

# Theoretical Tracing of a Novel Route from Molecular Precursors through Polymers to Dense, Hard C<sub>3</sub>N<sub>4</sub> Solids

Peter Kroll and Roald Hoffmann\*

Contribution from the Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

Received December 22, 1998

**Abstract:** We investigate theoretically a novel experimental polymer route to C<sub>3</sub>N<sub>4</sub> materials. Starting with simple molecules, we follow the initial steps of oligomerization of several carbodiimide based C<sub>3</sub>N<sub>4</sub> precursors. A sequence of hypothetical models with a chemically reasonable structure for the resulting low-density C<sub>3</sub>N<sub>4</sub> polymers is constructed. Simulating high pressures, we show that one hypothetical polymer structure might undergo a polymorphic transition into cubic C<sub>3</sub>N<sub>4</sub>. Another one is transformed into a novel dense 3/4-connected C<sub>3</sub>N<sub>4</sub> structure with odd-membered rings and C–C and N–N bonds.

## Introduction

Positioned as the problem is at the intersection of organic, inorganic, and physical chemistry, and of physics, geological, and materials science as well, the synthesis of hard carbon nitride materials perforce presents us with a truly interdisciplinary challenge. The concept of a carbon nitride whose hardness might exceed that of diamond<sup>1</sup> has stirred many computational<sup>2,3</sup> and synthetic<sup>4</sup> investigations. Much of this work is summarized in recent reviews<sup>5–7</sup>. Notwithstanding more than twenty papers claiming a synthesis, in our opinion no consensus has yet been reached as to whether pure crystalline C<sub>3</sub>N<sub>4</sub> has or has not been made.<sup>8,9</sup>

Though the incorporation of small amounts of nitrogen into a carbon phase appears to enhance certain important physical properties,<sup>10</sup> the ultimate goal in carbon nitride research has been to attain the stoichiometry. Structural models proposed for hard carbon nitride materials consist of 4-fold (sometimes approximately) tetrahedrally coordinated carbon (which is often very loosely called “sp<sup>3</sup>” carbon) and 3-fold approximately trigonal planar coordinated nitrogen (“sp<sup>2</sup>” nitrogen).<sup>2,11,12</sup> In these 3/4-connected networks carbon and nitrogen alternate, so that no C–C or N–N bonds are present.

The topology of these 3/4-connected phases is sufficient to guarantee dense networks. Moreover, they fulfill one requirement for hardness, that of short covalent bonds.<sup>1</sup> However, ab initio calculation indicates that graphite-like structures may be lower in energy than these dense networks.<sup>12,13</sup> The graphitic structures contain planar C as well as planar N, and the materials are considerably softer. The carbon system, of course, is similar;

soft graphite is energetically favored over hard diamond at ambient pressures and temperatures. Nevertheless, hard diamond-like phases of carbon can be synthesized. Unfortunately, in the binary C–N system the driving force toward graphitic structures appears to increase with the amount of nitrogen in the phase.

Consequently, a solid-state synthesis of tetrahedral carbon networks incorporating substantial amounts of nitrogen is not easy. Tetrahedral amorphous carbon (ta-C) can be doped and enriched with nitrogen, yielding CN<sub>x</sub> with  $x < 4/3$ . However, this has great effects on the bonding and structure of the material.<sup>14,15</sup> It is suspected that 10–15 at. % nitrogen is the amount sufficient to drive carbon from 4-fold to mainly 3-fold connectivity. Moreover, it reduces the density of the material from about 3.3 to 2.1 g/cm<sup>3</sup>.<sup>16</sup> The major difficulty arising in nitrogen-rich phases, CN<sub>x</sub> with  $x > 4/3$ , is the high content of 3-coordinated carbon right from the beginning. Furthermore, outgassing of excess dinitrogen damages the structure of the material, since the molecular volume of nitrogen is much higher than the atomic volume in the solid state. To summarize the “status quo”,<sup>16</sup> experimental results available so far suggest that physical deposition methods are unable to yield the desired (crystalline) hard material.

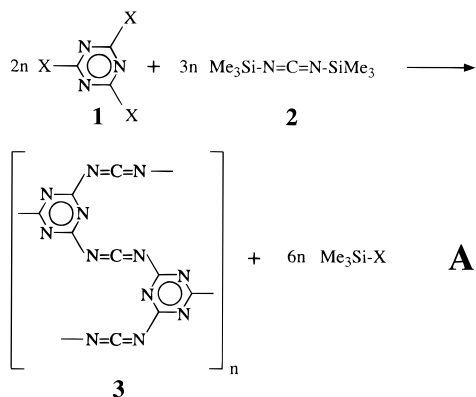
To attain an exact C<sub>3</sub>N<sub>4</sub> composition, chemists have conceived clever approaches via single-source carbon nitride precursors<sup>17–19</sup>. In this work an amine group is reacted with a perhalogenated triazine yielding (Me<sub>3</sub>M)<sub>2</sub>NC<sub>3</sub>N<sub>3</sub>X<sub>2</sub> (Me = CH<sub>3</sub>; M = Si, Sn; X = F, Cl). This molecule is then used for low-pressure chemical vapor deposition, leading eventually to thin films and bulk powders with a 3:4 carbon-to-nitrogen ratio. This method appears to be very promising, since the composition of the final product may be achieved in the precursor state. The desired hard material might then be obtained under high pressure. There is good reason to hope that hitherto unexplored parts of the

- (1) Cohen, M. L. *Phys. Rev. B* **1985**, *32*, 7988.
- (2) Liu, A.; Cohen, M. L. *Science* **1989**, *245*, 841.
- (3) Liu, A.; Cohen, M. L. *Phys. Rev. B* **1990**, *41*, 10727.
- (4) Niu, C.; Lu, Y. Z.; Lieber, C. M. *Science* **1993**, *261*, 334.
- (5) Sung, C.-M.; Sung, M. *Mater. Chem. Phys.* **1996**, *43*, 1.
- (6) Yacaman, M. J.; Gil, J. M.; Gil, F. J. M.; Sarikaya, M.; Qian, M. X. *Mater. Chem. Phys.* **1997**, *47*, 109.
- (7) Badding, J. V. *Adv. Mater.* **1997**, *9*, 877.
- (8) Wang, J.; Lei, J.; Wu, R. *Phys. Rev. B* **1998**, *58*, 11890.
- (9) DeVries, R. C. *Mater. Res. Innovat.* **1997**, *1*, 161.
- (10) Neuville, S.; Matthews, A. *MRS Bull.* **1997**, *9*, 22.
- (11) Liu, A. Y.; Wentzcovitch, R. *Phys. Rev. B* **1994**, *50*, 10362.
- (12) Teter, D. M.; Hemley, R. J. *Science* **1996**, *271*, 53.
- (13) Lowther, J. E. *Phys. Rev. B*. Submitted for publication.

- (14) Veerasamy, V. S.; Yuan, J.; Amarantunga, G. A. J.; Millene, W. I.; Gilkes, K. W. R.; Weiler, M.; Brown, L. M. *Phys. Rev. B* **1993**, *48*, 17954.
- (15) Wei, A.; Chen, D.; Ke, N.; Cheung, W. Y.; Peng, S.; Wong, S. P. *J. Phys. D: Appl. Phys.* **1998**, *31*, 1522.
- (16) Hu, J.; Yang, P.; Lieber, Ch. M. *Phys. Rev. B* **1998**, *57*, 3185.
- (17) Kouvetakis, J.; Bandari, A.; Todd, M.; Wilkens, B.; Cave, N. *Chem. Mater.* **1994**, *6*, 811.
- (18) Todd, M.; Kouvetakis, J.; Groy, T. L.; Chandrasekhar, D.; Smith, D. J.; Deal, P. W. *Chem. Mater.* **1995**, *7*, 1422.
- (19) Kouvetakis, J.; Todd, M. US Patent 5606056 A, 1997.

