital calculations (at the Hartree–Fock level of theory using 6-31G(d), 4-31G(d,p), and STO-3G(d) basis sets) for a series of methyl- and silyl-substituted amines, $\text{N}(\text{CH}_3)_{3-k}(\text{SiH}_3)_k$ ($k = 0, 1, 2, 3$). It has been shown that transformation of the structure about the nitrogen atom from a planar configuration in trisilylamine ($k = 3$) to a nearly tetrahedral one in trimethylamine ($k = 0$) occurs. Also, an important conclusion is that the optimized geometry about the nitrogen atom in trisilylamine reproduces well that observed in the hexagonal silicon nitride crystals, $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$.

In order to determine the most suitable molecular systems which could be used for the correct description of the structures of such covalent crystalline solids as the silicon–carbon nitrides

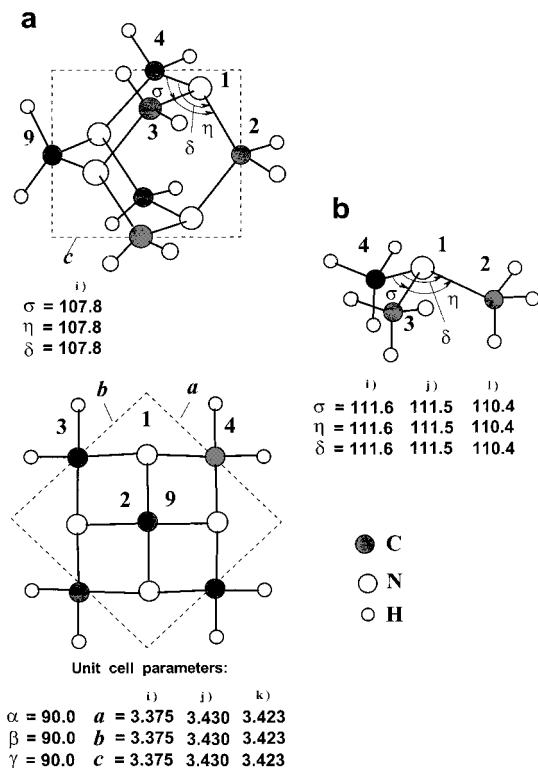


Figure 4. B3LYP/6-31G(d,p) optimized structures of the hexamethylenetetramine $N_4(CH_2)_6$ (model **a**) and trimethylamine $N(CH_3)_3$ (model **b**) molecules used to represent crystalline fragments of the cubic (defect zinc-blende) carbon nitrides $\text{Cz-C}_3\text{N}_4$ (compound **II**). (i) Calculated values of geometrical parameters (lengths in Å, angles in degrees, see Figure 1 and text), this work. Other calculations: (j) refs 40 and 41; (k) refs 19 and 24. (l) Experimental values: refs 40 and 41 (and references therein).

under consideration, we have carried out a detailed B3LYP/6-31G(d,p) analysis of the structural characteristics of the series of cubic (defect zinc-blende) crystalline compounds, diamond (**I**), silicon–carbon nitrides $\text{dz-Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0-3$) (**II-V**), and crystalline silicon (**VI**), using different molecular (cluster) models for the full geometry optimization. Model **a** is related to the 10 heavy-atom adamantane- and hexamethylenetetramine-like clusters (Figure 1a and 1b) having the topology of the diamond and zinc-blende cubic unit cells (Figure 1c and 1d), respectively. Models **b** and **c**, corresponding to the 4–5 heavy-atom molecular systems with trigonal-pyramidal and tetrahedral structures, were included for comparison with the results of the experiments and previous calculations^{40–42} (see Figures 3–8). Note that the adamantane and hexamethylenetetramine molecules were analyzed for the first time at the ab initio Hartree–Fock level by Guo and Goddard to obtain a force-field parameters (MSFF approach) suitable for predicting mechanical properties (bulk modulus) of carbon nitrides of the hexagonal structural phase, $\alpha\text{-C}_3\text{N}_4$ and $\beta\text{-C}_3\text{N}_4$.²⁰

Our optimized structures for the clusters $(\text{CH})_4(\text{CH}_2)_6$ (**I**, model **a**), $N_4(\text{CH}_2)_{6-n}(\text{SiH}_2)_n$ ($n = 0, 2, 4, 6$) (**II-V**, model **a**), and $(\text{SiH})_4(\text{SiH}_2)_6$ (**VI**, model **a**) as well as for a number of small molecular models $\text{HC}(\text{CH}_3)_3$ (**I**, model **b**), $\text{C}(\text{CH}_3)_4$ (**I**, model **c**), $\text{N}(\text{CH}_3)_{3-k}(\text{SiH}_3)_k$ ($k = 0, 1, 2, 3$) (**II-V**, model **b**), $\text{HSi}(\text{SiH}_3)_3$ (**VI**, model **b**) and $\text{Si}(\text{SiH}_3)_4$ (**VI**, model **c**) are illustrated in Figures 3–8. The relevant geometrical parameters calculated for these clusters and simple molecular systems, also shown in Figures 3–8, are summarized in Table 1, where $\sigma = \angle X(2)-A(1)-X(3)$, $\eta = \angle X(2)-A(1)-X(4)$, $\delta = \angle X(3)-A(1)-X(4)$ are the bond angles around the apical atom A(1) of the trigonal pyramid $A(1)-X(2)-X(3)-X(4)$ (see Figure 9);

