



What are the possible structures for CN_x compounds? The example of C_3N

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Abstract

It has been proposed that carbon nitride compounds could present abnormal mechanical properties. Until now, these compounds have only been synthesized as amorphous films and the search for their structure is a live topic. Using ab-initio calculations, we propose a few stable structures which could be in dynamical equilibrium. We suggest that CN_x ($x = 0.33$) structural arrangements dynamically equilibrate over the time which is necessary to perform a structural measurement and that more than one structure could be needed to describe them. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the original proposal and calculations on the ultra-hard material C_3N_4 by Liu and Cohen [1], a large effort has been directed towards the synthesis of this compound. Irrespective of the experimental procedure used to achieve this goal, almost every author has reported difficulty in obtaining high proportions of nitrogen in the final product. With respect to the stoichiometric formula CN_x , one usually obtains compounds with an $x < 0.33$ [2].

The search for ultra-hard materials is of interest because of the great number of potential applications which these systems have. C_3N_4 crystals or films should be ultra-hard as predicted. However, one

must ask whether a high Young modulus is a characteristic of all types of CN_x structures that may be synthesized on the way?

2. Calculations

In this Letter, we report theoretical calculations on prospective C_3N phases which present an obviously low compressibility in two of the three spatial directions. These 3-dimensional compounds were theoretically predicted by starting from the substitution in graphite of one carbon site out of four by nitrogen. We used a density functional theory (DFT) total energy scheme [3] based on ultra-soft pseudopotentials [4] with a plane-wave basis set cut-off energy of 320 eV. The exchange and correlation energy was calculated using the generalized gradient approximation (GGA) as given by Perdew and Wang [5]. The sets of irreducible k -points used in the Brillouin zone

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Table 1

Relaxed atomic structure of C_3N within the graphite structure.
Cell parameters: $a = 4.26 \text{ \AA}$; $b = 2.46 \text{ \AA}$; $c = 6.70 \text{ \AA}$. $\alpha = \beta = \gamma = 90^\circ$

	Fractional atomic coordinates		
C	0	0	1/4
C	1/6	1/2	1/4
C	1/2	1/2	1/4
C	0	0	3/4
C	1/2	1/2	3/4
C	5/6	1/2	3/4
N	2/3	0	1/4
N	1/3	0	3/4

integration were generated according to the Monkhorst–Pack scheme using a spacing of

0.05 \AA^{-1} which was found to be sufficient to converge the total energy. The total energy is minimized using a conjugate gradient and density mixing scheme [6].

Considering a double graphite sheet containing 8 atoms per unit cell which is built from two hexagonal graphite unit cells, one needs to substitute one carbon atom in each slab with nitrogen to reach the C_3N composition. Within the $P2/m$ space group, the corresponding relaxed atomic coordinates are given in Table 1 and the structure is represented schematically in Fig. 1a. Obviously, one expects the graphite structure to be stable (i.e. to correspond to a local minimum the total energy). However, one may wonder what happens if the nitrogen atoms are brought out their position in the flat sheet. If the

