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Carbon nitride: *Ab initio* investigation of carbon-rich phases

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We have examined the potential energy hypersurfaces for the carbon-rich phases of carbon nitride, CN and C_3N, and discovered low-energy structures different from those reported previously. Trends in the preferred local bonding environments have been analyzed as a function of nitrogen content. For each composition, several structures with similar energies were found, but they have very different equilibrium volumes; the structure produced during synthesis will strongly depend on the preparation conditions. When low densities are favored, conjugated planar-ring structures with sp^2 hybridized carbon are most likely to be formed. These structures are similar to those suggested as potential photocatalytic materials. At high pressures, the preferred structures contain three-coordinate nitrogen and sp^3 hybridized carbon, including the β-InS structure, which we predict to be the thermodynamically preferred structure for CN under positive hydrostatic pressures. This structure has a moderately high bulk modulus with a lower formation energy than β-C_3N_4 and so should be more easily synthesized.

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I. INTRODUCTION

There has been much interest in the synthesis of carbon nitrides. β-C_3N_4 has been a particular focus of synthetic work due to the prediction that it should have a very high bulk modulus (~430 GPa).[1] Unfortunately, success to date in the synthesis of this material has been limited to production of mixtures of α and β-C_3N_4 in the form of nanoparticles and nanocrystals embedded in an amorphous matrix.[2–4] Some success has been achieved toward the synthesis of graphitic forms of carbon nitride. The thermal decomposition products of melamine (as well as other C-N-H compounds including cyanamide) have been characterized and suggested as possible precursors to graphitic carbon nitride.[5–7] Zhang *et al.*[8] demonstrated the first bulk synthesis of a highly crystalline carbon nitride material with the production of a material with composition $C_6N_9H_3 \cdot HCl$ from triazine-based precursors including melamine. There have since been other demonstrations of the synthesis of graphitic carbon nitride with structures composed of melem (tri-*s*-triazine) units, formed by thermal decomposition of melamine and cyanamide.[9–11] Materials of this type have been shown to possess photocatalytic properties.[12] Further applications are anticipated in catalysis[10,13] and electronics—nitrogen-doped graphene is an *n*-type semiconductor, with many potential applications in electronic devices,[14] while two-dimensional carbon nitride graphenes are predicted to be wide band-gap semiconducting materials.[15]

It has been proposed that melamine, cyanamide, and other related triazine-based compounds could also be used as precursors for the dense C_3N_4 phases (including β-C_3N_4). For example, shock compression of these precursors has been used in attempts to prepare diamond-like carbon nitride.[16–18] However, this does not yet appear to have been successful, with results in dispute.[19] Further, it has been suggested that the amorphous and graphitic carbon nitride products of the decomposition of triazine-based materials could themselves be used as precursors for formation of dense carbon nitride phases,[8] for example by the application of high pressure,[20] although this has not yet been achieved.

The incentive for study of the β-C_3N_4 structure was the well-known analog β-Si_3N_4,[1] but it has subsequently been suggested[21] that the achievable nitrogen content in carbon nitride is lower than for silicon nitride, due not only to the relative bond energies of C-N and Si-N but also to the short C-N bonds that result in short N-N nonbonded distances and thus strong N-N repulsions. Consistent with this, products of attempts to synthesize β-C_3N_4 typically have a low ratio of nitrogen to carbon,[3,16,17,22,23] while carbon nitride films deposited by pulsed laser ablation have been found to have a limiting nitrogen content of 50 at. %.[24] This suggests the existence of carbon-rich phases that are more readily synthesized than C_3N_4 and *ab initio* investigation of possible carbon-rich crystal structures has been encouraged.[25] Thus, in this work we examine the C-N potential energy surfaces in more detail and in particular we investigate possible crystal structures for carbon-rich phases, specifically CN and C_3N, to predict the most likely crystal structures and to determine if these more readily synthesized phases also have interesting properties, such as high bulk moduli.

Some predictions of the possible crystal structures for CN and C_3N have already appeared in the literature.[26–28] However, these carbon-rich materials have not been investigated in detail and, in this work, we identify different structures that are lower in energy than those previously reported. We examine in detail a range of possible crystal structures for these two carbon-rich stoichiometries and analyze trends in their stability as a function of nitrogen content.

II. METHOD

Possible candidate crystal structures for CN and C_3N were investigated by plane-wave density-functional theory (DFT) calculations in the generalized gradient approximation

(GGA) as implemented in the CASTEP code[29] with the Perdew-Wang exchange correlation functional.[30] Only valence electrons were considered, with core electrons replaced with ultrasoft Vanderbilt pseudopotentials.[31] The energy cutoff for the plane waves was 310 eV. Cell parameters and atomic positions were relaxed by energy minimization with a conjugate-gradient algorithm. Results were checked for convergence with respect to k point spacing and basis set size. Periodic DFT calculations for a selection of the low-energy structures for both CN and C_3N were performed with CRYSTAL06,[32] with 6-21G* basis sets[33] and the B3LYP functional.[34,35] The relative energies of the structures calculated with CRYSTAL06 were the same as those calculated with CASTEP, so only the results from CASTEP are reported here.

Data for energy as a function of volume were obtained by applying a range of hydrostatic pressures to the structures and carrying out a full geometry optimization of all unit-cell parameters and basis atom positions. For all except layered structures, energy vs volume data were acquired by applying both positive and negative pressures. For layered structures, in the DFT calculations, either a positive hydrostatic pressure was applied or the interlayer separation was constrained during the geometry optimization, and calculations were performed for a range of interlayer separations; this was necessary because dispersion interactions are not included in DFT.[36] Corrections were then applied to the energy of the structures to account for dispersion interactions that are not included in the DFT calculation. The correction was calculated with a damped dispersion function:[37]

$$E = -\frac{C_6}{r^6}\left(1 - e^{-b_6 r}\sum_{k=0}^{6}\frac{(b_6 r)^k}{k!}\right)$$

using the GULP code,[38] with values for C_6 taken from Warne[39] and previously published damping coefficients, b_6.[40–42] The cutoff radius for the dispersion interactions was 12 Å.

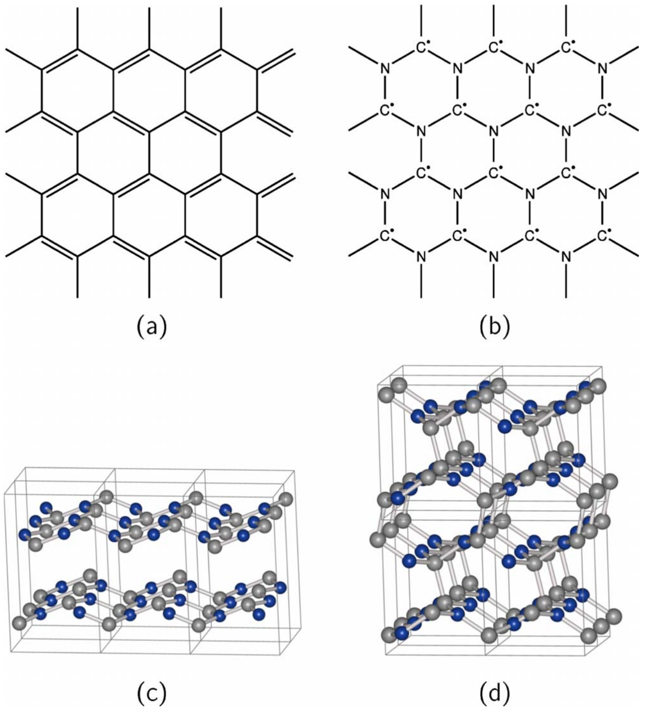
III. RESULTS AND DISCUSSION

A. CN

Structures that we have investigated for CN include those based on graphite, GaSe, and β-InS, as well as the body-centered tetragonal structure proposed by Kim *et al.*[28]

Graphite in which some nitrogen replaces carbon has been previously suggested as a low-energy structure for carbon nitrides.[26,43] In addition, a graphitic structure is predicted to be lowest in energy for C_3N_4.[44,45] We therefore begin our study by investigating nitrogen-substituted graphite as possible candidate structures for CN. The substitution of carbon by nitrogen in graphite must be carried out carefully to ensure that valencies are satisfied; replacing three-coordinate carbon in graphite with three-coordinate nitrogen may result in an unpaired electron on a neighboring carbon atom [e.g., Fig. 1(b)] and these structures are likely to be unphysical.