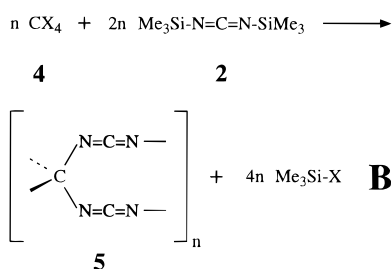
phase diagram will reveal a stable hard C<sub>3</sub>N<sub>4</sub> phase<sup>12</sup>—and that this material can then be quenched to ambient temperatures and pressures, while retaining its properties.

As an alternative to this approach, the synthesis of C<sub>3</sub>N<sub>4</sub> by a polymer route was recently proposed. Two promising reactions yielding polymeric C<sub>3</sub>N<sub>4</sub> have been suggested<sup>20–22</sup>, both based on reactions of common reagents with main group element carbodiimides. Reaction **A** below is that of 2,4,6-trihalo-1,3,5-triazine (**1**) with *N,N'*-bis(trimethylsilyl)-carbodiimide (**2**), yielding “polydi(triazine)tri(carbodiimide)” (**3**).



In reaction **A**, therefore, the triazines are linked through bridging carbodiimide units to form an extended structure. This reaction was examined using 2,4,6-trifluoro- as well as 2,4,6-trichloro-1,3,5-triazine, different solvents, and several reaction conditions. Depending on the process, yellow, green, brown, or black powders are formed. The elemental composition of the material varies from close to C<sub>3</sub>N<sub>4</sub> to samples strongly contaminated with silicon and/or halogens.<sup>22,23</sup> IR and Raman spectroscopy indicates the presence of cyanogen-like fragments in the material. In the course of a search of the literature, we found that more than 20 years ago Miyashita and Pauling already observed a “pale yellow solid” precipitated in a very similar reaction to **A**.<sup>24</sup> The purpose of their work was to find derivatives with antineoplastic or antibiotic actions.

In reaction **B**, tetrahalomethane (**4**) reacts with *N,N'*-bis(trimethylsilyl)carbodiimide (**2**) to form “polymethyldicarbodiimide” (**5**). This approach is analogous to the recent synthesis of ternary Si–C–N phases, Si(NCN)<sub>2</sub> and Si<sub>2</sub>N<sub>2</sub>(NCN).<sup>25</sup> Reaction **B** was only attempted with X = Br.<sup>20</sup> The elemental analysis of the black powder obtained showed a large amount of silicon and too little nitrogen.



Despite the limited success so far, the idea of synthesizing a C<sub>3</sub>N<sub>4</sub> polymer using either reaction **A** or **B**, or a related reaction, probably not based on the silylated carbodiimide, is appealing.

(20) Greiner, A. *Dissertation* (in German); Technical University Darmstadt, Germany, 1997; published as: *Keramiken aus Silylcarbodiimiden*; Shaker Verlag Aachen (ISBN: 3–8265–3247–3), 1998.

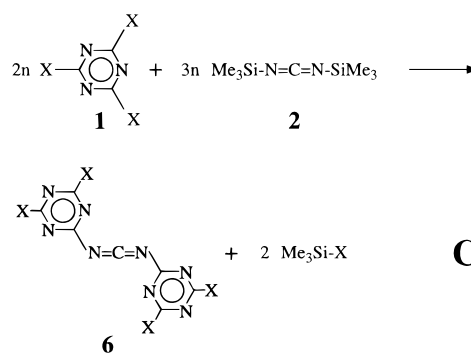
(21) Riedel, R.; Kroke, E.; Greiner, A. German Patent DE 19706028 C1, 1998.

(22) Riedel, R.; Kroke, E.; Greiner, A.; Gabriel, A. O.; Ruwisch, L.; Nicolich, J.; Kroll, P. *Chem. Mater.* **1998**, *10*, 2964.

In this paper we have used theory to follow reactions **A** and **B** in detail (we provide details about the calculations in the Appendix). We start the oligomerization with a simple initial reaction, in which carbodiimide units are transferred from the silylated carbodiimide to its reaction partner. The optimized geometries of the products provide information on potential polymers. We then propose hypothetical structures for the three-dimensional infinite polymers based on these molecular fragments. We also think about the effect of pressure on these polymers, the theory implying a direct conversion of one of the polymer precursors into the cubic C<sub>3</sub>N<sub>4</sub> phase, the one which is expected to have a hardness comparable to that of diamond. And pressure leads us theoretically to another unusual C<sub>3</sub>N<sub>4</sub> structure.

### The Initial Step: Molecular Precursors

*N,N'*-Bis(2,4-difluorotriazine)carbodiimide. We begin with the initial step of reaction **A**, in which the triazine **1** reacts with the carbodiimide **2** to yield the intermediate *N,N'*-bis(2,4-dihalotriazine)carbodiimide **6**, reaction **C**.



The halogenated product of reaction **C** may be very short-lived, as it is surrounded by an ample supply of further reaction partners. Nevertheless, we can simply calculate the heat of reaction for the (hypothetical) process. The resulting values are –130 and –100 kJ/mol for the fluorinated and the chlorinated product, respectively. Both reactions are thus exothermic.

Let us take a closer look at the carbodiimide product of reaction **C** (see Figure 1, top); its geometry is instructive for building models for polymeric C<sub>3</sub>N<sub>4</sub>.

As for so many other carbodiimides, the equilibrium structure of the molecule has C<sub>2</sub> symmetry.<sup>26</sup> Within the NCN group the C=N distance is 1.22 Å. Furthermore, there is a slight deviation from linearity; the NCN angle α being 169°. The triazine ring is nearly 3-fold symmetric and planar. The C–N intra-ring bond lengths are between 1.32 and 1.34 Å, and the endocyclic bond angles are between 112 and 113°, at the N's between 126 and 128° at the C's. This is a common pattern observed for triazine molecules<sup>27,28</sup> and consistent with calculations.<sup>29</sup> The exocyclic bond distance between the C of the triazine ring and the N of the carbodiimide is 1.38 Å.

(23) H. Jüngergermann, Bayer AG; M. Jansen, MPI Stuttgart, private communication.

(24) Miyashita, K.; Pauling, L. *J. Org. Chem.* **1976**, *41*, 2032.

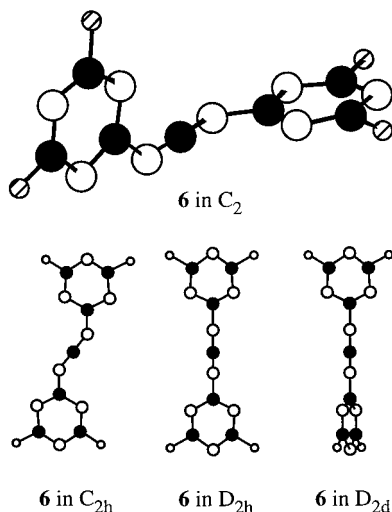
(25) Riedel, R.; Greiner, A.; Miehe, G.; Dressler, W.; Fuess, H.; Bill, J.; Aldinger, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 603.