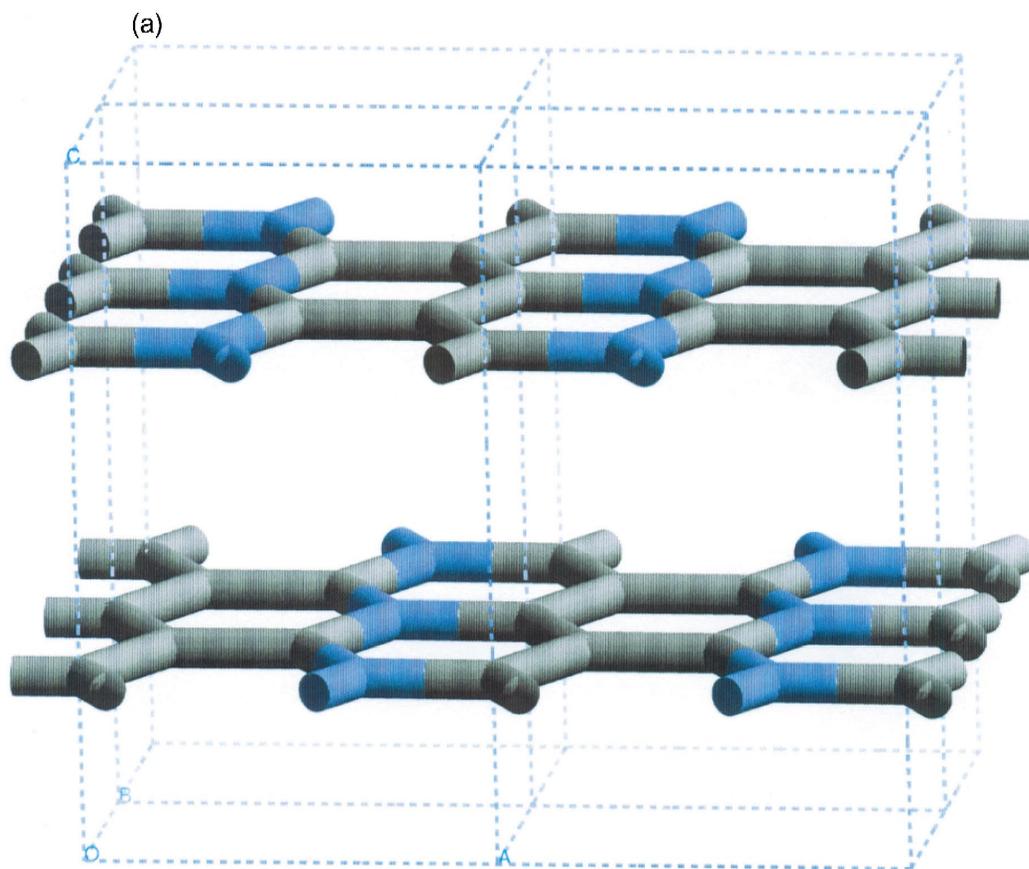


Fig. 1. (a) Structural arrangement for the flat N-substituted Graphite with composition C_3N . (b) Structural arrangement for dimerised N-substituted Graphite sheets with composition C_3N .