Indeed, we have found that the nitrogen-substituted graphite structure shown in Fig. 1(b), in which the valency of the carbon atoms is not satisfied (each has one unpaired electron), is unstable. This structure, obtained by simply alternating C and N around the six-membered rings in graphite, has been proposed by Miyamoto *et al.*[46] as a possible structure for CN and it is also analogous to the graphite-like structure for C_3N suggested by Sandré *et al.*[26] On optimization, the carbon atoms move out of the plane of the sheets [Fig. 1(c), Structure A]. If the interlayer separation of the optimized Structure A is reduced and geometry optimization repeated, interlayer C-C bonds form and a different energy minimum is found, lower in energy than Structure A by 0.36 eV/atom [Fig. 1(d) and Table I, Structure B].



(a) (b)
(c) (d)

FIG. 1. (Color online) (a) Structural motif of a single layer of pure graphite; (b) Structural motif of a single layer of CN obtained by nitrogen substitution in graphite such that the replacement of three-coordinate carbon with three-coordinate nitrogen results in the presence of unpaired electrons on the remaining carbon atoms; (c) Structure A: optimized geometry for a structure comprising the N-substituted sheets shown in (b); (d) Structure B: optimized geometry. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

The inclusion of N-N bonds can eliminate the problem of unpaired electrons and unsatisfied valencies in nitrogen-substituted graphite. Therefore, we have investigated starting structures that are related to graphite, of the type shown in Fig. 2(a), such that N-N bonds are present and all valencies are satisfied. The N-N bonds break during geometry optimization under negative hydrostatic pressure and are replaced with considerably stronger C-N double bonds. The optimized structure is the same as that proposed for paracyanogen,[47] consisting of one-dimensional chains [Fig. 2(b)] with the chains arranged such that there is a large N-N separation [Fig. 2(c), Structure C].

Several structures of this type were investigated, with Structure C the lowest in energy. Structure C contains two-coordinate nitrogen and sp^2 hybridized carbon. While for-

TABLE I. Dispersion-corrected, optimized unit-cell parameters, cell volumes, and energies of possible structures for CN. Energies are relative to the lowest-energy structure.

Structure	Space group	Cell parameters	Volume (Å^3 atom^{-1})	Energy (eV atom^{-1})
A	*Pbnm*	$a=4.05$ Å, $b=7.10$ Å, $c=2.33$ Å, $\alpha=90.5°$, $\beta=90.0°$, $\gamma=90.1°$	8.19	0.38
B	*Pmnn*	$a=2.35$ Å, $b=3.91$ Å, $c=5.21$ Å, $\alpha=\beta=\gamma=90.0°$	5.98	0.02
C	$P\bar{1}$	$a=4.85$ Å, $b=2.27$ Å, $c=5.46$ Å, $\alpha=96.2°$, $\beta=82.0°$, $\gamma=94.2°$	14.81	0.08
D	$P\bar{1}$	$a=2.32$ Å, $b=4.79$ Å, $c=8.26$ Å, $\alpha=78.6°$, $\beta=86.6°$, $\gamma=89.5°$	11.22	0
E	$P\bar{1}$	$a=b=7.08$ Å, $c=6.79$ Å, $\alpha=133.1°$, $\beta=93.1°$, $\gamma=120.0°$	13.99	0.08
F	*P63/mmc*	$a=b=2.37$ Å, $c=11.38$ Å	6.87	0.10
G	*C2/m*	$a=4.10$ Å, $b=2.37$ Å, $c=5.73$ Å, $\beta=101.7°$	6.86	0.07
H	*P1*	$a=10.41$ Å, $b=10.19$ Å, $c=2.56$ Å, $\alpha=89.7°$, $\beta=90.3°$, $\gamma=89.8°$	17.0	0.56

mally the electrons are delocalized, it is worth noting that the C-C bonds shown in Fig. 2(b) are 1.48 Å, closer to a single C-C bond length (1.54 Å) than the carbon-carbon separation in benzene (1.40 Å)[47] and thus the structure can be viewed as two conjugated (C=N) chains linked by C-C bonds.

A structure with slightly lower energy was found when Structure C was extended in the direction perpendicular to the chain axis by combining three chains [Table I and Figs. 2(d) and 2(e), Structure D]. The structure contains both two- and three-coordinate nitrogen. The common feature of Structures C and D is conjugation along the lines of C-N bonds at the outer edges of the one-dimensional chains. Note that it is not possible to continue extending the structure in this way, as doing so will result in unsatisfied valencies.

An alternative structure for CN, analogous to a structure that has been proposed for isoelectronic boron monoxide,[48] has a very similar energy to Structure C [Table I and Figs. 2(f) and 2(g), Structure E]. In common with Structure C, it has some formal electron delocalization (but this time around six-membered rings rather than along a line of C-N bonds), two-coordinate nitrogen and sp^2 hybridized carbon, but consists of two-dimensional sheets rather than one-dimensional chains.

These conjugated structures (C, D, and E) that contain planar rings, which we have found to be low in energy, were not investigated in previous studies of the possible crystal structures for CN.[27] We have found three structures of this type that have similar low energies (within 0.1 eV/atom of each other, Table I). It is likely that there are more in addition to those discussed here.

Other structures previously suggested to be low in energy for CN are GaSe-like and β-InS-like structures.[27] These consist of layers of the structural motif shown in Fig. 1(b), in which carbon and nitrogen atoms alternate around six-membered rings in a graphite-like sheet, with the unpaired electrons on the carbon atoms forming C-C bonds that join the sheets. These interlayer C-C bonds can be formed in two ways; first, the bonds can be formed such that the graphite-like sheets are joined in pairs, resulting in a layered GaSe-like structure, or alternatively the bonds can be formed in such as way as to join all of the graphite-like sheets in a complete three-dimensional network, resulting in a β-InS-like structure. In both cases, all of the carbon is sp^3 hybridized.

There are, in fact, two possibilities for the GaSe-like structure—one in which the two layers forming each bilayer are directly on top of each other [GaSe itself, for which the initial structure was taken from Côté and Cohen,[27] Fig. 3(a), Structure F], and a modified structure in which the two layers are rotated through 180° relative to each other [Fig. 3(b), Structure G]. In Structure G, the C-N bonds are no longer eclipsed (i.e., there are no longer N-C-C-N torsion angles of 0°) and this is the lower in energy of the two possibilities, although the energy difference is small (Table I). Structure F was investigated by Côté and Cohen[27] for CN, but Structure G was not. Both of these GaSe-like structures have a low bulk modulus because they are layered structures with only weak interlayer bonding.

Optimization of the β-InS-like structure (for which the initial structure was taken from the Chemical Database Service)[50] resulted in a structure identical to that which formed spontaneously during optimization of the N-substituted graphite sheets [Structure B, Fig. 1(d)], provided that the initial volume was sufficiently small; otherwise optimization resulted in either Structure A or E. Structure B has a moderately high bulk modulus of 320 GPa. While this is lower than the bulk moduli of diamond (442 GPa)[51] and β-C_3N_4 ($\sim$450 GPa),[45] it is higher than that of other "hard" materials, such as α-Al_2O_3 (252 GPa) and β-Si_3N_4 (259 GPa).[52] Although Côté and Cohen[27] began an optimization from the β-InS structure for CN, they found that the C-C bonds broke during optimization such that the final structure was the same as Structure A studied in this current work. However, Structure A is higher in energy than the β-InS-like structure (Structure B) investigated here, which contained C-C bonds both before and after geometry