(26) Kroll, P.; Hoffmann, R. Unpublished results.

(27) Bullen, G. J.; Corney, D. J.; Stephens, F. S. *J. Chem. Soc. Perkin Trans. 2* **1972**, 642.

(28) Höfs, H.-U.; Mews, R.; Noltemeyer, M.; Sheldrick, G. M.; Schmidt, M.; Henkel, G.; Krebs, B. *Z. Naturforsch. B* **1983**, *38*, 454.

(29) Walker, I. C.; Palmer, M. H.; Ballard, C. C. *Chem. Phys.* **1992**, *167*, 61.



**Figure 1.** Optimized molecular structures of bis(difluorotriazine)-carbodiimide (**6**, X = F). The top shows the lowest energy configuration in  $C_2$ . At the bottom are configurations of higher symmetry discussed in the text. Black atoms represent carbon, white atoms nitrogen, and small hatched atoms fluorine atoms.

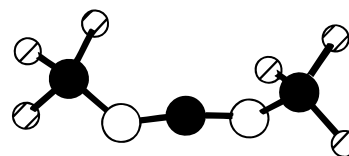
As for other carbodiimides, we can see bending at the N atom of the NCN group. This angle  $\varphi_N$  is  $139^\circ$ . The three atoms defining each  $\varphi_N$  angle span a plane. The dihedral angle  $\tau$ , defined as the angle between these two planes, is about  $85^\circ$ , i.e., these planes are almost perpendicular to each other. This is expected from the heterocumulene (allene-like)  $-\text{NCN}-$ .

If we look at the angle between the two vectors *normal* to the nearly planar triazine rings, we see that they are also almost perpendicular to each other. Both observations suggest some interaction of the  $\pi$ -systems of the rings with  $\pi$ -orbitals of the NCN fragment. This is confirmed by looking at the barrier to rotating these rings. Another very useful geometric descriptor we need in order to construct models of extended structures is the distance  $d_{V-V}$  (the index V here stands for vertex, the reason for the term in this context will become clear below) between the two centers of the two triazine rings, and this value is 6.8 Å.

The halogen-free counterpart of the carbodiimide product in reaction **3**, “bistriazinecarbodiimide”, should be easily accessible, but has not been synthesized so far. All calculated geometric parameters are very similar for the halogen-free product, with the biggest difference—due to the absence of the electron accepting fluorine atoms—in  $\varphi_N$ . The value of this angle is decreased to  $133^\circ$ . The variation of bond lengths and angles inside the ring is smaller, the atoms are even less distorted from ideal positions, and  $d_{V-V} = 6.9$  Å.

Now we compare the energy for the fluorinated molecule in its most stable  $C_2$  symmetry with the energy of more symmetric arrangements. Rotation around the C=N double bonds, thus changing  $\tau$ , moves the molecule into its enantiomeric geometry through a transition state with  $C_{2h}$  symmetry ( $\tau = 180^\circ$ ). This geometry (see Figure 1), which has coplanar triazine rings and a linear NCN fragment, is about 4.5 kJ/mol higher in energy. To make  $\varphi_N = 180^\circ$ , obtaining a linear C–NCN–C chain, costs 27 kJ/mol, if the triazine rings are perpendicular to each other (symmetry  $D_{2d}$ ), and 31 kJ/mol, if they are coplanar (symmetry  $D_{2h}$ ). The values of  $d_{V-V}$  for the different structures are 7.4 Å for  $C_{2h}$  and 7.8 Å for  $D_{2h}$  and  $D_{2d}$ .

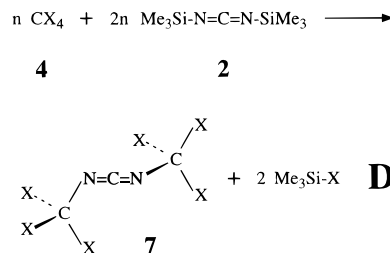
In contrast to silylated carbodiimides,<sup>30</sup> the energy difference between the most symmetric  $D_{2d}$  configuration and the one with



**Figure 2.** Molecular structure of bis(trifluoromethyl)carbodiimide from DFT calculations. Black atoms represent carbon, white atoms nitrogen, and small hatched atoms fluorine atoms.

the lowest energy in  $C_2$  is 2 orders of magnitude higher (although the values here are still not large). The bending potential at N is more pronounced in the hydrocarbon case.

***N,N'*-Bis(trifluoromethyl)carbodiimide.** The second molecular precursor we calculate is the (hypothetical) intermediate of reaction **B**: Tetrahalomethane **4** reacts with *N,N'*-bis(trimethylsilyl)carbodiimide **2** to yield *N,N'*-bis(trihalomethyl)-carbodiimide **7** and silicon trimethylhalide. This is reaction **D**.



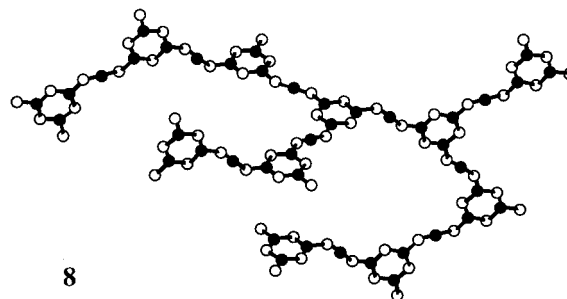
While the perhalogenated dimethylcarbodiimide again might be short-lived, its nonhalogenated counterpart is known.<sup>31</sup> Reaction **D** is also calculated to be exothermic, and the heat of reaction is  $-78$  kJ/mol for X = F and  $-127$  kJ/mol for X = Cl.

The molecular geometry of the carbodiimide product, which in its ground state possesses  $C_2$  symmetry, is shown in Figure 2. The C=N distance within the carbodiimide group is 1.22 Å, and the NCN angle  $\alpha$  is  $170^\circ$ . The bond length between the N of the NCN group and the C of the perhalogenated methyl is 1.41 Å. The bending angle  $\varphi_N$  is  $123^\circ$ ;  $\tau$ , the dihedral angle, is about  $88^\circ$ . The distance between the two terminal carbon atoms,  $d_{V-V}$ , is 4.6 Å. A  $D_{3d}$  “linear” geometry is 40 kJ/mol higher in energy.

The halogen-free molecule has very similar values for all geometric parameters, with some differences due to the lack of electron transfer to fluorine atoms. The distance C=N within the NCN group increases to 1.23 Å, and the bond length between the N of the carbodiimide and the C of the methyl increases to 1.46 Å. The bond angle  $\varphi_N$  is  $127^\circ$ .

### From Molecules to Polymers

“**Polydi(triazine)tri(carbodiimide)**”. Suppose the reaction initiated in equation **C** propagates by further connecting triazine rings with NCN groups via the halogen sites. Oligomers such as **8** might form and cross-link into polymers. The assembly of such structure-specific network topologies is a conjunction of polymer chemistry and supramolecular chemistry.<sup>32,33</sup>

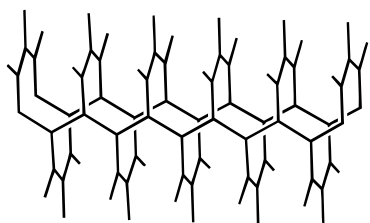


(30) Kroll, P.; Riedel, R.; Hoffmann, R. *Phys. Rev. B* Submitted for publication.