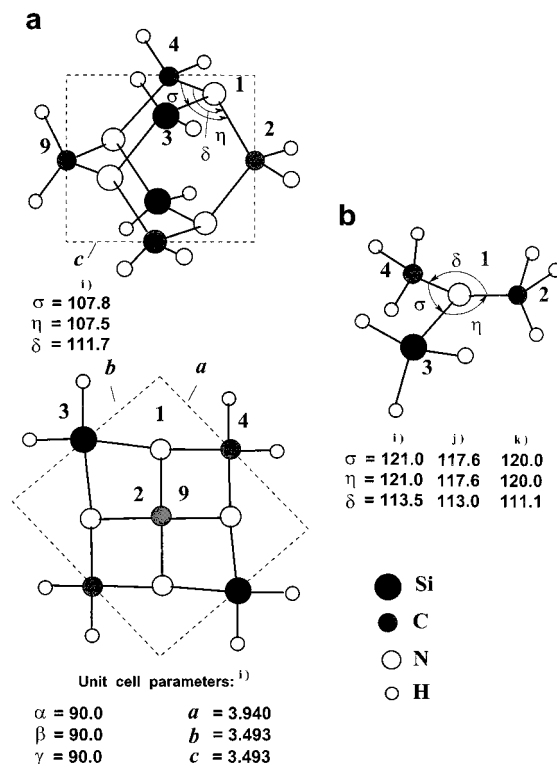


Figure 5. B3LYP/6-31G(d,p) optimized structures of the silylene-substituted derivative $N_4(\text{CH}_2)_{6-n}(\text{SiH}_2)_n$ ($n = 2$) (model **a**) of the hexamethylenetetramine molecule $N_4(\text{CH}_2)_6$ (constructed by replacement of 2 C atoms with the equivalent number of Si atoms) and the silyl-substituted amine $\text{N}(\text{CH}_3)_{3-k}(\text{SiH}_3)_k$ ($k = 1$) (model **b**) which have been used to represent crystalline fragments of the cubic (defect zinc-blende) silicon–carbon nitride $\text{dz-Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 1$) (compound **III**). (i) Calculated values of geometrical parameters (lengths in Å, angles in degrees, see Figure 1 and text), this work. (j) Other calculations: refs 40 and 41. (k) Experimental values: refs 40 and 41 (and references therein).

$R_{A(1)-X(2)}$, $R_{A(1)-X(3)}$, $R_{A(1)-X(4)}$ are the bond lengths between atom A(1) and basal plane atoms X(2), X(3), X(4) of this trigonal pyramid; $\Omega_{A(1)}$ is the sum of the σ , η , δ bond angles; A(1) denotes the (C or N or Si) atom at position 1; X(2), X(3), X(4) are the (C or Si) atoms at positions 2, 3, and 4, respectively (for A at position 5, 8, and 10, see Figures 3 and 9). Note that in the case of clusters (model **a**), atoms A(i) ($i = 1, 5, 8, 10$) are equivalent due to the symmetry of the systems. To quantitatively estimate the polyhedron structure variation, we have introduced the parameter Δh_A which represents the degree of pyramidity (nonplanarity) of the A atoms surrounding. For instance, $\Delta h_{A(1)}$ (see Figure 9) is determined as the shortest (\perp) distance between atom A(1) and a plane crossing the $A(1)-X(2)$, $A(1)-X(3)$, and $A(1)-X(4)$ bonds at the points separated from atom A(1) by 1 Å. The unit-cell parameters (a , b , c and α , β , γ) of compounds **I–VI** obtained using optimized cluster structures for model **a** are included in Figures 3–8. Some available experimental^{20,43–45} and theoretical²⁴ values of these parameters are presented in Figures 3, 4, and 8.

