

# Computation of Aromatic $C_3N_4$ Networks and Synthesis of the Molecular Precursor $N(C_3N_3)_3Cl_6$

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**Abstract:** The successful synthesis and structural characterization of molecules that represent segments of extended solids is a valuable strategy for learning metric and stereochemical characteristics of those solids. This approach has been useful in cases in which the solids are particularly difficult to crystallize and thus their atomic connectivity and overall structures become difficult to

deduce with X-ray diffraction techniques. One such class of materials is the covalently linked  $C_xN_y$  extended solids, where molecular analogues remain largely absent. In particular, structures

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of  $C_3N_4$  solids are controversial. This report illustrates the utility of a simple molecule,  $N(C_3N_3)_3Cl_6$ , in answering the question of whether triazine based  $C_3N_4$  phases are layered or instead they adopt 3D structures. Here, we present density functional calculations that clearly demonstrate the lower stability of graphitic  $C_3N_4$  relative to 3D analogues.

## Introduction

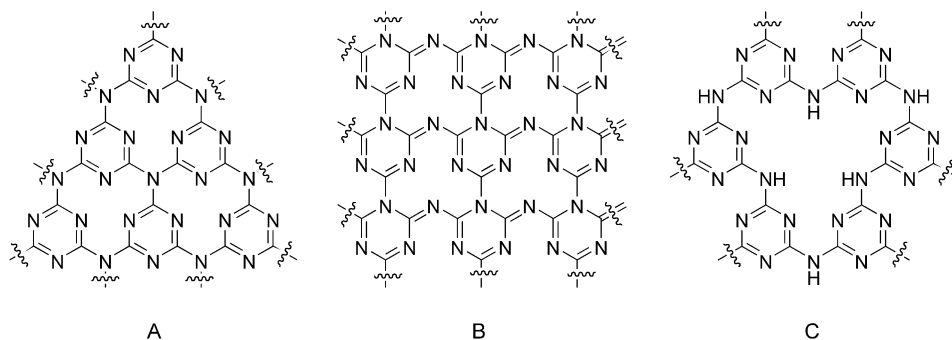
Over the last two decades, considerable research efforts have been devoted to the synthesis of carbon nitride networks for their promise as high-performance materials with hard, lightweight, and thermally stable properties.<sup>[1–4]</sup> In particular, 2D and 3D structures of  $C_xN_y$  composition have been proposed and, in many cases, syntheses have been reported.<sup>[5–8]</sup> However in the absence of single-crystal structure data the atomic connectivity and composition of these materials remain controversial. The inability to obtain definitive structural data for these materials has significantly slowed progress and frustrated attempts toward development of their synthetic chemistry.<sup>[9,10]</sup> Recently, we initiated a program aimed at the synthesis and study of CN-based molecules in an effort to produce discrete (molecular) structures that could closely resemble fragments of  $C_xN_y$  networks, and thus provide insight into the corresponding extended structures.

Our focus has been on linking rigid and stable trigonal triazine units into larger structures. Three important graphitic  $C_3N_4$  structures in which triazine is linked by nitrogen atoms have been proposed by others.<sup>[5–8]</sup> Conceptually, such structures are derived from the hypothetical CN graphitic structure by creating either carbon vacancies (A and B) or triazine vacancies (C). Other potential triazine-based structures include those proposed with carbodiimide (-NCN-) linkages<sup>[11]</sup> or tri-s-triazine ( $C_6N_7X_3$ ) building blocks.<sup>[12]</sup> However, these structures require different precursors than the one employed in the present study.