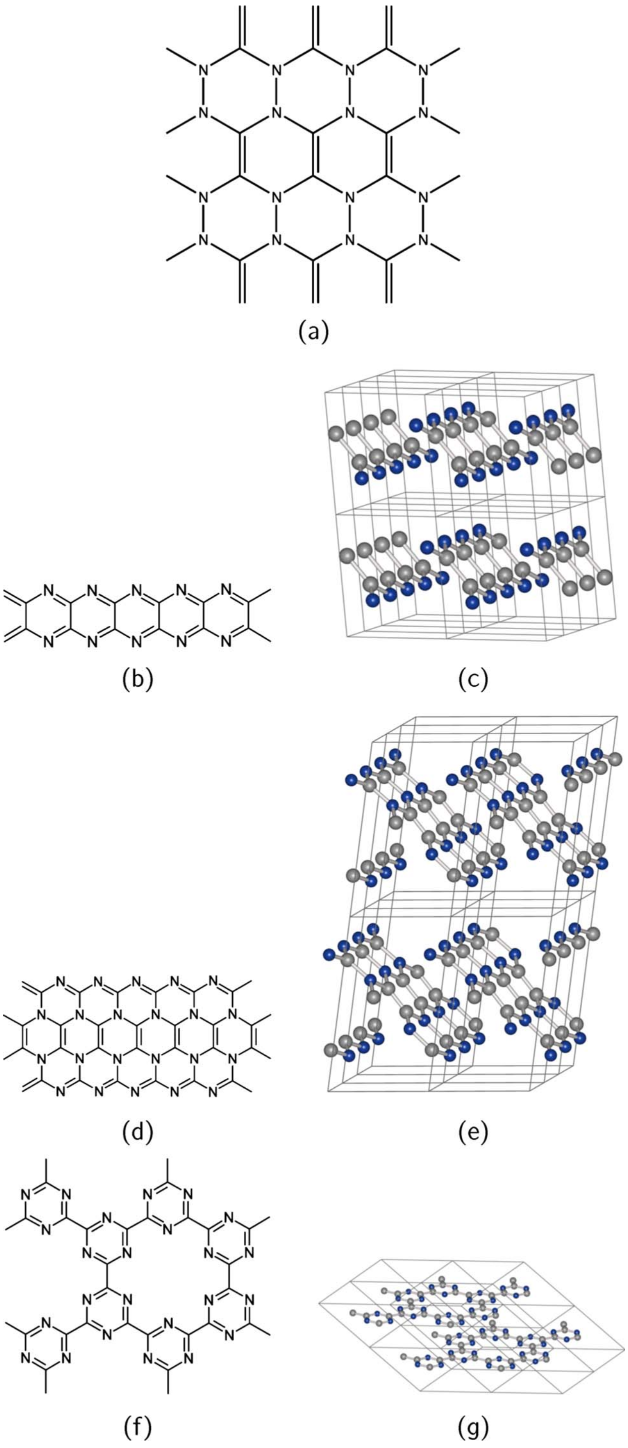


FIG. 2. (Color online) (a) Structural motif of a single layer of one possible nitrogen-substituted graphite with no unpaired electrons; (b) Structural motif of a single one-dimensional chain of the paracyanogen structure, the optimized bonding arrangement obtained from the sheets shown in (a); (c) Structure C: paracyanogen, optimized three-dimensional geometry for the one-dimensional chains shown in (b); (d) Structure D: optimized bonding arrangement for one-dimensional chains and (e) optimized geometry. (f) Structure E: optimized bonding arrangement and (g) optimized geometry for boron monoxide-like structure for CN. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

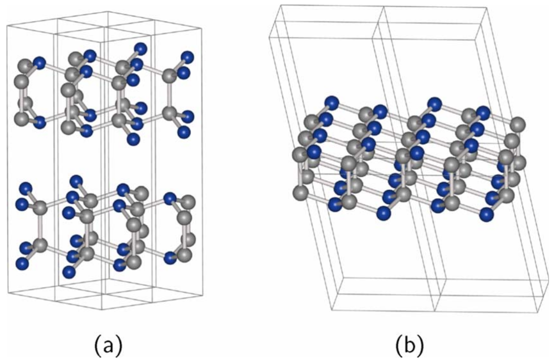


FIG. 3. (Color online) Optimized geometries of CN structures based on the GaSe structure: (a) Structure F (the GaSe structure itself, with the two sheets comprising each bilayer placed directly on top of each other); (b) Structure G (GaSe-like structure with the two sheets comprising each bilayer rotated through 180° relative to each other such that the C-N bonds are no longer eclipsed, as described in the text). The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

optimization. Our results for the relative energies of Structures A and F are in close agreement with those of Côté and Cohen.[27]

The final structure that we have investigated for CN is the body-centered tetragonal structure proposed by Kim *et al.*,[28] but we found it to be much higher in energy than the alternative structures that we have considered here (Table I, Structure H).

Thus, we have found three types of structures—conjugated planar-ring structures, GaSe-like, and β-InS-like—all with similarly low energies for CN (within 0.1 eV/atom of each other), but with very different equilibrium volumes [Table I and Fig. 4(a)]. This is due to the nature of the bonding—the β-InS-like structure (Structure B) has a complete three-dimensional network, while the conjugated (C, D, and E) and GaSe-like (F and G) structures are layered with dispersion interactions being of particular importance.

The energy of the β-InS-like structure is minimized at a volume of $\sim$6.0 Å^3/atom; at this volume, the C-C bond length is 1.57 Å, close to the diamond C-C bond length of 1.54 Å.[47] In contrast, the energy of the Structure D is minimized at a volume $\gtrsim$11 Å^3/atom, while the energy of Structures C and E is minimized at a volume of $\gtrsim$14 Å^3/atom. The β-InS-like structure is the lowest in enthalpy under positive hydrostatic pressures $\gtrsim$5 GPa [Fig. 4(b)] and it becomes less favorable relative to the layered structures as the pressure decreases. Structure D is the lowest in enthalpy under low and negative hydrostatic pressures, so either it or a similar conjugated structure is most likely to be formed under conditions that favor low densities and at high temperatures. The C-C bonds in the β-InS-like structure break when the volume is $\gtrsim$7 Å^3/atom. At lower densities than this, layered structures will be the most stable.

The β-InS-like and GaSe-like structures both consist of tetrahedral carbon (bonded to three nitrogen atoms and one other carbon atom) with nitrogen bonded to three carbon

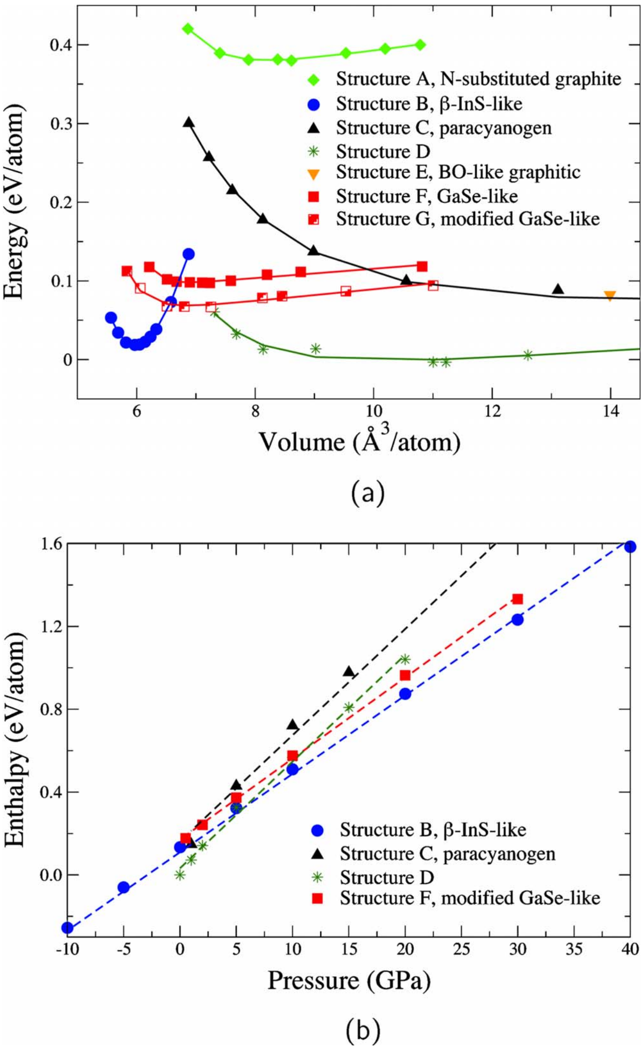


FIG. 4. (Color online) (a) Energy as a function of volume for possible CN structures. All energy values are relative to Structure D at zero pressure. The lines show the fits of the data to the Birch-Murnaghan equation of state (Ref. 49). (b) Enthalpy as a function of pressure for the lowest-energy structures; enthalpies are relative to Structure D at zero pressure. The lines are linear fits of the data and serve to guide the eye.