It can be seen from Table 1 and Figures 3 and 8 that B3LYP/6-31G(d,p) optimized structures of adamantane $(\text{CH})_4(\text{CH}_2)_6$ (**I**, **a**) (Figure 3a) and its silicon derivative $(\text{SiH})_4(\text{SiH}_2)_6$ (**VI**, **a**) (Figure 8a), i.e., silicon-substituted adamantane-like molecule, reproduce well the real geometry and unit-cell parameters for the diamond and silicon solid, respectively. For instance, the values of computed C–C and Si–Si bond lengths, $R_{\text{C-C}} = 1.544$ Å and $R_{\text{Si-Si}} = 2.365$ Å, as well as tetrahedral bond angles $\sigma = \eta = \delta \approx 109.5^\circ$ ($\Omega_A = \sigma + \eta + \delta \approx 328.0^\circ$, where A = C, Si)

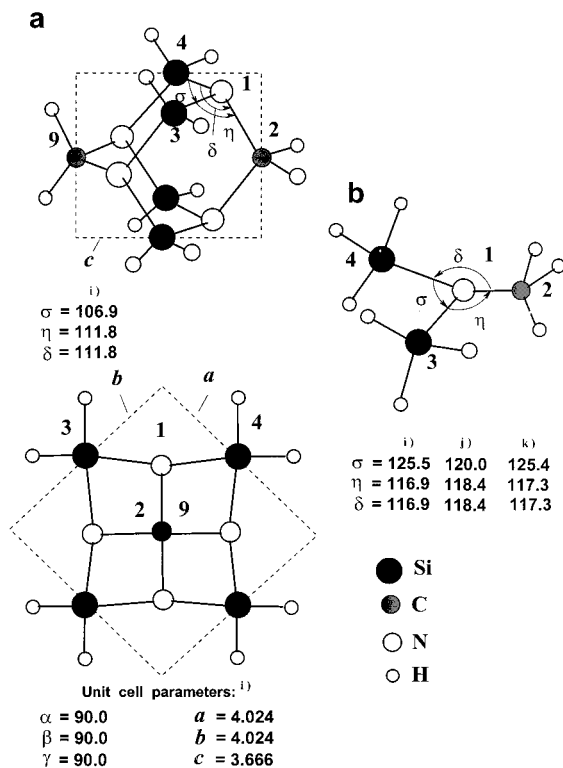


Figure 6. B3LYP/6-31G(d,p) optimized structures of the silylene-substituted derivative $N_4(CH_2)_{6-n}(SiH_2)_n$ ($n = 4$) (model **a**) of the hexamethylenetetramine molecule $N_4(CH_2)_6$ (constructed by replacement of 4 C atoms with the equivalent number of Si atoms) and the silyl-substituted amine $N(CH_3)_{3-k}(SiH_3)_k$ ($k = 2$) (model **b**) which have been used to represent a crystalline fragments of the cubic (defect zinc-blende) silicon-carbon nitride $dz-Si_xC_{3-x}N_4$ ($x = 2$) (compound **IV**). (i) Calculated values of geometrical parameters (lengths in Å, angles in degrees, see Figure 1 and text), this work. (j) Other calculations: refs 40 and 41. (k) Experimental values: refs 40 and 41 (and references therein).

are very close to the well-known experimental ones.^{1,15,46,47} The calculated lattice constants for these compounds $a = b = c = 3.562$ Å and $\alpha = \beta = \gamma = 90.0^\circ$ (**I, a**) and $a = b = c = 5.457$ Å and $\alpha = \beta = \gamma = 90.0^\circ$ (**VI, a**) are also in good agreement with experimental values for diamond^{20,43} $a = b = c = 3.567$ Å and $\alpha = \beta = \gamma = 90.0^\circ$ and for silicon solid^{44,45} $a = b = c = 5.451$ Å and $\alpha = \beta = \gamma = 90.0^\circ$. Moreover, Table 1 shows that to analyze the geometry of crystalline compounds of this type, the use of simpler models (**b** and **c**) is also possible. These results stimulated us to perform an analysis of the possible structures of the silicon-carbon nitride compounds (**II–V**) at the same level of theory. In these cases, we have chosen the hexamethylenetetramine molecule $N_4(CH_2)_6$ (**II, model a**) (Figure 1b) and its hypothetical derivatives $N_4(CH_2)_{6-n}(SiH_2)_n$ ($n = 2, 4, 6$) (**III–V, model a**) constructed from $N_4(CH_2)_6$ by replacement of 2, 4, or 6 C atoms with the equivalent number of Si atoms as model structures. Similarly, a number of small molecular models, namely, methyl- and silyl-substituted amines $N(CH_3)_{3-k}(SiH_3)_k$ ($k = 0, 1, 2, 3$) (**II–V, model b**) were also utilized, and the possibility of using these models has been analyzed.