The bonding topology of the hypothetical C<sub>3</sub>N<sub>4</sub> polymer product of reaction **A** can be described as a 3-connected net, where the triazine ring is a 3-vertex (call it V) and the carbodiimide unit is the link (L) between vertices. Such a net has the stoichiometry V<sub>2</sub>L<sub>3</sub> and the simplest model for a unit cell of V<sub>2</sub>L<sub>3</sub>, with triazine (6 atoms) at a vertex and the carbodiimide (3 atoms) in a link, has at least 21 atoms. In principle, an infinity of network configurations is possible. In practice, only a few regular 3-connected nets are common in solid-state chemistry and are described in Wells' book.<sup>34</sup>

For our specific choice we reason as follows: judging by the molecular models, the carbodiimide (–NCN–) units connect the triazine rings preferentially “perpendicular” to each other. Therefore, we expect the network to extend in three dimensions, instead of forming graphite-like structures. Moreover, the carbodiimide unit is a spacer of substantial size. We would thus expect the structure to be very open, probably allowing the interpenetration of identical networks.<sup>35</sup>

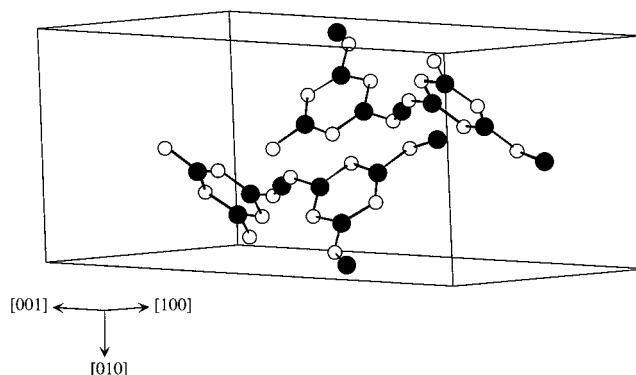
Consequently, the most appealing 3-connected net for our purpose (though not the only one possible) is the Si-sublattice **9** of ThSi<sub>2</sub>; Wells' nomenclature for it is (10,3)-b; it is also called the bct-4 net.

**9**

**9** is something like an ever-open purse of theoretical structural chemistry—one of us used it once to calculate a hypothetical polymorph of carbon which might be metallic.<sup>36</sup> The network topology of **9** is also a common motif in supramolecular chemistry; macrocycles of this structure have been synthesized.<sup>37</sup> Interpenetration in this context is often observed,<sup>38</sup> with examples ranging from 2-fold to 6-fold interpenetration.<sup>35</sup>

The space group symmetry of the (10,3)-b net is *I*4<sub>1</sub>/*amd* (141) in the conventional *I*-setting and there are eight vertices in the unit cell. Were we to construct a model for “polydi(triazine)tri(carbodiimide)” using this space group, it would consist of 84 atoms per unit cell. Using the motif of interpenetration of identical networks, we can reduce the number of atoms in the unit cell, and, what is even more essential for our calculation, also its volume.

A model of a 2-fold interpenetrating “polydi(triazine)tri(carbodiimide)” net is made up of two identical networks. An “ideal” structure (with  $\varphi_N = 180^\circ$ ) can be found in space group *P*4<sub>2</sub>/*n* (86); the unit cell contains only 42 atoms. The structure was constructed by “decorating” the 3-connected network with triazine rings and carbodiimide groups. We optimized the model



**Figure 3.** The unit cell of the optimized structure of a model of “polydi(triazine)tri(carbodiimide)”.

structure theoretically and in the course of the optimization it reduced its symmetry. The result is shown in Figure 3.

The calculated values are  $a = 7.9 \text{ \AA}$ ,  $c = 23.8 \text{ \AA}$ , and  $V = 1485 \text{ \AA}^3$ . The computed geometrical parameters are very similar to those of the molecular model we studied above: the mean distance C=N within the NCN group is 1.19 Å and that between the N of the carbodiimide and the C of the triazine ring is 1.34 Å. The angle  $\varphi_N$  ranges between 136 and 152°. The triazine rings are, as before, nearly trigonal planar, with C–N bond lengths inside the ring between 1.32 and 1.34 Å and endocyclic bond angles at the N's about 113° and at the C's between 126 and 127°. The shortest distance between the two identical nets is 5.1 Å, indicating no inter-net interaction. The total energy of the structure is about 80 kJ/mol higher than the total energy of  $\alpha$ -C<sub>3</sub>N<sub>4</sub> computed with the same method.<sup>39</sup> Nevertheless, the structure represents a local minimum of the C<sub>3</sub>N<sub>4</sub> energy surface, and there is certainly a substantial barrier in the way of its transformation to an energetically more favorable geometry.

We also constructed models with higher interpenetration. A 3-fold interpenetrating structure can be constructed in space group *C*2/*m* (12). Again, we optimized the structure, this time using the primitive unit cell with 42 atoms. Almost identical structural characteristics as before were obtained. The closest contact between any two nets is 4.1 Å in this case, still reasonable. The total energy of the structure per formula unit is essentially the same as for the 2-fold interpenetrating structure. One cannot continue this indefinitely; the model for 6-fold interpenetrating “polydi(triazine)tri(carbodiimide)” resulted in a too crowded structure; the closest contact for the “ideal” setting was 2.5 Å.

“Polymethylcarbodiimide”. The second molecular precursor may also react further, to form a polymer according to reaction **B**. Although CF<sub>4</sub> and CCl<sub>4</sub> are rather sluggish reagents, the reaction is clearly exothermic. Experimentally, we are optimistic that a suitable catalyst will be found to realize the reaction. The structure of the (hypothetical) resulting extended system is quite different from the structures discussed in the preceding section. If all halogens on the carbon atom of the methyl group are substituted by –NCN– units, this carbon atom becomes a 4-connected vertex and the carbodiimide units the links between vertices. Thus models can be borrowed from known 4-connected structures, such as diamond, lonsdaleite, CrB<sub>4</sub>, and zeolites.

The reason for thinking that a complete substitution reaction according to reaction **B** might take place comes from the analogous reaction of silicon tetrachloride with *N,N'*-bis-(trimethylsilyl)carbodiimide, which yielded the ternary Si–C–N

(31) Rapi, G.; Sbrana, G. *J. Am. Chem. Soc.* **1971**, *93*, 5213.

(32) Desiraju, G. R. *Crystal Engineering: the Design of Organic Solids*, Elsevier: New York, 1994.

(33) MacDonald, J. W.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383.

(34) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, **1977**; pp 33ff.

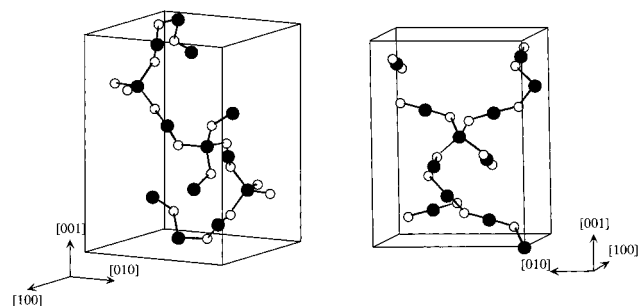
(35) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460 and references therein.