atoms. This is the bonding arrangement that we might expect for CN structures containing only sp^3 carbon because it avoids the presence of any relatively high energy N-N bonds. The β-InS-like structure has the lower dispersion corrected, optimized energy of the two, although the energy difference is small [Table I and Fig. 4(a)]. The most significant difference in the bonding arrangement between these two structures is that the nitrogen is bonded in an approximately planar arrangement in the β-InS-like structure (the sum of the C-N-C bond angles is 357.1°), whereas it is pyramidal in the GaSe-like (the sum of the C-N-C bond angles is 328.2° in Structure F and 327.6° in Structure G). All other bond lengths and angles are very similar between the two structures and they are close to those observed in strain-free environments. There is an energy increase associated with the planarization of nitrogen, although this increase is relatively small (24.7 kJ/mol, compared with 155 kJ/mol for phosphorus).[47] Given this, at first sight it is somewhat surprising that the dispersion corrected, optimized energy of the β-InS-like structure is very similar to, rather than higher than, those of the GaSe-like structures.

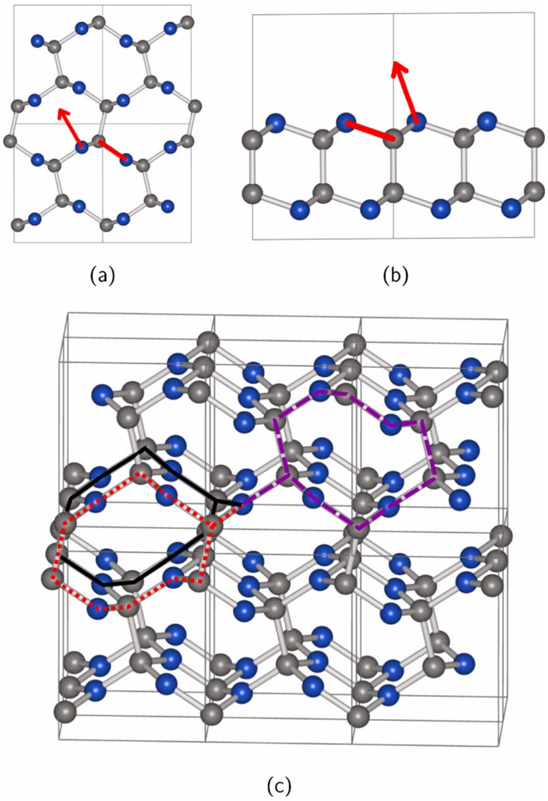


FIG. 5. (Color online) (a) β-InS-like structure and (b) GaSe-like structure for CN. The red arrow indicates the nitrogen lone pair, with the red line indicating a neighboring C-N bond; the torsion angle here is important for the "anomeric" effect discussed in the text. (c) β-InS-like structure, with three colored (solid, dashed, and dotted) lines showing the three C_6N_4 rings to which each nitrogen atom is attached. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

The "anomeric" effect, well-known in molecular chemistry,[53–55] can be used to rationalize the stabilization of the β-InS-like structure relative to the GaSe-like structures. The conventional explanation of this effect involves a stabilizing π interaction between the nitrogen lone pair and an antiperiplanar σ^* orbital on an adjacent C-N bond. Thus, structures in which the N-C-N-(lone-pair) dihedral angle is close to 180° are often preferred to those in which this angle is 30−90°.[56] In the β-InS-like structure, this angle is either $\sim$150° or $\sim$60° whereas it is always $\lesssim$80° in the GaSe-like structures [Figs. 5(a) and 5(b)].

Another possibility is that a steric effect may counter the energy increase associated with planarization of nitrogen in the β-InS-like structure. In this structure, each nitrogen is connected to three bulky C_6N_4 rings [Fig. 5(c)], the separation of which will be increased as the C-N-C bond angle increases. However, this effect is difficult to quantify because there is no energy minimum associated with the β-InS-like structure without planar nitrogen. It has previously been argued[57] that steric effects may play a role in stabilizing nitrogen in a planar geometry.

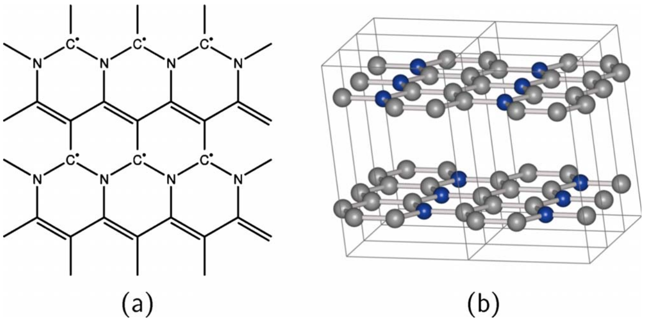


FIG. 6. (Color online) (a) Structure J: bonding arrangement and (b) optimized geometry for nitrogen-substituted graphite, proposed by Sandré *et al.* (Ref. 26) as a structure for C_3N. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

The β-InS-like structure is the thermodynamically favored structure at high densities (e.g., under positive hydrostatic pressures), suggesting that structures with planar nitrogen may become favorable at high densities, a point to which we will return in Sec. III C.

B. C_3N

For C_3N, the structures we study include those proposed by Sandré *et al.*,[26] as well as structures analogous to those suggested by Claeyssens *et al.*[58] for C_3P. In some of these C_3P structures, the phosphorus is hypervalent; these structures are, therefore, not possible for C_3N and are not considered here.

We begin by investigating the nitrogen-substituted graphite structure reported by Sandré *et al.*[26] as the lowest-energy structure for C_3N [Fig. 6(a), Structure J]. However, as for the N-substituted graphite structure for CN, some of the atomic valencies are not satisfied in this structure—there are unpaired electrons on some carbon atoms. Although this structure is stable, in that the bonding arrangement does not change during geometry optimization [Fig. 6(b)], it was thought that there are likely to be other structures with lower energy. We have searched for these structures by looking for analogs to those that are low in energy for CN.

A conjugated structure analogous to the low energy paracyanogen structure for CN, in which all carbon atoms are sp^2 hybridized and formally there is electron delocalization, can be created for C_3N by including additional sp^2 carbon between the nitrogen atoms [Fig. 7(a), Structure K]. The optimized structure consists of one-dimensional chains, which, as for CN, are arranged such that there is a large N-N separation [Fig. 7(b)]. This structure has approximately the same energy as the N-substituted graphite (Structure J) proposed by Sandré *et al.*[26] [Table II and Fig. 8(a)]. However, there is some strain in this paracyanogen-like structure (Structure K) caused by the presence of a chain of conjugated carbon-carbon bonds running in parallel to a chain of conjugated carbon-nitrogen bonds that constrains the length of these bonds. The C-N bonds are stretched relative to those observed in a similar environment in Structure C for CN (1.35 Å, compared with 1.33 Å), while the conjugated C-C bonds are shorter than those observed in benzene (1.37 Å, compared with 1.40 Å). As for the analogous structure for CN (Structure C), the length of the C-C bonds that link the chains of conjugated bonds (1.44 Å) is between a single C-C bond length (1.54 Å) and the carbon-carbon separation in benzene (1.40 Å),[47] suggesting that electrons are not fully delocalized. These conjugated structures for both C_3N and CN are similar to those suggested as potential photocatalytic materials and also to the graphene nanoribbons doped with nitrogen at the edges that have been found to be *n*-type semiconductors.[14]