It was found (see Figures 4–7 and Table 1) from our full geometry optimization that the N–C and N–Si bond lengths and bond angles σ , η , and δ (as well as $\Omega_N = \sigma + \eta + \delta$) are increased, whereas the degree of pyramidality Δh_N of the N atoms surrounding is decreased, with an increase of the number of Si atoms in both the $N_4(CH_2)_{6-n}(SiH_2)_n$ ($n = 0, 2, 4, 6$) clusters (**II–V, model a**) and the substituted series of four

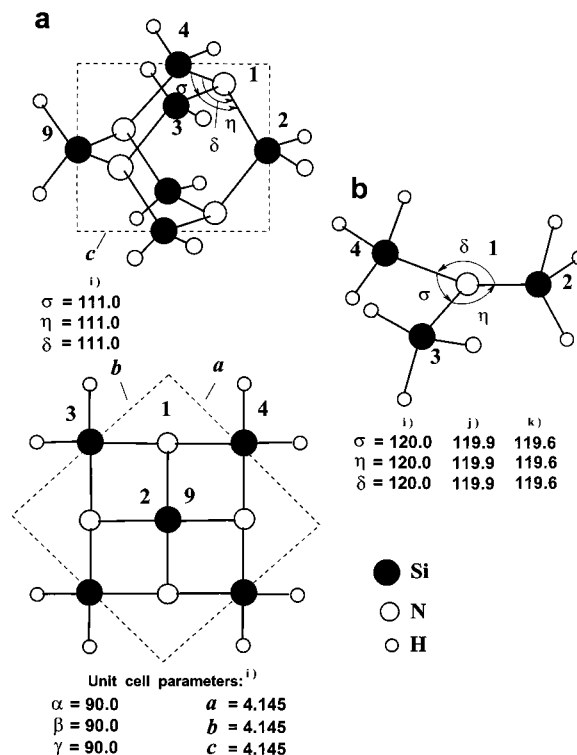


Figure 7. B3LYP/6-31G(d,p) optimized structures of the silylene-substituted derivative $N_4(SiH_2)_6$ (model **a**) of the hexamethylenetetramine molecule $N_4(CH_2)_6$ (constructed by replacement of all C atoms with the equivalent number of Si atoms) and the trisilylamine $N(SiH_3)_3$ (model **b**) which have been used to represent crystalline fragments of the cubic (defect zinc-blende) silicon nitride $dz-Si_3N_4$ (compound **V**). (i) Calculated values of geometrical parameters (lengths in Å; angles in degrees, see Figure 1 and text), this work. (j) Other calculations: refs 40 and 41. (k) Experimental values: refs 40 and 41 (and references therein).

amines, $N(CH_3)_{3-k}(SiH_3)_k$ ($k = 0, 1, 2, 3$) (**II–V, model b**). At the same time, increasing the bond angles Ω_N and decreasing the pyramidality Δh_N are significantly sharper in the case of simple molecular systems than for the hexamethylenetetramine-like clusters. As can be seen, the B3LYP/6-31G(d,p) optimization of the geometry in the clusters (model **a**) results in a pronounced pyramidal arrangement of the $N(Si)_k(C)_{3-k}$ ($k = 0–3$) fragment atoms ($\Omega_N = 323.4^\circ, 327.0^\circ, 330.4^\circ, \text{ and } 332.9^\circ$, Δh_N (Å) = 0.312, 0.300, 0.282, 0.267), whereas for small molecular systems (model **b**), the optimized structures $N(SiH_3)_k(CH_3)_{3-k}$ ($k = 0–3$) are flatter ($\Omega_N = 334.7^\circ, 355.4^\circ, 359.2^\circ, \text{ and } 360.0^\circ$, Δh_N (Å) = 0.258, 0.110, 0.043, 0.0) and correspond to the pure planar geometry of the N atom surrounding in the $N(SiH_3)_3$ system. This means that prediction of structures of the crystalline compounds of such type based on the geometry of the small molecules (or simplified molecular fragments) can lead to incorrect results.

To estimate the reliability of our structural predictions for this series of silicon-carbon nitrides, we have compared the values of lattice constants (a, b, c and α, β, γ) obtained from optimized geometry of the $N_4(CH_2)_6$ cluster with previous calculations^{19,24} of the cubic (defect zinc-blende) structural phase of the carbon-nitride solid carried out in the framework of ab initio molecular dynamics (MD) with a variable-cell-shape (VCS) algorithm and density-functional techniques within the local density approximation (LDA) to electron exchange and correlation. The results of our comparison are very promising. Our lattice constants ($a = b = c = 3.375$ Å and $\alpha = \beta = \gamma = 90.0^\circ$) corresponding to the minimum of the cluster's energy

TABLE 1: B3LYP/6-31G(d,p) Optimized Geometrical Parameters^a and Charge Distributions^b for the Series of Model Structures (a, b, c) of Different Cubic (Defect Zinc-Blende) Crystalline Compounds: Diamond (I), Silicon–Carbon Nitrides Si_xC_{x-3}N₄ (x = 0, 1, 2, 3; II–V), and Silicon Solid (VI)