Examination of structures A–C reveals unusually short and hence high-energy  $N\cdots N$  nonbonded distances,<sup>[13]</sup> thus prompting us to pursue the synthesis and structure of their molecular analogues to evaluate whether planar structures of this sort are likely. Specifically, we chose as an initial object, structure A in which trigonal nitrogen atoms are each linked to three triazine units. At the outset of this study, crystal structures of molecules with this arrangement had not been reported. Here, we describe the synthesis and crystal structure of the first such molecular compound,  $N(C_3N_3)_3Cl_6$  (tris(2,4-dichloro-1,3,5-triazine)amine, TDT) in which the metrics and stereochemical arrangement of three triazine rings around a central nitrogen atom provide important information that has been used to shed light on the likelihood of the proposed graphitic forms of  $C_3N_4$  (g- $C_3N_4$ ).<sup>[5–8]</sup> These findings led us to undertake computational studies in which two *new* extended 3D networks based on the  $N(C_3N_3)_3$  unit have been investigated and found to indeed have lower energy than the proposed g- $C_3N_4$  (A).

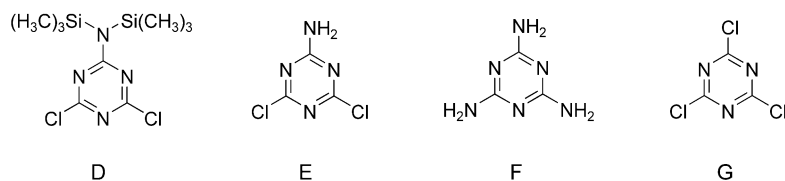
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Supporting information for this article is available on the WWW under <http://www.chemeurj.org> or from the author. Calculated crystallographic parameters and atomic positions for all triazine-based  $C_3N_4$  networks and their respective simulated X-ray powder diffraction patterns.



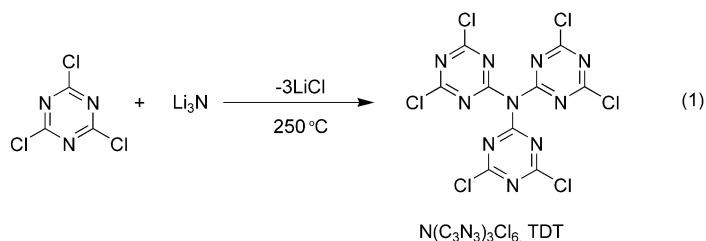
## Results and Discussion

**Synthesis and crystal structure of  $N(C_3N_3)_3Cl_6$  (TDT):** To synthesize models for triazine-containing network A, we followed an intriguing method that has been pursued in the synthesis of carbon nitrides, which employs simple molecular precursors having the triazine core (D–G), such as 2,4-dichloro-6-bis(trimethylsilyl)imido-1,3,5-triazine (D), 2-amino-4,6-dichloro-1,3,5-triazine (E), melamine (F), and cyanuric chloride (G). Of particular interest are recent reports on



reactions involving the self-condensation of D and E,<sup>[5, 7, 8]</sup> and the heterocondensation of F with G.<sup>[7, 14]</sup> When these reactions are driven to completion, amorphous or poorly crystalline products are invariably obtained, precluding full characterization of their atomic connectivity. We chose to study one of these reactions in some detail, namely the recently reported reaction of cyanuric chloride (G) with lithium nitride.<sup>[15]</sup>

In the present study, the reaction was carried out at a lower temperature than in the earlier preparation to yield colorless needle-like crystals of TDT: specifically, this compound was isolated from a reaction of cyanuric chloride with lithium nitride, using a 1:1 mole ratio, in a Pyrex tube at 250 °C [Eq. (1)].



The crystals were analyzed by single-crystal X-ray diffraction techniques to reveal a molecular compound of the composition  $N(C_3N_3)_3Cl_6$ . Each molecule is composed of

three dichlorotriazine rings linked to a central nitrogen atom as shown in Figure 1a. Although there are many examples of a central nitrogen atom surrounded by three phenyl rings, this is the first example of a structurally characterized compound in which three triazine rings are linked to a central nitrogen atom.