(36) Hoffmann, R.; Hughbanks, T.; Kertész, M.; Bird, P. H. *J. Am. Chem. Soc.* **1983**, *105*, 4831.

(37) Wu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 297.

(38) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562.

(39) We have chosen the energy of  $\alpha$ -C<sub>3</sub>N<sub>4</sub> as a reference here. However, there are proposed graphitic structures of C<sub>3</sub>N<sub>4</sub>, which are about 5 kJ/mol lower in energy.<sup>12,13</sup>



**Figure 4.** Unit cells for our models of  $\alpha$ -C(NCN)<sub>2</sub> (on the left) and  $\beta$ -C(NCN)<sub>2</sub> (on the right).

phase Si(NCN)<sub>2</sub>≡SiC<sub>2</sub>N<sub>4</sub>.<sup>25</sup> Though carbon and silicon often have very different chemistries, we feel somewhat attracted to the thought that a C<sub>3</sub>N<sub>4</sub> polymer (C(NCN)<sub>2</sub>) may be achievable with this analogous reaction.

What structure might such a polymer have? For Si(NCN)<sub>2</sub> the observed structure is related to the structure of  $\beta$ -cristobalite, the high-temperature modification of cristobalite SiO<sub>2</sub>. This leads us to consider cristobalite-like networks. The beauty and simplicity of the resulting structures, which are closely related to that of diamond, are intriguing.

We constructed two models for our C(NCN)<sub>2</sub> polymer using the analogy to  $\alpha$ - and  $\beta$ -cristobalite. Setting up the structures is a fairly easy task, because we can use the geometric data calculated for the molecular precursor and O’Keeffe’s and Hyde’s comprehensive structural analysis of cristobalite structures.<sup>40</sup> After optimization we obtain a structure for “ $\alpha$ -C(NCN)<sub>2</sub>” within space group  $P4_12_12$  (94) with  $a = 7.4$  Å,  $c = 10.5$  Å, and  $V = 581$  Å<sup>3</sup> ( $Z = 4$ ), and a structure for “ $\beta$ -C(NCN)<sub>2</sub>”, space group  $I\bar{4}2d$  (122) with  $a = 7.1$  Å,  $c = 10.1$  Å, ( $Z = 4$ ), and  $V = 508$  Å<sup>3</sup>. These two structures are illustrated in Figure 4.

The geometries are (again) similar to those computed for the molecular model: The distances C=N within the carbodiimide group are 1.21 Å, and the bond lengths between the N of the NCN group and the C of the methyl are 1.44 Å and are similar for both  $\alpha$  and  $\beta$  structures. The bending angle  $\varphi_N$  is 128° for  $\alpha$  (122° for  $\beta$ ), and the NCN angle is 170° for  $\alpha$  (175° for  $\beta$ ).  $\varphi_C$ , the parameter making the connection to the cristobalite phases of SiO<sub>2</sub>, is 150° (133°). The distance between the two adjacent 4-vertices,  $d_{V-V}$  is 4.6 Å (4.3 Å). The density of the polymer is low, about 1.0 and 1.2 g/cm<sup>3</sup> for the  $\alpha$  and  $\beta$  structures, respectively. The computation of the total energy for these two models and four additional closely related structures (including interpenetrating structures) for C(NCN)<sub>2</sub> based on cristobalite structures reveals minimal energy differences between them. They are all within 5 kJ/mol of each other. However, the computed total energy is about 180 kJ/mol higher than that of  $\alpha$ -C<sub>3</sub>N<sub>4</sub>. These polymers represent metastable configurations; they are thermodynamically unstable, but have local minima with substantial barriers to rearrangement.

#### “A Little In-Between Something”<sup>41</sup>

Let us review what we have achieved up to now. We have explored the intermediate stages of oligomerization of several carbodiimide-based C<sub>3</sub>N<sub>4</sub> precursors, constructing a sequence of models with a chemically reasonable structure. All structures considered so far are high in energy, indicating that they are not thermodynamically stable. Yet they are local minima on

the C<sub>3</sub>N<sub>4</sub> potential energy surface, and we think they are likely to exist and persist.

The polymers studied are by no means the desired hard material. On the contrary, they are very soft matter. This is mainly due to the flexibility of the bonding angle  $\varphi_N$  at the nitrogen sites of the carbodiimide unit. Furthermore, we do not have a completely 3/4-connected network, but many 3-connected and even 2-connected carbons. The densities are also low. On the theoretical side, our situation seems to be no better than that of many other research groups, who have synthesized amorphous phases of carbon nitride with substantial unsaturation (3-connected centers). However, all these properties, the high energy, the softness, and the unsaturated bonds, may not be as negative as they sound.

Consider the advantages these polymers offer: Both products already have the desired stoichiometry C<sub>3</sub>N<sub>4</sub> in the precursor state. Thus we do not need to worry about incorporation of additional elements into the solid-state structure, nor about the release of gaseous species to attain the 4:3 carbon-to-nitrogen ratio. Another desired feature of the material is the alternation of carbon and nitrogen in the structure. There are no homovalent bonds, in particular no N–N bonds of any kind. These are at least two properties in which the polymers already resemble the desired hard carbon nitride material.

This is why we believe that these polymers are ideal candidates for high-pressure synthesis. Since all molecules or solids containing unsaturation are likely to form further bonds when compressed, we surely have appropriate precursors to generate (under pressure) more saturated networks—in this case a 3/4-connected carbon nitride phase. We propose that all these quite open structures we have constructed will exhibit pressure-induced phase transformations at moderate pressures, yielding much denser phases of carbon nitride.

#### Simulating High Pressures

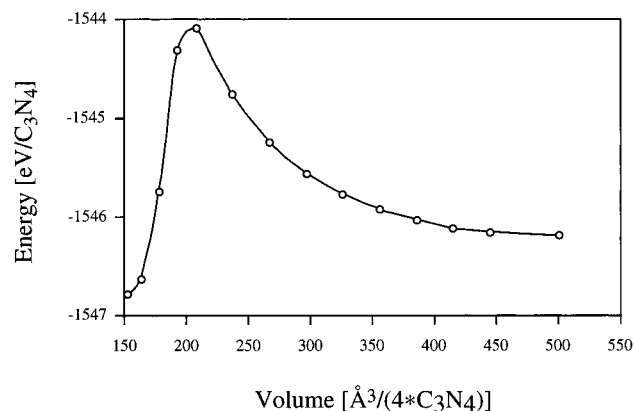
We can go beyond the computer synthesis of polymers in carbon nitride materials and study the transformations likely to happen under high pressure. The space group of “ $\beta$ -C(NCN)<sub>2</sub>”,  $I42d$ , is a subgroup of  $I43d$  (220), the space group of the hypothetical cubic structure of C<sub>3</sub>N<sub>4</sub>.<sup>12</sup> It is this polymorph,  $c$ -C<sub>3</sub>N<sub>4</sub>, that is proposed to have a hardness comparable to that of diamond. The energy of  $c$ -C<sub>3</sub>N<sub>4</sub> relative to  $\alpha$ -C<sub>3</sub>N<sub>4</sub> is about +130 kJ/mol.

The question now is: Can the structure of  $\beta$ -C(NCN)<sub>2</sub> be transformed into that of  $c$ -C<sub>3</sub>N<sub>4</sub>?