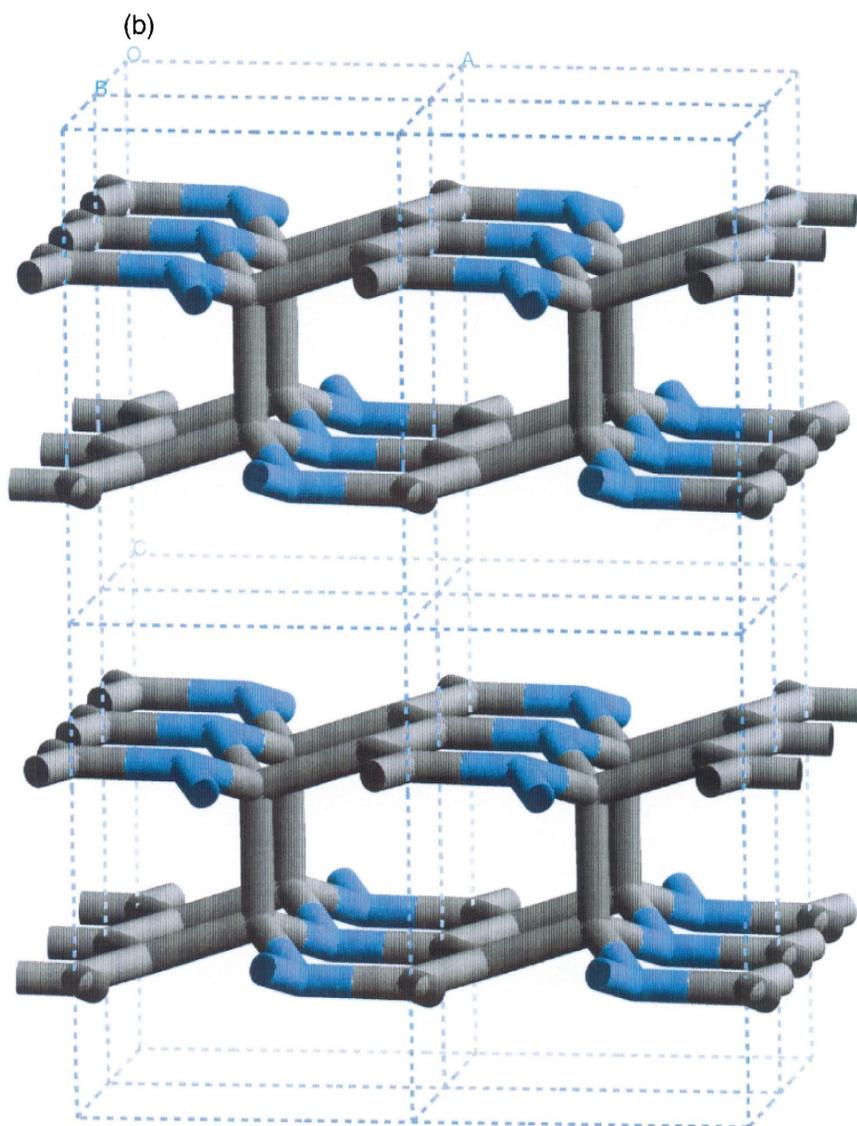


Fig. 1 (continued).

nitrogen atoms are brought only a few tenths of an angstrom out of the planes, the flat structure is unstable and undergoes a transformation.

Because 3-fold coordinated nitrogen atoms have a tendency to stabilize in a pyramidal conformation, the planes first corrugate and one of the adjacent carbon atoms has to adjust and consequently also adopts a pyramidal conformation. Since a 3-fold coordinated carbon atom is unstable in such a pyramidal conformation, the stabilization is achieved by

increasing the coordination number of the bent carbon atoms, which then become 4-fold coordinated as two adjacent slabs come close to one another. The relaxed structure is formed of dimerised sheets (Fig. 1b and Table 2). In other words, the extra electron which is brought to the graphite sheet by the substituted nitrogen atom is counterbalanced by the extraction of one carbon electron which is removed from the conjugated system when an sp^2 carbon is transformed into sp^3 . By considering electronic rules

only, the system is still considered to be a 2-D conjugated system. This is confirmed by the relaxed carbon–carbon distances inside the 6-atom rings which appear to be within the distances which are expected for double and single bond.

3. Discussion

Knowing that nitrogen-substituted graphite can dimerise through the transformation of some sp^2

carbon atoms into sp^3 carbon atoms, one can expect that some simple three-dimensional (3-D) C_3N structures are stable. In this case, we should not speak of dimerization but of polymerization of graphite-like sheets. Two examples of predicted stable structures are given in Fig. 2a,b. Corresponding atomic coordinates are given in Tables 3 and 4. For each sheet, both structures were constructed considering an alternative formation of sp^3 bonds with neighbouring sheets on either side. The structure in Fig. 2a was