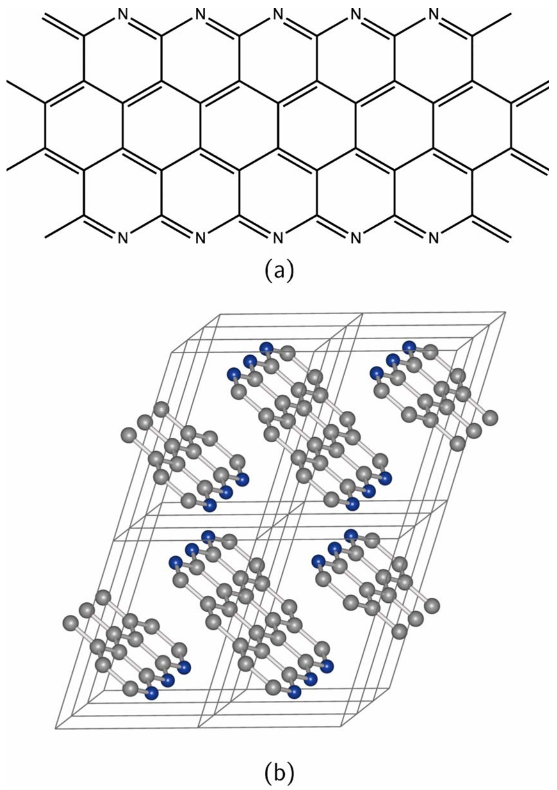


FIG. 7. (Color online) Structure K: (a) optimized bonding arrangement and (b) optimized geometry for the paracyanogen-like structure of C_3N. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

We have investigated the three other structures proposed by Sandré *et al.*[26] (Structures L, M, and N, Fig. 9). These are related to the N-substituted graphite sheets shown in Fig. 6(a), with the unpaired electrons on the carbon atoms used to form C-C bonds between the layers such that all atomic valencies are satisfied. These C-C bonds can be formed such that the N-substituted graphite sheets are joined in pairs to form a bilayer structure [Structure L, Fig. 9(a)], analogous to the GaSe-like structures (Structures F and G) for CN. Alternatively, the C-C bonds can be formed such that all of the N-substituted graphite sheets are connected in a three-dimensional network. Sandré *et al.*[26] have suggested two ways in which this can be done [Structures M and N, Figs. 9(b) and 9(c)], one of which (Structure M) is analogous to the β-InS-like structure (Structure B) for CN. In all three structures, the ratio of sp^2 to sp^3 carbon is 2:1.

TABLE II. Dispersion-corrected, optimized unit-cell parameters, cell volumes and energies of possible structures for C_3N at the equilibrium volume. Energies are relative to the lowest-energy structure.

Structure	Space group	Cell parameters	Volume ($Å^3$ atom^{-1})	Energy (eV atom^{-1})
J	$P\bar{1}$	$a=4.15$ Å, $b=2.39$ Å, $c=6.72$ Å, $\alpha=97.6°$, $\beta=94.0°$, $\gamma=90.0°$	8.07	0.04
K	$P\bar{1}$	$a=2.35$ Å, $b=6.18$ Å, $c=6.90$ Å, $\alpha=117.8°$, $\beta=122.9°$, $\gamma=78.7°$	9.55	0.05
L	$P\bar{1}$	$a=4.15$ Å, $b=2.39$ Å, $c=6.21$ Å, $\alpha=85.5°$, $\beta=109.9°$, $\gamma=90.0°$	7.05	0.07
M	*Pbam*	$a=8.09$ Å, $b=6.17$ Å, $c=2.39$ Å, $\alpha=\beta=\gamma=90.0°$	7.47	0.01
M2	*Pbam*	$a=6.75$ Å, $b=7.92$ Å, $c=2.39$ Å, $\alpha=\beta=\gamma=90.0°$	8.09	0
N	*Pmna*	$a=4.74$ Å, $b=4.12$ Å, $c=5.40$ Å, $\alpha=89.8°$, $\beta=\gamma=90.0°$	6.63	0.06
O	$P1$	$a=b=2.42$ Å, $c=9.99$ Å, $\alpha=85.2°$, $\beta=89.9°$, $\gamma=120.0°$	6.32	0.08
P	$P2/m$	$a=3.62$ Å, $b=2.41$ Å, $c=5.26$ Å, $\beta=97.1°$	5.70	0.16
Q	$P21/m$	$a=3.55$ Å, $b=2.39$ Å, $c=6.14$ Å, $\beta=104.7°$	6.32	0.08

For Structure M, we used the same initial structure as Sandré *et al.*[26] but found that a different geometry was obtained when a negative hydrostatic stress was applied [Structure M2, Fig. 9(d)]. When this geometry was reoptimized with no hydrostatic stress, we found it to be slightly lower in energy than the geometry reported by Sandré *et al.* who did not investigate the effect of pressure and therefore did not find this alternative geometry (Structure M2).

Comparing our results for Structures J, L, M, and N with those of Sandré *et al.*,[26] we found (prior to applying the dispersion correction to our results) the same energy ordering for the four structures that they considered, with similar energy differences, but we have also found two additional low energy structures: (1) a conjugated paracyanogen-like structure with sp^2 carbon (Structure K) and (2) Structure M2, which has the same bonding arrangement as Structure M, investigated by Sandré *et al.*, but in an alternative geometry. With the inclusion of dispersion interactions, we find Structure M2 to be lower in energy than any of the structures reported in this previous work.[26]

As for CN, several structures have been found with very similar energies, but they have different equilibrium volumes and, therefore, the conditions favoring their formation will be different. Structure M2 is the lowest in enthalpy under positive hydrostatic pressures up to ~10 GPa [Fig. 8(b)], but, as for the analogous β-InS-like structure for CN, it becomes less favorable relative to the paracyanogen-like structure (Structure K) with decreasing pressure. The C-C bonds in Structure M2 break when the volume is $\gtrsim 10$ $Å^3$/atom.

Structure N becomes lower in enthalpy than Structure M2 at hydrostatic pressures ≥ 10 GPa [Fig. 8(b)] and the C-C bonds in this structure break when the volume is $\gtrsim 8$ $Å^3$/atom. Thus, Structure N is the preferred structure under conditions that favor high densities, while the paracyanogen-like structure with formally delocalized electrons will be favored under conditions that favor low densi-

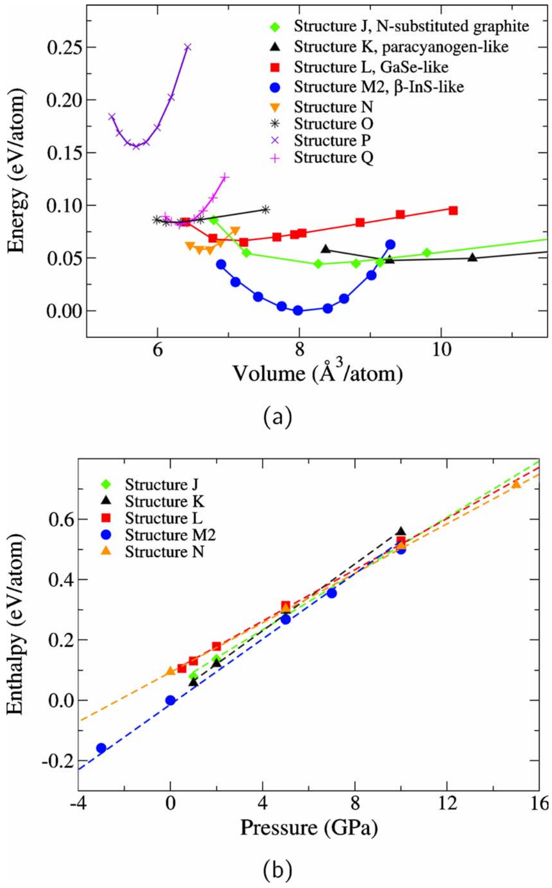


FIG. 8. (Color online) (a) Energy as a function of volume for possible C_3N structures. The lines show the fits of the data to the Birch-Murnaghan equation of state (Ref. 49). (b) Enthalpy as a function of pressure for the five lowest-energy structures; enthalpies are relative to that of Structure M2 at zero pressure and lines are guides to the eye only.