compound	models	$R_{A(1)-X(2)}$ A(1)–X(2)	$R_{A(1)-X(3)}$ A(1)–X(3)	$\Omega_{A(1)}$ A(1)	$\Delta h_{A(1)}$	$Q_{A(1)}$ A(1)	$Q_{X(2)}$ X(2)	$Q_{X(3)}$ X(3)	
I	diamond	a; (CH) ₄ (CH ₂) ₆	C–C 1.544		C 328.0	0.291	C 0.0072	C –0.0048	
		b; HC(CH ₃) ₃	C–C 1.535		C 333.4	0.264	C 0.0342	C –0.0114	
		c; C(CH ₃) ₄	C–C 1.540		C 328.4	0.289	C 0.0404	C –0.0101	
II	Si ₀ C ₃ N ₄	a; N ₄ (CH ₂) ₆	N–C 1.477		N 323.4	0.312	N –0.3863	C 0.2575	
		b; N(CH ₃) ₃	N–C 1.455		N 334.7	0.258	N –0.3902	C 0.1301	
III	Si ₁ C ₂ N ₄	a; N ₄ (CH ₂) ₄ (SiH ₂) ₂	N–C 1.492	N–Si 1.764	N 327.0	0.300	N –0.5172	C 0.2681	Si 0.4982
		b; N(CH ₃) ₂ SiH ₃	N–C 1.456	N–Si 1.735	N 355.4	0.110	N –0.5196	C 0.1561	Si 0.2073
IV	Si ₂ C ₁ N ₄	a; N ₄ (CH ₂) ₂ (SiH ₂) ₄	N–C 1.512	N–Si 1.771	N 330.4	0.282	N –0.6546	C 0.2927	Si 0.5083
		b; N(CH ₃)(SiH ₃) ₂	N–C 1.475	N–Si 1.744	N 359.2	0.043	N –0.6659	C 0.1872	Si 0.2392
V	Si ₃ C ₀ N ₄	a; N ₄ (SiH ₂) ₆	N–Si 1.779		N 332.9	0.2670	N –0.8040	Si 0.5361	
		b; N(SiH ₃) ₃	N–Si 1.754		N 360.0	0	N –0.8236	Si 0.2746	
VI	silicon	a; (SiH) ₄ (SiH ₂) ₆	Si–Si 2.365		Si 327.9	0.291	Si –0.0537	Si 0.0358	
		b; HSi(SiH ₃) ₃	Si–Si 2.357		Si 333.2	0.266	Si –0.1323	Si 0.0441	
		c; Si(SiH ₃) ₄	Si–Si 2.360		Si 328.2	0.290	Si –0.2791	Si 0.0700	

^a Bond lengths $R_{A(1)-X(2)}$ and $R_{A(1)-X(3)}$ (in Å) between atom A(1) and atoms X(2), X(3), respectively; sum of bond angles $\Omega_{A(1)} = \sigma + \eta + \delta$ (in deg) around the A(1) atom; degree of pyramidity $\Delta h_{A(1)}$ (in Å) of atoms A(1) surrounding; see Figures 3–8 and 9). ^b Total effective charges $Q_{A(1)}$, $Q_{X(2)}$, and $Q_{X(3)}$ localized on the atoms A(1), X(2), and X(3), respectively (with hydrogens charges included in heavy atoms).

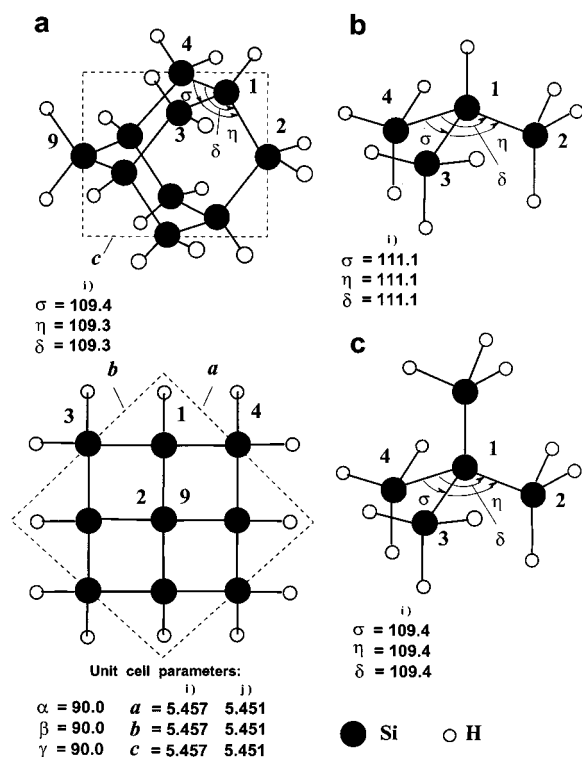


Figure 8. B3LYP/6-31G(d,p) optimized structures of the silicon derivative (SiH)₄(SiH₂)₆ (model a) of the adamantane (CH)₄(CH₂)₆, the trisilylsilane HSi(SiH₃)₃ (model b), and the tetrasilylsilane Si(SiH₃)₄ (model c) molecules which have been used to represent crystalline fragments of silicon solid (compound VI). (i) Calculated values of geometrical parameters (lengths in Å, angles in degrees, see Figure 1 and text), this work. (j) Experimental values: refs 40 and 41 (and references therein).