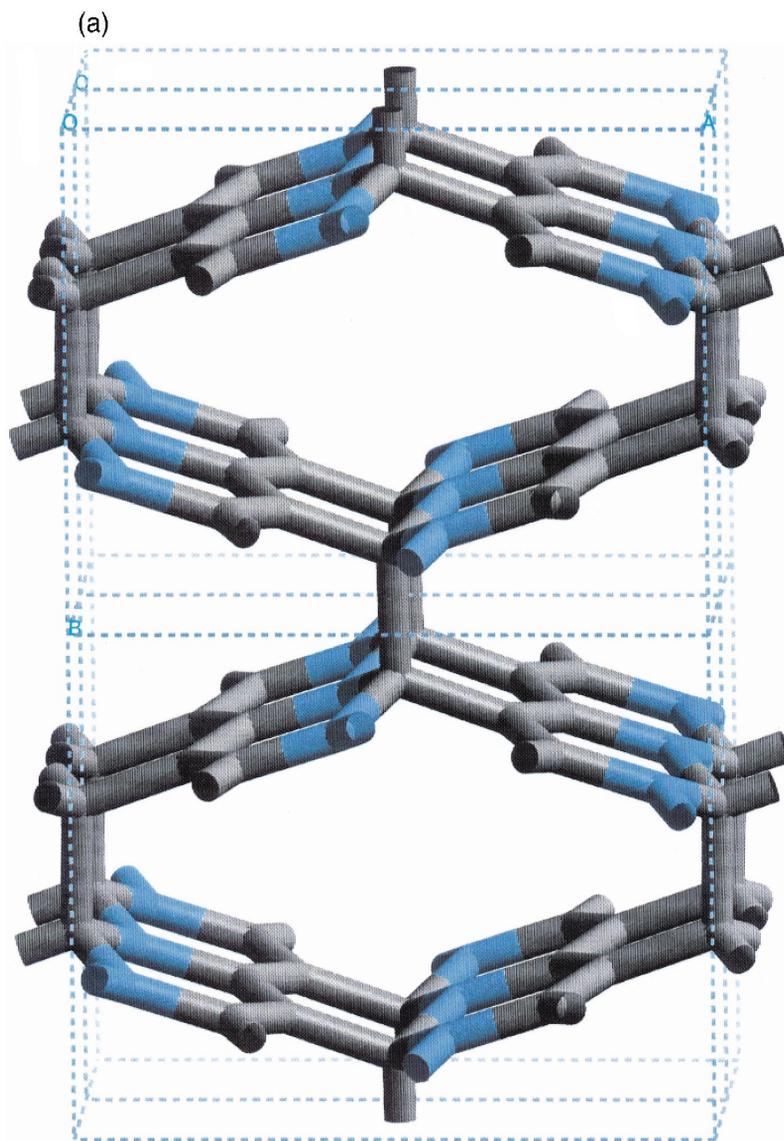


Fig. 2. (a) Structural arrangement of a-poly- C_3N . (b) Structural arrangement of b-poly- C_3N .