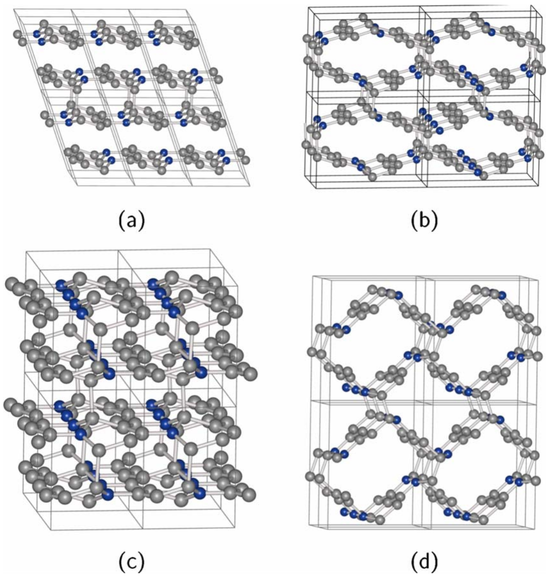


FIG. 9. (Color online) (a) Structure L; (b) Structure M; (c) Structure N; (d) Structure M2. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

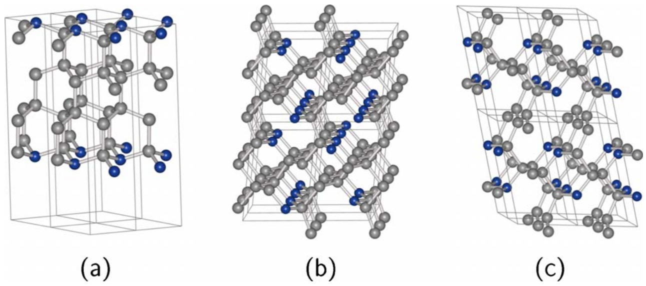


FIG. 10. (Color online) (a) Structure O: GaSe-like structure for C_3N; (b) Structure P; (c) Structure Q. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

ties. Conditions intermediate between these two extremes are likely to favor Structure M2.

The three-coordinate nitrogen adopts a more pyramidal geometry in the low energy C_3N structure (Structure M2) than in the analogous CN structure (Structure B). The sum of the C-N-C bond angles is 344° in Structure M2, compared with 357° in Structure B. Also, the nitrogen adopts a more planar geometry in Structures L and N (the sum of the C-N-C bond angles is 348° and 360°, respectively), which are higher in energy than Structure M2. This suggests that, for C_3N, structures in which nitrogen can adopt a strain-free pyramidal geometry are preferred over those in which nitrogen is constrained to a planar geometry. Structure N becoming thermodynamically favorable with increasing pressure is consistent with the observation for CN that structures with planar nitrogen become favorable at high densities.

For CN, it was argued that the structure with planar nitrogen could be stabilized relative to the structure with pyramidal nitrogen by anomeric and steric effects. The anomeric effect cannot play any role in these C_3N structures because there are no neighboring C-N bonds to interact with nitrogen lone pairs. It also does not seem plausible for steric effects to be playing a role in these structures because the nitrogen atoms are not attached to bulky groups. Thus, anomeric and steric effects cannot act to counter the planarization energy of nitrogen in C_3N structures and the lowest-energy structures are those with pyramidal nitrogen.

Structure M2 has a bulk modulus of ~120 GPa, considerably lower than that of the analogous CN structure (the β-InS-like Structure B), which is consistent with a lower concentration of sp^3 hybridized carbon and, hence, a lower density of C-C bonds joining the N-substituted graphite sheets. Structure N has a moderately high bulk modulus of ~250 GPa.

We have also studied several structures with an increased sp^3 carbon content. In particular, it was anticipated that structures with a high sp^3 carbon content may have a high bulk modulus and high equilibrium density. Structures of this type that we have investigated include one related to the GaSe-like structure of CN but with additional layers of sp^3 carbon [Structure O, Fig. 10(a)], another with only sp^3 carbon [Structure P, Fig. 10(b)] and one containing a 1:2 ratio of sp^2 to sp^3 carbon [Structure Q, Fig. 10(c)]. While the energy minima for these structures occur at lower volumes than for the structures with a lower sp^3 carbon content (particularly Structure P, which contains only sp^3 carbon and has a complete three-dimensional bonding network) and the bulk moduli are high (~400 GPa for Structure P and ~290 GPa for Structure Q), these structures are all highly strained and have high energies [Table II and Fig. 8(a)].

C. Variation in thermodynamic stability with composition

Formation energies have been investigated as a function of nitrogen content (Fig. 11), considering not only CN and C_3N but other compositions ($C_{3+8n}N_4$ with n taking integer values between 0 and 3). For $C_{3+8n}N_4$, we consider both graphitic structures [layered structures consisting of two-dimensional sheets with only sp^2 carbon and formally delocalized electrons, Fig. 12(a)] and pseudocubic-like structures [containing only sp^3 carbon, Fig. 12(c)] and have calculated

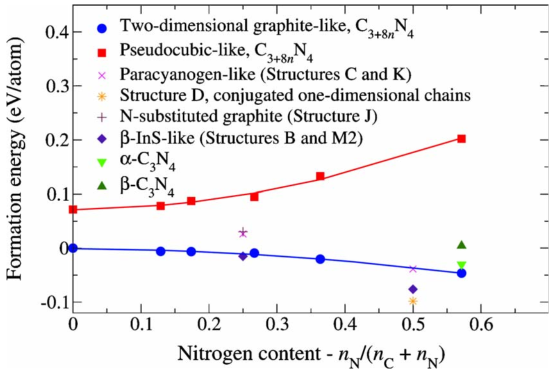


FIG. 11. (Color online) Formation energy of carbon nitride as a function of composition; lines are quadratic fits of the data and serve to guide the eye. Formation energies were calculated with energy values of −156.31 eV/atom for graphite and −271.98 eV/atom for N_2 gas and include a dispersion correction.

formation energies including the dispersion interactions. These two types of structures were produced for different compositions as discussed in previous publications.[59,60] Formation energies of α- and β-C_3N_4 are also included in Fig. 11 for comparison.

For CN and C_3N, the formation energies of the β-InS-like structures (made from N-substituted graphite sheets with C-C bonds between the sheets) are included in Fig. 11, as well as those for the conjugated structures consisting of one-dimensional chains with sp^2 carbon. Formation energies for the N-substituted graphite structures are also included for comparison.

For all compositions, the formation energy of the graphitic structures with $C_{3+8n}N_4$ compositions, consisting of two-dimensional sheets with formally delocalized electrons [of the type shown in Fig. 12(a)] is low, as expected in view of the known chemical preferences of carbon and nitrogen for multiple bonding (sp^2 hybridization).[47] The formation energy of these structures is approximately constant (or decreases slightly) as the nitrogen content increases.

The conjugated planar-ring structures for CN (e.g., Structures C and D made from one-dimensional chains, and the boron monoxide-like Structure E, which is not shown in Fig. 11) have a similar local bonding environment to the graphitic structures with $C_{3+8n}N_4$ compositions (e.g., both carbon and nitrogen are sp^2 hybridized and formally there are delocalized electrons). The formation energies of these structures fit with the trend observed for the two-dimensional $C_{3+8n}N_4$ graphitic structures (although the formation energy of Structure D is slightly lower, Fig. 11), suggesting that there is no significant strain present.

The formation energy of the paracyanogen-like structure for C_3N is higher than the trend would suggest. This is consistent with the presence of strain in the bonds, as discussed in Sec. III B.

These results suggest that all strain-free, conjugated carbon nitride structures in which both carbon and nitrogen are sp^2 hybridized and formally there is some electron delocalization will have approximately the same energy for a given composition, with that energy consistent with the trend shown in Fig. 11. As seen for CN, electrons can be delocalized either around six-membered rings or along lines of carbon-nitrogen bonds, and the energy is very similar for the two possibilities. The same is also seen for C_3N_4; the energy of the graphite-like structure shown in Fig. 12(b), in which electrons are delocalized across the two-dimensional sheets along lines of carbon-nitrogen bonds, is very similar to that of the structure shown in Fig. 12(a), in which electrons are delocalized around six-membered rings. These results are in agreement with those of Mattesini *et al.*,[62] who also found that the energies of these two structures are very close. Furthermore, it has been suggested that graphitic carbon nitride structures are more likely to be composed of tri-*s*-triazine (melem) units, rather than *s*-triazine units as in the graphite-like structures shown in Fig. 12.[5] In line with the argument outlined above, structures composed of tri-*s*-triazine, in which both carbon and nitrogen are sp^2 hybridized and formally there is some electron delocalization, have been predicted to have similar (slightly lower) energies than those composed of *s*-triazine units.[63] It is likely that there is a range of possible conjugated structures for each composition all with similar energies, making prediction of the exact crystal structure difficult.