are quite close to (even a few percent smaller than) those calculated in the mentioned works ($a = b = c = 3.430$ Å and $\alpha = \beta = \gamma = 90.0^\circ$)¹⁹ and ($a = b = c = 3.423$ Å and $\alpha = \beta = \gamma = 90.0^\circ$).²⁴

Estimation of Hardness. The bulk modulus (hardness) of the SiCN_x crystals was estimated using the empirical expression (1), proposed by Cohen, involving the average coordination number, $\langle N_C \rangle$, bond length, d , and ionicity parameter, λ . To evaluate the degree of ionicity of the silicon–carbon nitrides II–V, we analyzed (in the framework of the Mulliken formula-

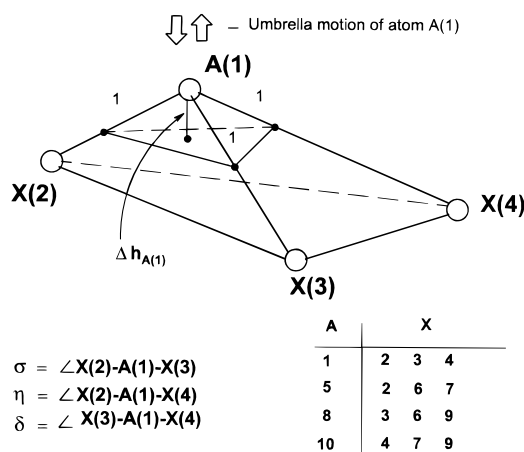


Figure 9. Trigonal-pyramidal fragment A(1)–X(2)–X(3)–X(4) of the cubic adamantane-like molecular systems I–VI (see Figures 3–8). A(1) is the apical (C or N or Si) atom at position 1; X(2), X(3), X(4) are the basal plane (C or/and Si) atoms at positions 2, 3, and 4, respectively (for A at positions 5, 8, and 10, see Figure 3 and the table included). Geometrical parameter $\Delta h_{A(1)}$ represents the degree of pyramidity (nonplanarity) of the A(1) atoms surrounding. It is determined as the shortest (\perp) distance between atom A(1) and a plane crossing the A(1)–X(2), A(1)–X(3), and A(1)–X(4) bonds at the points separated from atom A by 1 Å.

tion) the total effective charges Q_N , Q_C , and Q_{Si} centered on the N, C, and Si atoms of the trigonal-pyramidal (or trigonal planar, in the case of V, b) N(Si)_k(C)_{3-k} fragments of the model structures considered. For simplicity, the effective hydrogen charges were included into heavy atoms. The values of Q_C and Q_{Si} in the case of purely covalent crystalline compounds, diamond (I) and silicon solid (VI), were calculated to estimate the ability of the different model structures (a, b, and c) to predict the actual charge distribution in these compounds. The results obtained are listed in the last columns of the Table 1 and plotted in Figure 10. Here $Q_{A(1)}$ is total effective charge of an apical atom A(1) of the trigonal pyramid (see Figures 3–8 and Figure 9); $Q_{X(2)}$ and $Q_{X(3)}$ are the effective charges of the nearest-neighbor atoms X(2) and X(3) which reside on the basal plane of such a pyramid. As shown in Table 1 and Figure 10, compounds I–VI exhibit a local electroneutrality of the fragments involving the apical (central, in the case of model c) A(1) = C, or Si, or N atom surrounded by its three (model a and b, $i = 2-4$) or four (model c, $i = 2-5$) nearest neighbors

TABLE 2. Values of the Bond Lengths d (Å), Ionicity λ_s and Modified Ionicity $\lambda_m = |Q_{A(i)}|/3$ ($A(i) = \text{C, N, or Si}, i = 1, 5, 8, 10$, see Figures 3–8), Force Constants k (mDyne/Å) for Umbrella Motion of the Four $A(i)$ Atoms, Bulk Modulus (Hardness) B (GPa) for Different Cubic (Defect Zinc-Blende) Crystalline Compounds (Model **a**)^a

	compound	d	λ_s	$B(\lambda_s) \langle N_c \rangle = 4$	$B(\lambda_s) \langle N_c \rangle = 3.43$	λ_m	$B(\lambda_m) \langle N_c \rangle = 3.43$	k	B other calc	B exp
I	diamond	1.544	0	430.9		0		4.156	430.1 ^b 436.0 ^c 444.0 ^d	442.0 ^e
II	Si ₀ C ₃ N ₄	1.477	0.5	475.2	407.5	0.13	425.3	3.996	425.0 ^f 448.0 ^g	
III	Si ₁ C ₂ N ₄	1.583	0.5	372.9	319.7	0.17	332.2			
IV	Si ₂ C ₁ N ₄	1.685	0.5	299.7	257.0	0.22	265.5			
V	Si ₃ C ₀ N ₄	1.779	0.5	247.8	212.5	0.27	218.3	2.921		
VI	silicon	2.365	0	96.9		0		0.895	99.1 ^b 98.0 ^h	98.0 ^b 99.0 ⁱ

^a Diamond (**I**), silicon–carbon nitrides Si_{*x*}C_{3–*x*}N₄ ($x = 0, 1, 2, 3$) (**II–V**), and silicon solid (**VI**). $\langle N_c \rangle$ is average coordination number. ^b Reference 15. ^c Reference 20. ^d Reference 3. ^e References 1, 15, 20, 43. ^f Reference 19. ^g References 14, 24. ^h Reference 44. ⁱ References 44, 48, 49.