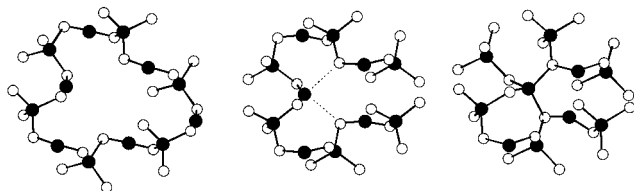
We can perform a theoretical experiment. Our structural model of “ $\beta$ -C(NCN)<sub>2</sub>” is related to that of  $\beta$ -cristobalite SiO<sub>2</sub>, which is tetragonal and has an ideal  $c/a$  ratio of  $\sqrt{2}$ . For the cubic polymorph  $c$ -C<sub>3</sub>N<sub>4</sub> we have a  $c/a$  ratio of 1. Our computer experiment is to take the model of “ $\beta$ -C(NCN)<sub>2</sub>” with its four formula units in the unit cell and compress it from its original volume  $V = 500$  Å<sup>3</sup> to  $V = 152$  Å<sup>3</sup>, the (optimized) volume of the  $c$ -C<sub>3</sub>N<sub>4</sub> structure. This corresponds to a density increase from 1.2 to about 3.9 g/cm<sup>3</sup>. The volume decrease is simultaneously accompanied by a linear decrease of the  $c/a$  ratio from  $\sqrt{2}$  to 1, and, of course, we allow the atoms in the structure to relax. Thinking chemically, what we are doing is investigating “intramolecular reactivity” of  $\beta$ -C(NCN)<sub>2</sub>, and as a reaction coordinate taking the unit cell volume (with additional constraints of tetragonal unit cell geometry and a given  $c/a$  ratio<sup>42</sup>). Figure 5 shows the total energy of the system along the reaction coordinate.

(40) O’Keeffe, M.; Hyde, B. G. *Acta Crystallogr. B* **1976**, *32*, 2923.

(41) After: Milne, A. A. *Winnie-the-Pooh*; Dutton Childrens Book: New York, 1926; p 79.



**Figure 5.** Variation of the total energy with the unit cell volume along the specified reaction coordinate for the reaction of “ $\beta$ - $C(NCN)_2$ ”  $\rightarrow$   $c$ - $C_3N_4$ .



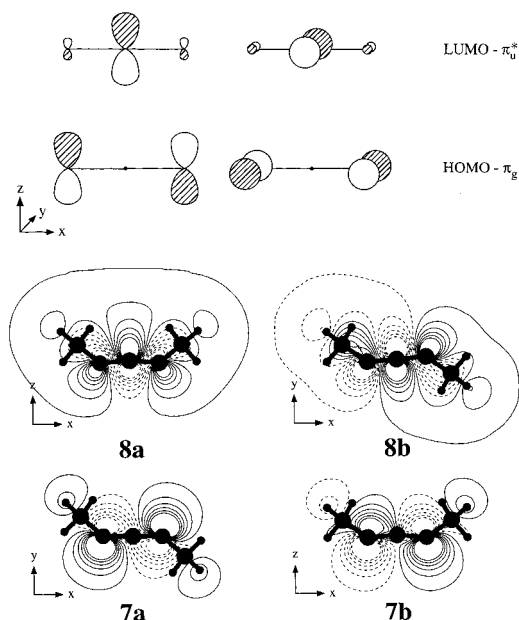
**Figure 6.** Three steps in the solid-state reaction showing the change in the environment of the carbon atom in the carbodiimide group. For the sake of clarity, atoms and bonds which are not involved in the change of the local environment have been omitted. At the left is the structure with a unit cell volume of  $V = 300 \text{ \AA}^3$  (60% of the zero-pressure volume). The polymer structure is still intact. The situation ( $V = 210 \text{ \AA}^3$ ) just before the solid-state transformation is shown in the middle. The angle in the carbodiimide unit widens up. The dashed lines help to see the adjacent nitrogen atoms, which bond to the carbon. At the right ( $V = 193 \text{ \AA}^3$ ) the new phase with the connectivity of the  $c$ - $C_3N_4$  structure is shown.

The result is intriguing: there is a direct path from one structure to the other. Both phases of  $C_3N_4$  are indeed smoothly connected. Figure 6 represents in atomic detail what is happening in the phase transformation.

Down to a volume of about  $300 \text{ \AA}^3$  (Figure 6, left), the structure compensates for energy increase induced by the applied pressure only by changing the bond angle at the nitrogen atoms of the carbodiimide unit down to  $110^\circ$ . This is accompanied by a rotation of the  $CN_2$  tetrahedra, but not by shortening of bond lengths. Indeed, the bond length  $C=N$  is still  $1.21 \text{ \AA}$ , and the bond length  $C-N$  is  $1.46 \text{ \AA}$ . At  $V = 210 \text{ \AA}^3$  (Figure 6, middle) the bond lengths are still  $1.23$  and  $1.45 \text{ \AA}$ , respectively. However, the bond angle at the carbon atom within the carbodiimide group widens up significantly; it is now  $214^\circ$ . The linearity of the  $-NCN-$  groups is lost, the “ $sp$ ” hybridization at C effectively gone. At this point, the distance from the central C to the adjacent nitrogen atoms, which soon will become bonded to it, is still over  $2.2 \text{ \AA}$ .

Decreasing the unit cell volume slightly further changes the situation drastically (Figure 6, right). The previously 2-connected carbon forms two additional bonds to nitrogen atoms. This results in a 4-fold-coordinated, approximately tetrahedral carbon and a 3-fold-coordinated, almost trigonal planar nitrogen in the final structure.

(42) Actually, neither the restricted symmetry nor the decrease of the  $c/a$  ratio is necessary to get the result. We also performed the experiment keeping the  $c/a$  ratio fixed at  $\sqrt{2}$  and allowed the atoms to move freely in the rectangular box. The result was the same connection pattern the  $c$ - $C_3N_4$  structure exhibits.



**Figure 7.** The top shows the iconic representation of the frontier orbitals of the  $NCN^{2-}$  fragment. Contour plots of the corresponding frontier orbitals of dimethylcarbodiimide ( $H_3C-NCN-CH_3$ ) are on the bottom. The two HOMO's (**7a**, **7b**) as well as the two LUMO's (**8a** and **8b**) are almost degenerate.

Thinking again chemically, what we are observing is a simple acid–base or donor–acceptor interaction in the solid state. Recall the frontier orbitals of the carbodiimide fragment. The HOMO is the  $\pi_g$  set, localized at the nitrogens, making up the “lone pairs”. The LUMO is the  $\pi_u^*$  set, which is mainly located on the central C (see Figure 7, top).