The structure showed that the central nitrogen atom, which lies on a threefold axis, and its three carbon neighbors are coplanar. The planes of the three  $C_3N_3$  rings are each at a dihedral angle of  $34.33(6)^\circ$  to the central plane. The  $N \cdots N$  nonbonded distance on adjacent rings of the same molecular unit is  $2.809(2) \text{ \AA}$ , a value within the range ( $2.670\text{--}2.840 \text{ \AA}$ ) found in a Cambridge Structural Database search of nitrogen-containing organic compounds.

The molecules are chiral with  $C_3$  (very close to  $D_3$ ) point group symmetry; however, they pack in columns with the opposite-handed molecules alternating (Figure 1b) and are separated by  $3.722(4) \text{ \AA}$  (distance between trigonal nitrogen atoms in the stack). The columns are stacked in a hexagonal array to give an overall centrosymmetric rhombohedral arrangement. The shortest intermolecular nonbonded distances are  $N \cdots Cl = 3.071(1) \text{ \AA}$  and  $Cl \cdots Cl = 3.610(7) \text{ \AA}$ , typical values for these interactions.<sup>[16]</sup>

The dihedral angle and the  $N \cdots N$  nonbonded distance are two metric features of this compound that we find relevant to the  $g\text{-}C_3N_4$  structures (A–C), which have been proposed by others for the products of the reactions mentioned above. It is important to note that structure A has an identical connectivity to that observed in  $N(C_3N_3)_3$  core structure of TDT, and the latter ones (B and C) have a closely related one.

TDT is a potential compositional and structural building block for structure A, as its further condensation with  $Li_3N$  would yield the  $C_3N_4$  composition. However, it is doubtful that planar structures similar to those previously proposed (in particular A but also B and C) would be easily accessible as they have unusually short  $N \cdots N$  nonbonded distances ( $2.380\text{--}2.436 \text{ \AA}$ , vide infra), which are not observed in the molecular analogue TDT (compare  $2.809(2) \text{ \AA}$ ) or other nitrogen-containing organic compounds.

## Computational Methods

**TDT:** In view of the pronounced difference in planarity between the  $N(C_3N_3)_3$  subunits in TDT and those in the proposed structures (A–C), we sought to confirm that the dihedral angles in TDT were not due to the presence of the chlorine atoms or intermolecular  $N \cdots Cl$  and  $Cl \cdots Cl$  inter-

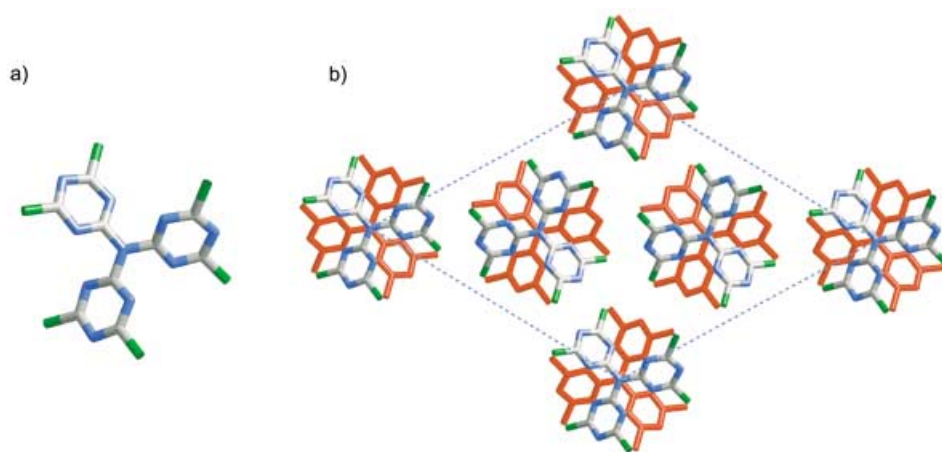


Figure 1. Crystal structure of  $N(C_3N_3)_3Cl_6$  (TDT): a) drawing of a single molecule and b) representation of its stacking in the crystal perpendicular along  $c$ . (C: gray; N: blue; Cl: green; the enantiomers are drawn in red for contrast).