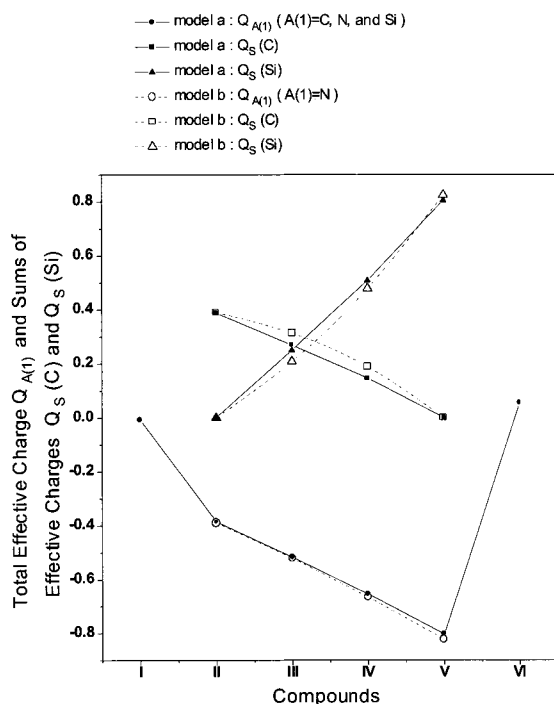


Figure 10. Calculated values of the total effective charge (in the framework of Mulliken formulation) $Q_{A(1)}$ centered on the C or N or Si atom $A(1)$ and the sums $Q_S(X) = \sum_i Q_{X(i)}/2$ (and $Q_S(X) = \sum_i Q_{X(i)}$ in the case of models **b** and **c**) of the effective charges located on the nearest-neighbor carbon ($X(i) = \text{C}$) and, separately, silicon ($X(i) = \text{Si}$) atoms surrounding $A(1)$ atom ($i \in 2, 3, 4$ for models **a** and **b**; $i = 2, 3, 4, 5$ for model **c**).

$X(i) = \text{C or/and Si, i.e.}$

$$Q_{A(1)} = - \sum_{i=2}^4 Q_{X(i)}/2 \quad (\text{model a})$$

$$Q_{A(1)} = - \sum_{i=2}^{4(\text{or } 5)} Q_{X(i)} \quad (\text{models b and c})$$

The use of cluster model **a** for the charge distribution analysis allows one to reproduce the nonpolarity $|Q_{A(1)}| \approx 0$ of the covalent bonds C–C and Si–Si in the diamond and silicon crystalline solids quite well, whereas the transition to model **b** and then to model **c** leads to less reliable results. In the case of silicon–carbon nitrides (**II–V**), the quantitative results for charge polarization obtained for cluster **a** and small molecular **b** models are comparable. The negative effective charge is centered on the apical N atom of the trigonal pyramid, and the

absolute values of this charge grow practically linear with increasing the number of surrounding Si atoms. It is obvious that the values $\lambda_m = |Q_N|/3$ (because N links three nearest-neighbor C and/or Si atoms) will characterize the degree of ionicity (or heteropolarity) of chemical N–C and N–Si bonds of the compounds **II** and **V**, respectively. For compounds **III** and **IV**, the magnitude of λ_m will correspond to the averaged (over the N–C and N–Si bonds) ionicity of the chemical bonds.

In Table 2 we compare the results of our calculations of the bulk modulus $B(\lambda_s)$ and $B(\lambda_m)$ for the compounds under investigation, using empirical expression (1), with those obtained from experimental measurements^{1,15,20,43,44,48,49} and calculations performed in the framework of solid-state methodology.^{14,19,20,24} Here d is the B3LYP/6-31(d,p) optimized value of the C–C, N–C, N–Si, or Si–Si bond length in compounds **I**, **II**, **V**, and **VI**, respectively. In the case of compounds **III** and **IV**, parameter d corresponds to the averaged value of the three bond lengths N–C and N–Si; λ_s is the value of the ionicity of compounds proposed by Cohen;^{1,13,15} $\langle N_c \rangle$ is the average coordination number for the cubic (defect zinc-blende) structures with composition Si_{*x*}C_{3–*x*}N₄ ($x = 0, 1, 2, 3$);¹³ $\lambda_m = |Q_N|/3$ is the modified ionicity value which takes into account the increase in the average heteropolarity of chemical bonds while going from compound **II** to **V**; k is the force constant for an umbrella motion of the $A(i) = \text{C, N, or Si}$ ($i = 1, 5, 8, 10$) atoms.