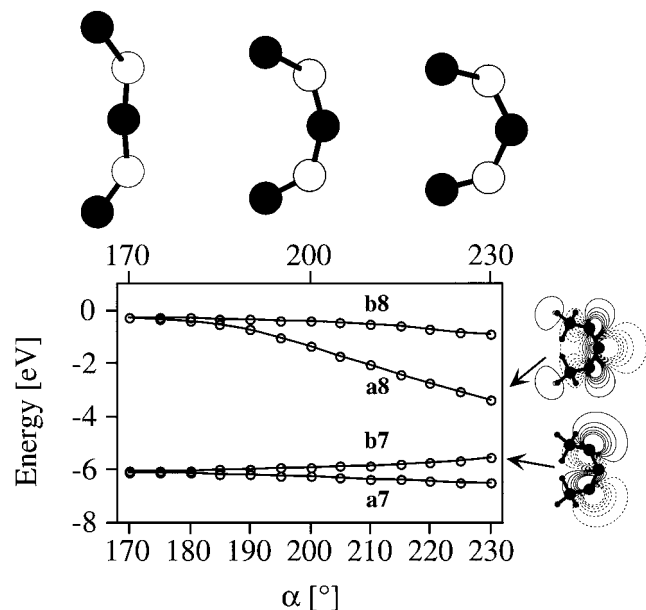
Adding the R ligands in  $R-NCN-R$  (here we choose  $R = CH_3$ ) changes the orbitals a little, in both energy and shape, as in Figure 7, bottom. Note the nice lone pair character of **7a** and **7b**. The two highest filled orbitals as well as the two lowest unfilled orbitals remain almost degenerate. If we go on and bend the molecule at C, this approximate degeneracy gets lost and the HOMO–LUMO gap decreases. In particular one of the former  $\pi_u^*$  levels comes down and one of the former  $\pi_g$  levels moves up in energy. Figure 8 shows the energy evolution of the frontier orbitals.

To summarize, the central carbon, where the low-lying unfilled orbital is localized, is a strong acidic (electrophilic) site, longing for some electrons, and the nitrogens (through their lone pairs) are strongly basic (nucleophilic).

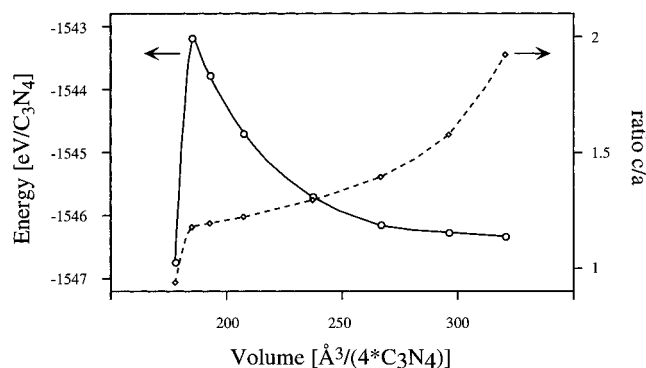
We also looked at the orbitals in a molecular model, the large ring molecule in Figure 6 on the left, with hydrogens terminating the 4-fold carbons. The same pattern is observed: splitting of the near degeneracy of orbitals making up the  $\pi$  bonds, unfilled orbitals localized at the carbons of the  $NCN$  unit coming down in energy, and lone pairs on the nitrogens moving up. We showed for extended  $Si(NCN)_2$  that the crystal states more or less reflect the molecular levels.<sup>30</sup> Thus, the discrete molecules model the essential trends of the solid-state reaction. It is, of course, a special feature of the structure that the lone pairs approach the carbon in such a way as to yield an approximately tetrahedral carbon.

The pressure needed for this phase transformation can be estimated from the data given in Figure 5. We calculate it to be about  $16 \text{ GPa}$ . This value should be no problem for a diamond–anvil press.

We can provide another example of a high-pressure transformation, this time using a structure related to the “ $\alpha$ -



**Figure 8.** The energy of the frontier orbitals for dimethylcarbodiimide as a function of the angle  $\alpha$  within the NCN group. The geometries of the molecule are given above the graph; hydrogen atoms are omitted. Contour plots of the two frontier orbitals for  $\alpha = 230^\circ$ . (HOMO, **7b**; and LUMO, **8a**) are given at the right.

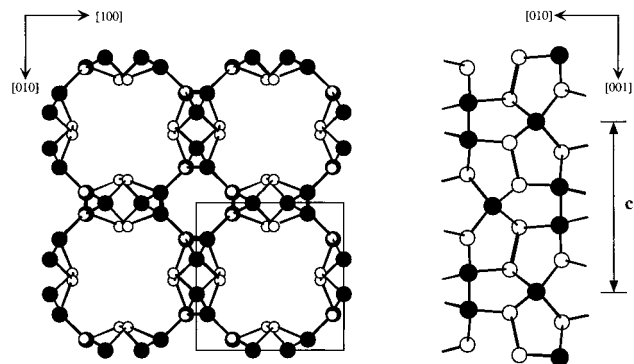


**Figure 9.** Variation of the total energy with the unit cell volume along the specified reaction coordinate for the reaction of " $\alpha$ -C(NCN) $_2$ "  $\rightarrow$   $\lambda$ -C $_3$ N $_4$ .

C(NCN) $_2$ ". If we make this structure interpenetrating, it can be described within space group  $P4_322$  (95). As before, we reduce the volume of the unit cell in a computer experiment. In each step the relaxed coordinates of the previously optimized structure at a higher volume are used as the starting configuration. This time we also optimize the  $c/a$  ratio for each volume.<sup>43</sup> Although the atoms were allowed to move without symmetry constraints in a rectangular box, the symmetry of the system was conserved at all times. Figure 9 shows the change of the total energy and of the  $c/a$  ratio in the course of the reaction.

Again we have (at a pressure of about 50 GPa) a phase transformation. Surprisingly, this time the situation is a little bit more complicated than before. Initially, the structure is compressed and compensates by bending  $\varphi_N$ . Down to a volume of about 210  $\text{\AA}^3$  nothing else happens. At this point the angle  $\alpha$  inside the carbodiimide units starts to widen. However, this time the carbon winds up with only *one* nitrogen bonded to it, because there is only one within reach. For steric reasons, connection to another nitrogen is impossible. What happens instead, and at the same volume, is that another symmetry-

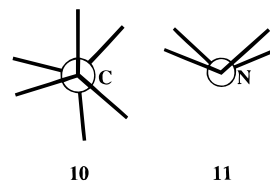
(43) This implies that we are thinking of an experiment using a single crystal.



**Figure 10.**  $\lambda$ -C $_3$ N $_4$ : (Left) Projection along [001]. The structure might be described as connected columns running along [001], every other one rotated by  $90^\circ$  and shifted by  $(0,0,1/4)$ . (Right) One of these columns projected along  $[100]$ , showing the five-membered rings. Filled circles represent carbon and open circles nitrogen.

equivalent C approaches and the two carbon atoms form a bond. At the same time two nitrogens (also symmetry equivalent) also bond. The last point is certainly surprising. The final structure is a  $3/4$ -connected net with odd-membered rings. It is therefore not alternating. We call this phase  $\lambda$ -C $_3$ N $_4$ , and its zero-pressure volume is 202.5  $\text{\AA}^3$  in a unit cell with 4 formula units and its density is 3.0 g/cm $^3$ . The energy of this structure relative to  $\alpha$ -C $_3$ N $_4$  is about +90 kJ/mol, thus about 40 kJ/mol lower relative to  $c$ -C $_3$ N $_4$ . The structure is shown in Figure 10.

The structure contains 28 atoms in the unit cell, with two crystallographically independent carbon and two nitrogen atoms. One of these two carbon atoms is bonded to four N's, with bond angles between  $102^\circ$  and  $120^\circ$ . The other C is bonded to one symmetry equivalent C as well as to three nitrogens. The Newman projection **10** shows the bonding of the C–C pair along the C–C bond, whose length is 1.49  $\text{\AA}$ . The configuration is closer to staggered than eclipsed.