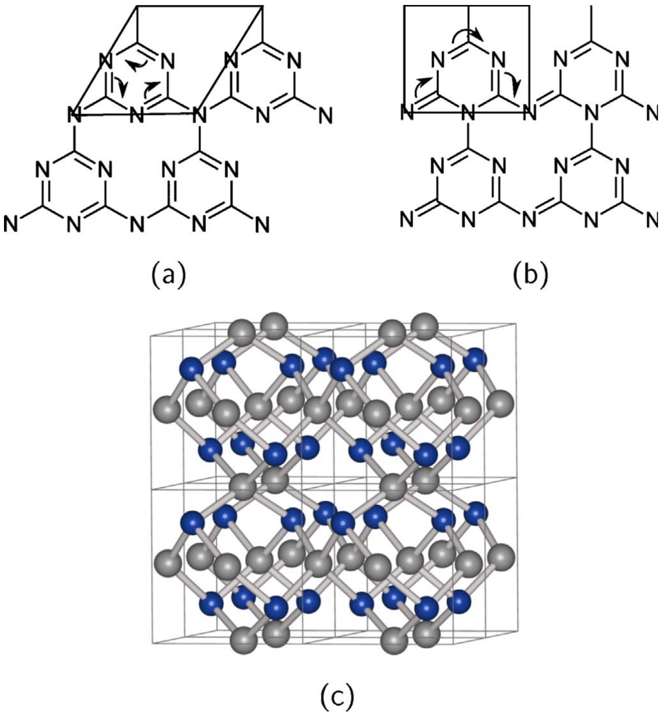


FIG. 12. (Color online) (a) One layer of graphitic-C_3N_4 proposed by Teter and Hemley (Ref. 45) with sp^2 carbon and formally delocalized electrons; electrons are delocalized around the six-membered rings. This structure can be considered to consist of graphite sheets with carbon vacancies surrounded by nitrogen atoms. An equivalent structure can be produced for a wide range of compositions (from pure carbon to C_3N_4) by adjusting the vacancy concentration. (b) An alternative graphitic-C_3N_4 structure proposed by Alves *et al.* (Ref. 61), in which electrons are delocalized across the two-dimensional sheets along lines of carbon-nitrogen bonds rather than around the six-membered rings. (c) Pseudocubic C_3N_4; this structure can be considered to consist of diamond with carbon vacancies surrounded by nitrogen atoms and the composition can be adjusted as for the graphitic structures. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

For C_3N, the formation energy of the structure made from N-substituted graphite sheets with unpaired electrons on the carbon atoms (Structure J), previously reported to be the lowest-energy structure,[26] is approximately equal to that of the paracyanogen-like C_3N structure with formally delocalized electrons (Structure K) in which all valencies are satisfied but there is some strain. Therefore, a *strain-free* conjugated structure for C_3N in which all valencies are satisfied would be expected, if such a structure exists, to have lower formation energy than both Structures J and K. For CN, N-substituted graphite structures with unpaired electrons were found to be unstable. This suggests that structures of this type are highly unlikely to form when the nitrogen content is high and, even when the nitrogen content is low, their formation is unlikely to be favorable relative to strain-free conjugated structures.

Of the structures in which all of the nitrogen is three-coordinated (rather than at least some being two-coordinated as it is in the conjugated structures) and there is at least some sp^3 hybridized carbon, it might be expected that the pseudocubic-like structures would be low in energy because the nitrogen adopts a pyramidal geometry (the sum of the C-N-C bond angles is $\sim 332°-337°$, depending on the nitrogen content). It has been argued previously that three-coordinate nitrogen should prefer to be sp^3 hybridized rather than sp^2 hybridized in carbon nitride structures.[57,64] However, it has been found in this work that the formation energy of the pseudocubic-like structures is relatively high and increases as the nitrogen content increases (Fig. 11). This is consistent with small N-N separations, which are only 2.50 Å when the nitrogen atomic fraction is 0.13 (the smallest nitrogen content investigated) and decrease further as the nitrogen content increases, reaching 2.43 Å for C_3N_4. These pseudocubic-like structures can be usefully viewed as diamond-like with carbon vacancies surrounded by nitrogen atoms. As the nitrogen content increases, the bonding arrangement becomes thermodynamically less favorable as C-C bonds are replaced with weaker C-N bonds and the vacancy concentration increases, which also contributes to the increase in the formation energy with increasing nitrogen content.

The β-InS-like structures are considerably more favorable than the pseudocubic-like structures for all compositions (although different compositions were investigated for the two types of structure, this can be clearly seen by interpolation), consistent with the significantly larger N-N separations. The formation energy of the β-InS-like structures decreases as the nitrogen content increases.

The formation energies of α and β-C_3N_4 are considerably less than that of the pseudocubic structure for C_3N_4 (all of these structures have three-coordinate nitrogen and four-coordinate carbon), even though the nitrogen adopts a pyramidal geometry in the pseudocubic structure, but a planar (or almost planar) geometry in the α and β phases. The higher formation energy is consistent with the much shorter N-N separations in the pseudocubic structure. Further evidence for the effect of N-N separations is that, in the pseudocubic structure, the C-N bonds are stretched compared with those in α and β-C_3N_4, consistent with there being significant repulsion between the nitrogen atoms.

The β-InS-like structure for CN has a lower formation energy than α and β-C_3N_4. This is consistent with both longer N-N separations and a more thermodynamically favorable bonding arrangement (e.g., the presence of strong C-C bonds). Its formation energy is also very close to those of the graphite-like structures, in contrast to α and β-C_3N_4 for which the formation energies are significantly higher than the graphite-like structures. This suggests that the β-InS-like structure for CN should be more easily formed than α and β-C_3N_4. This structure has a moderately high bulk modulus, although not as high as α and β-C_3N_4.

For both CN and C_3N_4, the preferred structure under positive hydrostatic pressures is one in which the three-coordinate nitrogen is close to planar. In contrast, for C_3N, the nitrogen adopts a pyramidal geometry in the lowest-energy structure. This suggests that as the nitrogen content is increased three-coordinate nitrogen becomes increasingly planar in the structures that are low in energy under positive pressures. It is likely that this trend is related to the N-N separations, which become increasingly important as the nitrogen content and density increase.

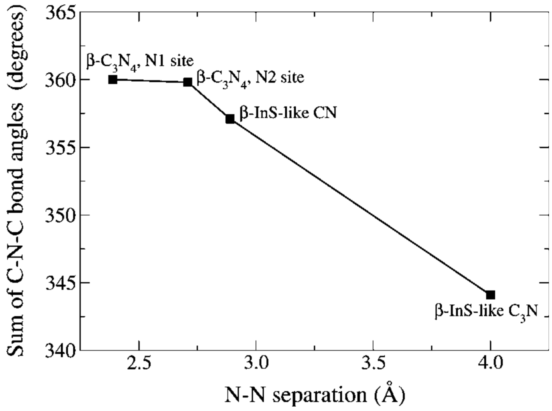


FIG. 13. Sum of the C-N-C angles at each distinct crystallographic site versus N-N separation for various carbon nitride structures.