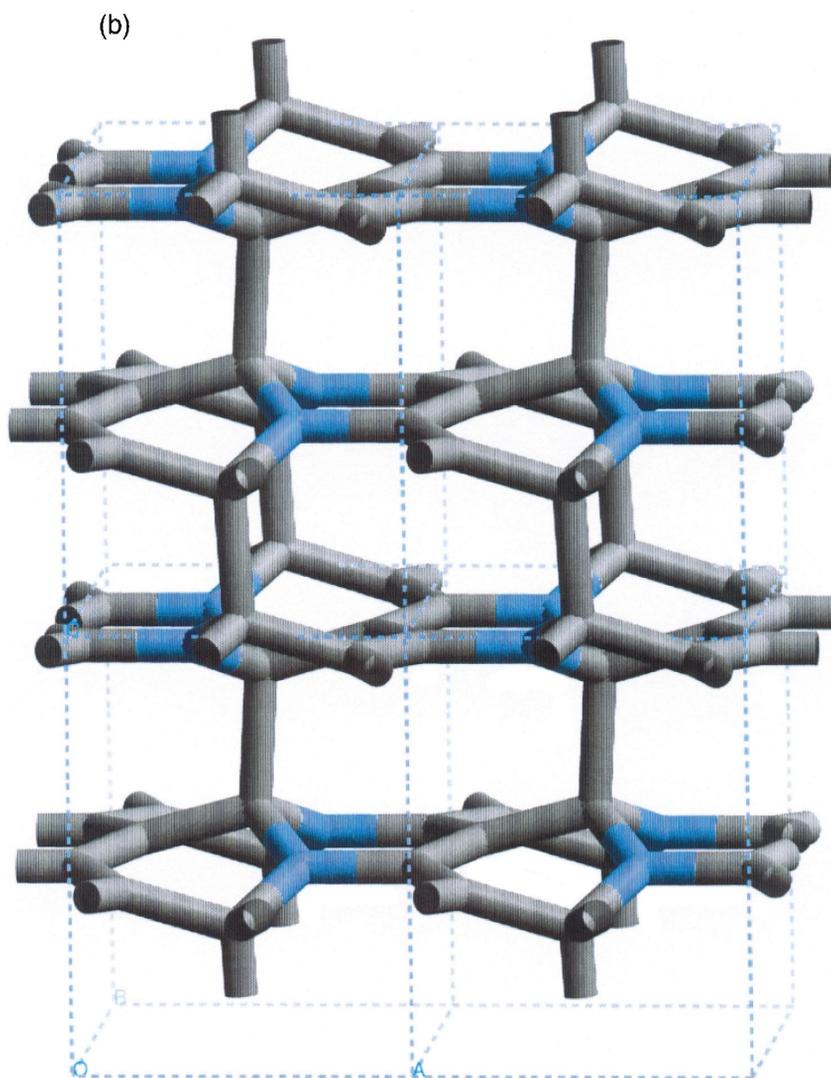


Fig. 2 (continued).

constructed alternating sp^3 bonds along the 'a' direction of the cell (which we then call a-poly- C_3N), and the structure in Fig. 2b was constructed alternating sp^3 bonds along the 'b' direction of the cell (which we then call b-poly- C_3N). Fig. 3a,b give the density of states corresponding to the flat N-substituted graphite and the a-poly- C_3N . By considering the density of states at the Fermi level, the flat graphite-type structure is metallic and the 3D-a-poly- C_3N is semimetallic. Hence, the structural transformation is also accompanied by a complete reformation of the

electronic structure, which is certainly of importance for characterization techniques probing electronic states in systems.

Because the structural constraints on the 6-atom rings are different in all of these C_3N structures, one would expect their stability to be different. Table 5 gives the stabilization energies at a temperature of 0 K for the different phases (compared to that of the flat nitrogen-substituted graphite with composition C_3N). Although the flat configuration appears to be the most stable one, all these structures appear to

Table 2

Atomic structure of the dimerised C_3N sheets. Optimization performed within the $P2/m$ symmetry. Cell parameters: $a = 4.16 \text{ \AA}$; $b = 2.40 \text{ \AA}$; $c = 6.05 \text{ \AA}$. $\alpha = \beta = \gamma = 90^\circ$

Fractional atomic coordinates			
C	0	0	0.72
C	0.16	1/2	0.71
C	0.50	1/2	0.64
C	0	0	0.28
C	0.50	1/2	0.38
C	0.84	1/2	0.29
N	0.67	0	0.71
N	0.33	0	0.29

have very similar stabilization energies (a difference of a few 10^{-2} eV per atom or a few kJ/mol is calculated). Consequently, we suggest that the relative stabilization of the polymerized or flat conformation is governed by entropic effects during any synthesis process (Table 5).

As far as hardness properties are concerned, the Young moduli for the three most stable phases are

Table 3

Structure of a-poly- C_3N . Cell parameters: $a = 8.06 \text{ \AA}$, $b = 6.41 \text{ \AA}$, $c = 2.40 \text{ \AA}$. $\alpha = \beta = \gamma = 90^\circ$ space group: Pbam

Fractional atomic coordinates			
C	0	0.63	0.5
C	0	0.38	0.5
C	0.25	0.75	0
C	0.32	0.80	0.5
C	0.75	0.74	0
C	0.82	0.70	0.5
C	0.75	0.24	0
C	0.68	0.20	0.5
C	0.5	0.87	0.5
C	0.5	0.13	0.5
C	0.26	0.26	0
C	0.18	0.3	0.5
N	0.08	0.7	0
N	0.58	0.8	0
N	0.92	0.3	0
N	0.42	0.2	0

given Table 6. Because the structures are far from being isotropic, one notices that the compression