actions. Accordingly we examined the influence of this substitution on the geometry around the central nitrogen; semiempirical calculations were carried out to determine the inherent geometric preference of this unit. With the AM1 method both the TDT and parent model tris(1,3,5-triazine)-amine ( $N(C_3N_3)_3H_6$ ) were found to be twisted from planarity by  $37.0^\circ$  and  $36.5^\circ$  respectively.<sup>[17]</sup> Furthermore, the planar forms of these molecules are destabilized by  $33.1 \text{ kcal mol}^{-1}$  for TDT and  $31.7 \text{ kcal mol}^{-1}$  for the parent-unsubstituted structure indicating the minimal role of Cl in dictating the geometry of this unit.

Additionally, the energy of the unsubstituted model  $N(C_3N_3)_3H_6$  was determined using density functional calculations on the molecule optimized in  $D_3$  symmetry and contrasted with a planar ( $D_{3h}$ ) conformation. At the B3LYP/6-31G\*\* level the twisted geometry ( $36.2^\circ$ ) was found to be favored by  $32.2 \text{ kcal mol}^{-1}$ , which implies a considerable repulsion between the nitrogen atoms when separated by the optimized value of  $2.484 \text{ \AA}$  in the  $D_{3h}$  structure.<sup>[17]</sup> Since a similar interaction is present in the proposed planar g- $C_3N_4$  extended solids (A–C), and in particular the extended analogue of TDT (A), it was anticipated that they would be significantly destabilized relative to corrugated (out-of-plane) deformations<sup>[18]</sup> and 3D analogues.

#### Triazine-based C<sub>3</sub>N<sub>4</sub> networks:

To examine the energy of extended C<sub>3</sub>N<sub>4</sub> structures in which TDT is a potential building block, density functional calculations were carried out on six polymorphs of C<sub>3</sub>N<sub>4</sub> containing triazine rings joined by 3-coordinate nitrogen atoms both in idealized symmetry and corrugated in  $P1$  (Figures 2 and 3). Extended calculations on the planar AA-type graphitic arrangement and three AB-type structures showed that these four structures were the highest energy aromatic forms (Figure 2, Table 1). In all of the graphitic structures, each triazine nitrogen experiences re-

pulsion from two other nitrogen atoms at a distance of approximately  $2.45 \text{ \AA}$ . Not surprisingly,<sup>[13, 18]</sup> in  $P1$  the energies of the graphitic structures were reduced substantially by adopting corrugated structures with  $N \cdots N$  nonbonding distances =  $2.44, 2.50, 2.59 \text{ \AA}$  (g-AA),  $2.49, 2.55, 2.49, 2.47, 2.57 \text{ \AA}$  (g-AB1),  $2.46, 2.48, 2.61, 2.45, 2.48, 2.60 \text{ \AA}$  (g-AB2), and  $2.44, 2.50, 2.59 \text{ \AA}$  (g-AB3) (Figure 2, Table 1).