In Fig. 13, the sum of the C-N-C angles is shown as a function of N-N separation in various structures. Data are included for the two different nitrogen sites in β-C_3N_4 (Refs. 21, 65, and 66) as well as the β-InS-like structure for both CN and C_3N. These results suggest that there is a relationship between the N-N separation and the geometry of three-coordinate nitrogen in carbon nitride. Nitrogen tends to adopt a planar geometry when the N-N separations are small. As the N-N separation increases, the repulsive energy between nitrogen atoms reduces and the optimum trade-off between the repulsive energy and the planarization energy is such that the nitrogen geometry becomes nonplanar. Small N-N separations, and hence planar nitrogen, are most likely to occur in high density structures with high nitrogen content. We also note in passing that, for the nitrogen sites in β-C_3N_4 at which the nitrogen geometry is slightly nonplanar, the direction in which the nitrogen atoms move away from planarity is such to reduce the N-N separation, contradicting the possibility that these sites become pyramidal to reduce N-N interactions, as has been previously suggested.[21]

As mentioned in the discussion of C_3N structures (Sec. III B), we have searched for a low-energy, high-density structure for C_3N in which all of the carbon is sp^3 hybridized, but all of the structures that we have found in this category are high in energy. Based on the trend discussed above, it is likely that, if such a structure exists, the N-N separations will be small and the nitrogen will adopt a planar geometry.

For CN, it was argued that steric effects could play a role in offsetting the energy increase associated with planarization of nitrogen; this is also true for β-C_3N_4. For one of the two different types of nitrogen sites (N1 sites) in β-C_3N_4, all C-N-C angles are 120.0°. The nitrogen atoms in these sites are attached to three bulky C_6N_6 rings[57] the separation of which is maximized by the nitrogen adopting a planar geometry with C-N-C angles of 120°. For the second type of ni-

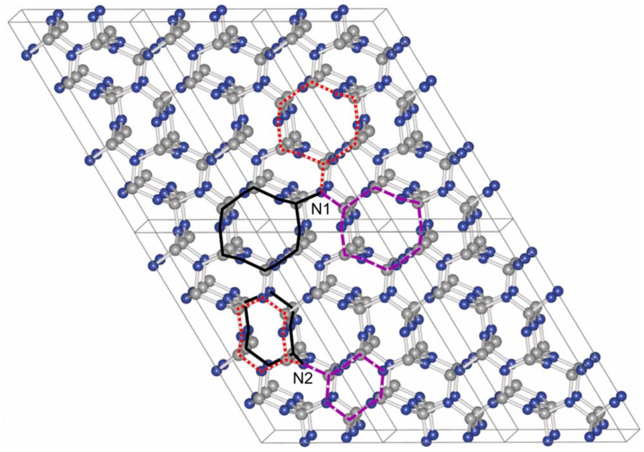


FIG. 14. (Color online) β-C_3N_4, with three colored (solid, dashed, and dotted) lines showing the three C_6N_6 rings to which each N1 nitrogen atom is attached and the three C_4N_4 rings to which each N2 nitrogen atom is attached. The light gray and the darker blue atoms are C and N, respectively, and the black lines show the unit-cell boundaries.

trogen site (N2 sites), the nitrogen atoms are attached to three C_4N_4 rings (Fig. 14); the geometry of these sites is very similar to that of the nitrogen sites in the β-InS-like structure for CN [Fig. 5(c)]. The N-C-N-(lone-pair) dihedral angle reaches values of 180° and 148.6° for the N2 sites sites and 152° for the N1 sites, whereas it is $\lesssim 60°$ in the pseudocubic structure, suggesting that, as for CN, the anomeric effect may also play a role in stabilizing the β phase of C_3N_4 relative to the pseudocubic.

The low-energy structures that contain at least some sp^3 hybridized carbon for both CN and C_3N (i.e., Structures B and M2, respectively) are related to the lowest energy structures for PC and PC_3, respectively,[58,67] except that in the phosphorus carbide structures phosphorus occupies the four-coordinate sites and carbon the three-coordinate sites. Thus, all carbon is sp^2 hybridized in the phosphorus carbide structures, whereas it is both sp^2 and sp^3 hybridized in the C_3N structure and all sp^3 hybridized in CN. This is consistent with the stronger preference of phosphorus, in comparison with nitrogen, for sp^3 hybridization,[47] which is more easily satisfied at the four-coordinate sites in these structures, as well as the preference of carbon for sp^2 rather than sp^3 hybridization. To occupy these four-coordinate sites, the phosphorus must be hypervalent; thus, it is not possible for nitrogen to occupy the four-coordinate sites.

D. Correlation with experiment

Based on our analysis of formation energies, it is possible to predict the most likely local bonding environments for both carbon and nitrogen in carbon nitride. At low pressures or high temperatures, the most likely synthesis products are conjugated systems, where the chemical structure indicates some formal electron delocalization. However, the exact arrangement of the bonds cannot be determined because several possibilities have been investigated and all have similar energies. Thus, synthesis is likely to result in the production of a disordered mixture of planar-ring conjugated structures. Alternatively, under conditions that favor higher densities, synthesis may result in structures based on N-substituted graphite sheets (e.g., β-InS-like structures) with the formation of C-C bonds between the sheets becoming increasingly favorable as the nitrogen content increases.

Both of these possibilities are consistent with experimental reports. For example, it has been found that a transition from sp^3 to sp^2 carbon occurs as the nitrogen content in carbon nitride films increases, at least for nitrogen atomic fractions ≤ 0.25.[68,69] There have also been several reports of the synthesis of graphitic carbon nitride[9–13,70] and nitrogen bonded to two carbon atoms in a graphitic structure has been reported as one of the most likely nitrogen environments in carbon nitrides.[43] These experimental reports are consistent with the low formation energies calculated in this work for structures with formally delocalized electrons and sp^2 hybridized carbon. Furthermore, our prediction that synthesis is likely to result in the production of a mixture of planar-ring conjugated structures is consistent with experimental reports of disordered and amorphous synthesis products that have a graphitic nature and contain sp^2 hybridized carbon and nitrogen.[16,17,20]

In addition, it has been suggested[71] that, at low nitrogen content, nitrogen-substituted graphite forms, but at a nitrogen atomic fraction between ~0.05 and ~0.15 these nitrogen-substituted graphite sheets become unstable and C-C bonds form between the sheets. Consistent with this, we have found N-substituted graphite sheets without C-C bonds to be stable for C_3N, but with a higher energy than structures with C-C bonds. Structures made from N-substituted graphite sheets without C-C bonds are unstable for CN due to the presence of unpaired electrons on the carbon atoms; C-C bonds formed spontaneously between graphite sheets during optimization of this structure. Nitrogen substituted into graphite with one neighboring sp^3 carbon has been reported as another commonly occurring nitrogen environment in carbon nitrides with a nitrogen atomic fraction of ~0.2,[43] in agreement with the structural transformation proposed by Hellgren *et al.*[71] This is the local bonding environment in the β-InS-like structures, which we have found to be low in energy for both C_3N and CN. In the case of the β-InS-like structure for CN, the formation energy is lower than that of β-C_3N_4, suggesting that it can be more easily synthesized, and the bulk modulus is moderately high.

IV. CONCLUSIONS

Low-energy structures have been predicted for CN and C_3N and the results compared with those predicted for C_3N_4. For each composition, there are several structures with similarly low energy but very different equilibrium volumes. Hence, the structure that is produced will be strongly dependent on the synthesis conditions. At low pressures (or high temperatures), the thermodynamically preferred carbon nitride structures are conjugated and contain sp^2 hybridized carbon. These structures are similar to those that have been suggested as potential photocatalytic materials. At higher pressures, the preferred structures are related to β-InS and contain three-coordinate nitrogen and at least some sp^3 hybridized carbon (depending on the nitrogen content). As density and nitrogen content increases, N-N separations appear to become increasingly important in determining the lowest-energy structure and nitrogen becomes increasingly planar in the thermodynamically preferred structures. Structures in which all of the carbon is sp^3 hybridized and there is a complete three-dimensional network of bonds tend to have high bulk moduli. These structures become thermodynamically favorable at high densities so their formation may be possible under high pressure.

The local bonding environments in the structures that we predict to have the lowest formation energies are consistent with those reported in experimental work. Specifically, our finding that conjugated structures with some formal electron delocalization are low in energy is consistent with experimental reports of the synthesis of graphitic carbon nitride. In addition, the β-InS-like structure for CN has a lower formation energy than α and β-C_3N_4 suggesting that it could be synthesized more easily. This CN structure is predicted to have a bulk modulus of 320 GPa, which, despite being lower than that predicted for β-C_3N_4, is moderately high and so this structure is of particular interest since it is likely to be more accessible than β-C_3N_4.

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