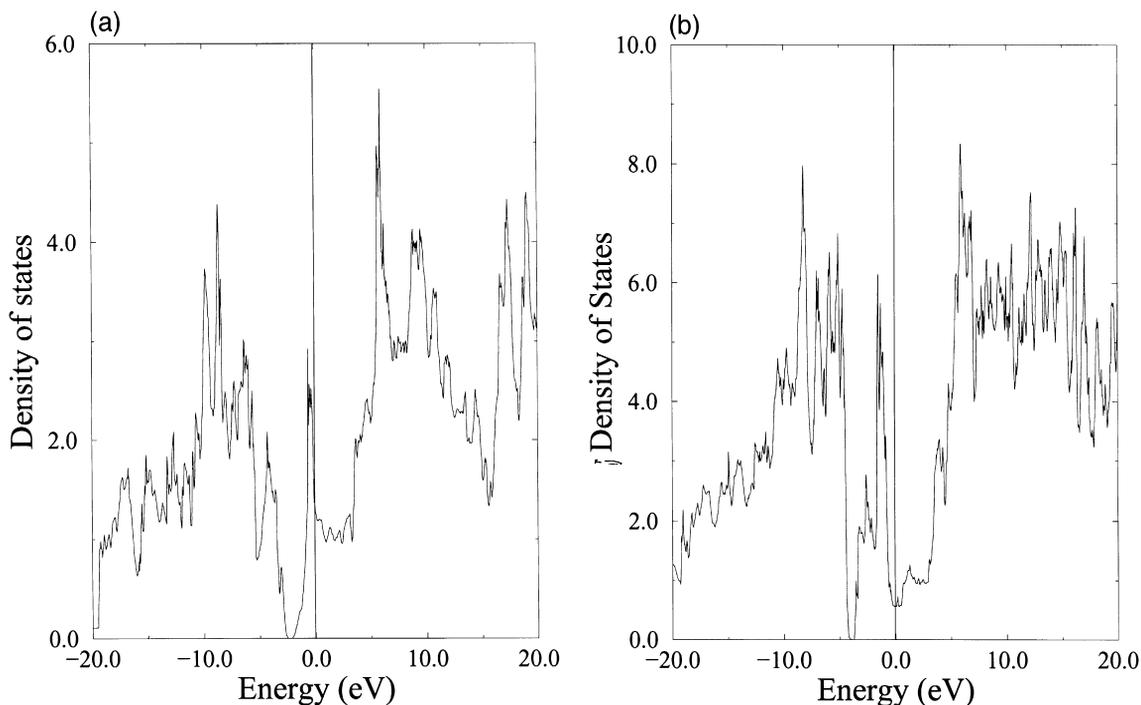


Fig. 3. (a) Electronic density of state for N-substituted graphite with composition C_3N . The Fermi level is at 0. (b) Electronic density of state for a-poly- C_3N . The Fermi level is at 0.

Table 4

Structure of b-poly-C₃N. Cell parameters: $a = 4.78 \text{ \AA}$, $b = 4.12 \text{ \AA}$, $c = 5.35 \text{ \AA}$. $\alpha = \beta = \gamma = 90^\circ$. Space group: Pmna

Fractional atomic coordinates			
C	0.5	0.51	0.84
C	0	0.85	0.73
C	0	0.51	0.66
C	0.5	0.85	0.76
C	0.25	0.02	0.75
C	0.75	0	0.25
C	0	0.15	0.26
C	0	0.49	0.34
C	0.5	0.49	0.16
C	0.5	0.15	0.24
C	0.15	0.49	0.16
C	0.25	0.98	0.25
N	0.25	0.65	0.25
N	0.75	0.65	0.25
N	0.25	0.35	0.75
N	0.75	0.35	0.75

parameters should be very different according to the chosen crystallographic direction. Indeed, the hardness appears to vary a lot and to span the whole range between diamond-type hardness and interlayer graphitic one. This result does not contradict the hardness measurements, which indicate no particular hardness properties to the films [7].