One of the two crystallographically independent nitrogen atoms is nearly planar; the three angles are  $111^\circ$ ,  $121^\circ$ , and  $126^\circ$ . The other nitrogen is more pyramidal (bond angles of  $106^\circ$ ,  $108^\circ$ , and  $110^\circ$ ) and bonded to two C's and to one symmetry equivalent N. The N–N bond length is 1.43  $\text{\AA}$ . The two N's therefore form a hydrazine unit in an extended structure, a structural feature that appears to be unknown so far. A Newman projection of an N–N pair is shown in **11**; the local rotational conformation is difficult to characterize. The angle between the two lines bisecting each C–N–C angle is  $20^\circ$ . For a gauche configuration it would be  $60^\circ$ . The nitrogen lone pairs are thus not orthogonal to each other, as found for the simple hydrazine molecule.<sup>44,45</sup> However, from structures of fluorinated hydrazines it is known that electronegative (and  $\pi$ -donating) substituent transfer can influence the potential energy surface for N–N rotation substantially.<sup>46</sup>

The structure of  $\lambda$ -C $_3$ N $_4$  shown in Figure 10 exhibits channels along the [001] direction with a diameter of 4  $\text{\AA}$ , tempting us

(44) DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576.

(45) Werpinski, K. S.; Cook, M. J. *J. Chem. Phys.* **1997**, *106*, 7124.

(46) Juršić, B. S. *J. Mol. Struct. (THEOCHEM)* **1998**, *434*, 67.

to fill them with a Lewis acid. Were we to introduce a transition metal atom inside the channels, its distance to the center of an N–N bond would be about 2.1 Å. Due to the presence of a 4-fold screwaxis, however, the coordination is complicated. In another construction strategy we can, however, exchange (on paper) the N's pointing to the channels in the model by C–H units, since there is enough space around to accommodate the hydrogen atoms. The model thus constructed would have the stoichiometry C<sub>5</sub>N<sub>2</sub>H<sub>2</sub>. We will discuss the electronic structure for this and related materials in a separate contribution.

**A “Caveat”.** Are we naive in our way of thinking? Our protocol allows us only to look at polymorphic transitions. We left out any consideration of shear instabilities during the reaction, which may lead us to amorphous phases. Or to put it into molecular terms: we did not look for different reaction pathways, branching from our chosen reaction coordinate. We may have missed some minima.<sup>47</sup> A more realistic modeling of the phase transformation might also show that the process of forming new bonds does not happen instantaneously at all sites, but propagates through the crystal. This immediately gives rise to the question as to whether the excess heat of reaction may cause local damage, and even induce some unwanted diffusion processes, probably resulting in gaseous N<sub>2</sub>. Be that as it may, the final states are mechanically stable; our method opens new opportunities in structural research by suggesting new alternative C<sub>3</sub>N<sub>4</sub> structures.

## Summary

The quest for a synthetic route to hard carbon nitride materials with stoichiometry C<sub>3</sub>N<sub>4</sub> continues. In this paper we have proposed two hypothetical, though chemically reasonable, polymers with the stoichiometry C<sub>3</sub>N<sub>4</sub>. We followed theoretically the progression from a single-source precursor to an extended structure. The hypothetical C<sub>3</sub>N<sub>4</sub> polymers we generated are neither dense nor hard. The potential of these polymers for a high-pressure synthesis of hard carbon nitride materials is demonstrated in one case, the utility of the theoretical method used to find new exciting structures in another. Whether or not the cubic C<sub>3</sub>N<sub>4</sub> or the λ-C<sub>3</sub>N<sub>4</sub> phase will be within reach must still be investigated. Our aim is to encourage chemists to take up the thread and develop these and other new polymer precursors for advanced systems.

**Acknowledgment.** The authors gratefully acknowledge the generous support by the National Science Foundation (Grant No. CHE 94-08455). We also thank the Deutsche Forschungsgemeinschaft, Bonn (Germany) for granting a research fellowship (contract Kr 1805/1-1). We acknowledge the useful discussions with and suggestions of Axel Greiner and Davide Proserpio. For computer time we thank the Cornell Theory Center.

(47) We also stayed always on the adiabatic potential energy surface. Thus we did not, could not, investigate influences of excited states. Fortunately, in our extended state calculations the band gap always was higher than 2 eV.

## Appendix: Theoretical Methods

The calculations used for the total energy and atomic structures are of the density functional theory (DFT) type.<sup>48–51</sup> For the calculation of molecular properties we used the Amsterdam Density Functional (ADF) program.<sup>52–54</sup> The valence atomic orbitals were expanded in a set of Slater-type orbitals (STOs). For all atoms we used a triple-ζ basis set with two polarization functions (type V).<sup>55</sup> The core shell was treated in the frozen core approximation.<sup>56</sup> We used the local density approximation (LDA) as parametrized by Vosko, Wilk, and Nusair (VWN).<sup>57</sup> Gradient corrections were applied using the approach of Becke<sup>58,59</sup> for exchange and of Perdew<sup>60</sup> for correlation. The reported values for energy differences are not corrected for zero-point vibrations, since one cannot do (with our resources) a complete frequency calculation for the huge silylated carbodiimide. ADF was run on a Silicon Graphics Power Challenge.

For the extended structure calculations we used the local-density approximation<sup>61,62</sup> with soft separable,<sup>63</sup> norm-conserving, nonlocal pseudopotentials<sup>64–66</sup>. The electronic wave functions were expanded into plane waves with an energy cutoff of  $E_{\text{cut}}^{\text{PW}} = 40$  ryd for preliminary and  $E_{\text{cut}}^{\text{PW}} = 80$  ryd for final optimizations of the internal coordinates. In the integration over the Brillouin Zone special points were used.<sup>67</sup> Here, all calculations were carried out using the program fhi96md of the Fritz-Haber Institut in Berlin (Germany).<sup>68</sup> This part of the work was done by running the program on nodes of the SP2 of the Cornell Theory Center.

JA984406B

- 
- (48) Hohenberg, P.; Kohn, W. *Phys. Rev. A* **1964**, *136*, 864.  
 (49) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.  
 (50) Dreizler, R. M.; Gross, E. K. U. *Density Functional Theory*; Springer-Verlag: Berlin, 1990.  
 (51) Parr, R. G.; Wang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.  
 (52) ADF 2.3.0, Theoretical Chemistry, Vrije Universiteit, Amsterdam, 1997.  
 (53) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1993**, *99*, 84.  
 (54) Fonseca Guerra, C.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. In *Methods and Techniques for Computational Chemistry*; Clementi, E., Corongiu, G., Eds.; (STEF: Cagliari, Italy, **1995**; pp 305–395.  
 (55) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483.  
 (56) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.  
 (57) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.  
 (58) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.  
 (59) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.  
 (60) Perdew, J. P. *Phys. Rev. B* **1985**, *33*, 8822. Erratum: *ibid.* **1986**, *34*, 7406.  
 (61) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 1814.  
 (62) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.  
 (63) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425.  
 (64) Hamann, D. R. *Phys. Rev. B* **1989**, *40*, 2980.  
 (65) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.  
 (66) Fuchs, M.; Scheffler, M. *Comput. Phys. Commun.* In press.  
 (67) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.  
 (68) Bockstedte, M.; Kley, A.; Neugebauer, J.; Scheffler, M. *Comput. Phys. Commun.* **1997**, *107*, 187.