As shown in Table 2, the estimated values of the bulk modulus $B(\lambda_s)$ (using parameters $\langle N_c \rangle = 4$ and $\lambda_s = 0$) for diamond (430.9 GPa) and silicon solid (96.9 GPa) are very close to those obtained from experiments (442.0 and 98.0 GPa, respectively).^{1,15,20,43,44,48,49} Moreover, the results of our calculations for carbon nitride, dz-C₃N₄ (**II**) ($B(\lambda_s) = 407.5$ GPa and $B(\lambda_m) = 425.3$ GPa), compare quantitatively with the previous calculations of the cubic structural phase of the defect zinc-blende carbon–nitride solid carried out in the framework of the ab initio molecular dynamics approach (425.0 GPa)¹⁹ and density-functional techniques within the local density approximation (448.0 GPa).^{14,24}

It is clear from a general point of view that the magnitude of a force constant for a vibrational mode corresponding to umbrella (inversion) motion of the atoms $A(i) = \text{C, N, or Si}$ (at position $i = 1, 5, 8, 10$) in the cubic clusters (CH)₄(CH₂)₆ (**I**), N₄(CH₂)_{6–*n*}(SiH₂)_{*n*} (**II, V**) ($n = 0, 6$), and (SiH)₄(SiH₂)₆ (**VI**) can give us additional indirect information concerning the “hardness” of the compounds considered. For instance, the magnitude of the force constant for umbrella motion of the four $A(i)$ ($i = 1, 5, 8, 10$) atoms for adamantane (model system for diamond **I**) is expected to be larger than that for the silicon derivative of adamantane (model system for silicon solid **VI**). Indeed, Table 2 shows that the values of force constants k

calculated for cubic structures **I**, **II**, **V**, and **VI** correlate well with the values of the bulk modulus for these compounds (in the case of structures **III** and **IV** with tetragonal distortion, there are no vibrational modes strongly corresponding to the umbrella motion of atoms N). This allows us to conclude that the predicted values of the bulk modulus ($B(\lambda_m) = 425.3, 332.2, 265.5,$ and 218.3 GPa) for silicon–carbon nitrides with composition $\text{Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0, 1, 2, 3$) are reliable and that compounds of this type are promising for designing novel class of crystalline solids with variable values of hardness.

IV. Conclusion

The results presented above (see Figures 3–8, Tables 1 and 2) on the optimized structural characteristics (bond lengths and angles, unit cell parameters) as well as vibrational (force constants for umbrella motion of the N atoms) and mechanical (bulk modulus) properties of the series of cubic (defect zinc-blende) crystalline compounds, diamond (**I**), silicon–carbon nitrides with composition $\text{Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0, 1, 2, 3$) (**II–V**), and silicon solid (**VI**) show that (a) the quantum-chemical calculations at the B3LYP/6-31G(d,p) level of theory for the clusters with the topology of the adamantane molecule (model **a**) allow us to reproduce quite well the structures, unit cell parameters, and bulk modulus (hardness) of real crystals (**I** and **VI**) and to predict the structural and mechanical properties of the hypothetical zinc-blende crystalline compounds $\text{dz-Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0, 1, 2, 3$) (**II–V**). (b) Prediction of the structures of the crystalline compounds such as silicon–carbon nitrides **II–V** based on the geometry of the small molecules (like $\text{N}(\text{CH}_3)_{3-k}$ (SiH_3) $_k$ ($k = 0, 1, 2, 3$), model **b**) can lead to incorrect results. For instance, our full optimization of the geometry for clusters **II–V** (model **a**) results in a pronounced pyramidal arrangement of the $\text{N}(\text{Si})_k(\text{C})_{3-k}$ ($k = 0–3$) fragment atoms, whereas for the small molecular systems (model **b**), the optimized structures $\text{N}(\text{SiH}_3)_k(\text{CH}_3)_{3-k}$ ($k = 0–3$) are flatter and correspond to the pure planar geometry of the N atom surrounding in the case of the $\text{N}(\text{SiH}_3)_3$ system. (c) As in the case of hypothetical hexagonal $\beta\text{-Si}_x\text{C}_{3-x}\text{N}_4$ ($x = 0–3$) compounds,³¹ an increase of the number of C atoms (decrease of the number x) in the defect zinc-blende silicon–carbon nitrides, $\text{dz-Si}_x\text{C}_{3-x}\text{N}_4$, results in an increase of the bulk modulus values from ~ 218 GPa for $\text{dz-Si}_3\text{N}_4$ to ~ 425 GPa for $\text{dz-C}_3\text{N}_4$.

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