Furthermore, it is certainly of great interest to determine the energy barrier between these different types of structures. Indeed, by construction one understands that the flat structure can transform into a 3D structure without the breaking of any bond. Using the method described by one of us in [8], we have calculated the barrier (within the GGA approximation) separating the flat nitrogen-substituted graphite and the a-poly-C₃N. As shown in Fig. 4 and according to the calculation, the barrier is found to be around 0.63 eV per created carbon–carbon bond

Table 5

Stabilization energies for different C₃N stable structures in eV/atom. The reference structure is the flat N-substituted graphite (C₃N)

Flat N-substituted graphite (C ₃ N):	0.0
Dimerised N-substituted graphite (C ₃ N):	0.0875
a-poly-C ₃ N:	0.02
b-poly-C ₃ N:	0.095

Table 6

Young moduli of the three most stable phases calculated along the main axis directions as given in Table 1–4 (eV/Å²)

Flat N-substituted graphite (C ₃ N):	(13.6; 41.2; 0.4)
a-poly-C ₃ N:	(20.0; 0.6; 123)
b-poly-C ₃ N:	(23.5; 30.5; 3.7)

(63 kJ per bond) which is quite a low value. Indeed, such range of energies is in the order of magnitude of what is calculated for catalytic room-temperature organic reactions for instance (the energy barrier given in Ref. [9] for the catalytic conversion of methanol into dimethyl ether is 0.72 eV). Consequently, it may well be that the room-temperature C₃N compound transforms dynamically from one structure to the other one during a limited period of time (i.e. the time needed for an industrial organic catalytic reaction to take place, i.e. $\ll 1$ s). This possibility may explain the difficulty in studying the

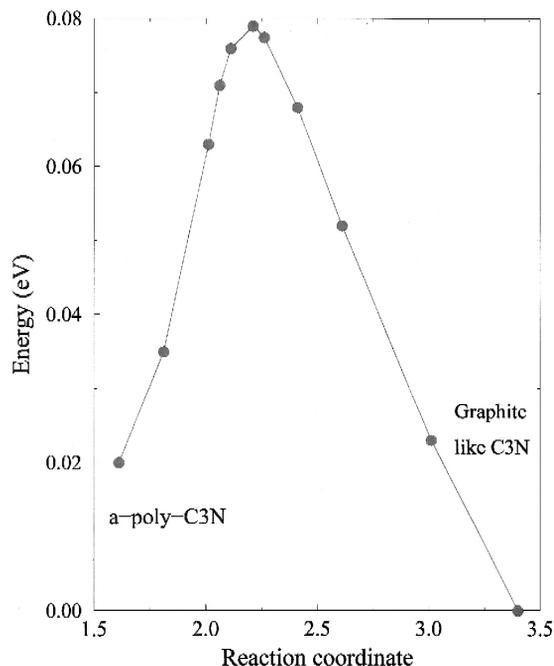


Fig. 4. Activation energy barrier separating the N-substituted graphite and a-poly-C₃N structures. The energies are given per 8 atoms, which correspond to one formed carbon–carbon bond. The x-axis is the reaction coordinate which corresponds to the interatomic distance between the two sp³ carbon atoms located on two adjacent sheets (see Ref. [6]).

structure of such materials. Indeed if studying the electronic structure (using EELS for instance), one can see in Fig. 4a,b that the electronic structure varies dramatically and that no clear electronic signature should be expected if the structure actually changes dynamically between the 2D and 3D structures. Since the atom could change position dramatically, trying to study the atomic structure directly may be equally difficult. The amorphous structure of CN_x compounds is certainly related to a disordered arrangement of atoms. It could also come from the existence of different structures, which could coexist dynamically. Such a hypothesis might be consistent with the fact that these compounds present intriguing (but not super hard) mechanical properties [7].

4. Conclusion

To summarize our results, we have shown that nitrogen-substituted graphite compounds could be stable with different structures. Amongst these, some are 2D and some are 3D. These two types of structure have similar low-temperature stabilization energies and their relative stability at higher temperature could be governed by entropic effects. We have shown that the barrier separating both the flat N-substituted graphite and the polymerized C_3N -sheet structure is fairly low which can allow a dynamical transformation of one structure into the other and, thus, faster than the time needed to perform an

experiment to study their structure. The problem of defining an atomic structure for CN_x compounds can consequently be greater than thought originally, and can also originate in the possible dynamics of structure transformations inside the films as synthesized by experimentalists.

Acknowledgements

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