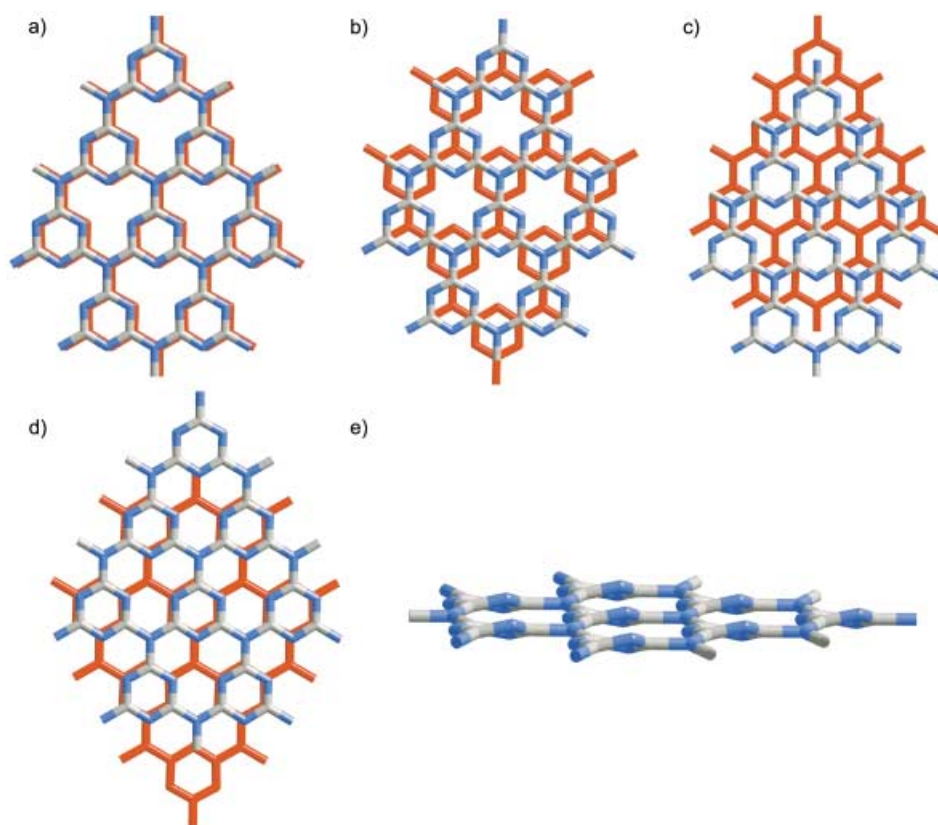


Figure 2. Idealized model structures of graphitic C<sub>3</sub>N<sub>4</sub> (g-C<sub>3</sub>N<sub>4</sub>) in which the layers are a) eclipsed (g-AA), b) rotated  $60^\circ$  (g-AB1), c) translated by  $\frac{1}{2}$  unit cell (g-AB2), and d) rotated by  $60^\circ$  and translated by  $\frac{1}{2}$  unit cell (g-AB3), including an example e) of the corresponding corrugated structures emphasizing the out-of-plane distortions of nitrogen atoms. (In a)–d) adjacent layers are colored in red for contrast)

Table 1. Energy and density of  $C_3N_4$  planar (idealized symmetry) and corrugated structures ( $P1$ ).<sup>[a]</sup>

Structure type of $C_3N_4$	Energy [eV]	Planar structures		Density [g mL <sup>-1</sup> ]	Energy [eV]	Corrugated structures	
		Relative energy [kcal mol <sup>-1</sup> ]				Relative energy [kcal mol <sup>-1</sup> ]	$\Delta E$ from symmetry-enforced structure
g-AA	-1555.7697	0.53		2.19	-1556.0629	-6.23	-6.76
g-AB1	-1555.7361	1.3		2.39	-1555.9922	-4.60	-5.9
g-AB2	-1555.7925	0		2.21	-1556.1050	-7.21	-7.21
g-AB3	-1555.8198	-0.63		2.33	-1556.0935	-6.94	-6.31
3D-srs	-1556.0115	-5.05		1.59	-1556.0655	-6.29	-1.24
3D-ths	-1556.5732	-18.00		1.65	-1556.6017	-18.65	-0.65

[a] Optimized geometries, absolute energies, and densities were calculated by using CASTEP with the GGA-PW91 functional on the  $C_3N_4$  polymorphs in idealized symmetry (see Methods section). The  $\Delta E$  value from the symmetry enforced structure to the  $P1$  space group reveals that the 3D-srs and 3D-ths structures undergo substantially less reorganization than their graphitic counterparts. Energy values are per mole of  $C_3N_4$ . This is consistent with the large degree of nitrogen-nitrogen repulsion present in the planar g- $C_3N_4$ .

Considerably more favorable than the planar  $C_3N_4$  polymorphs is the structure based on the Si network of  $SrSi_2$  (named 3D-srs)<sup>[19]</sup> where no adjacent triazine rings are coplanar (Figure 3a) but rather are twisted by  $69.3^\circ$  from

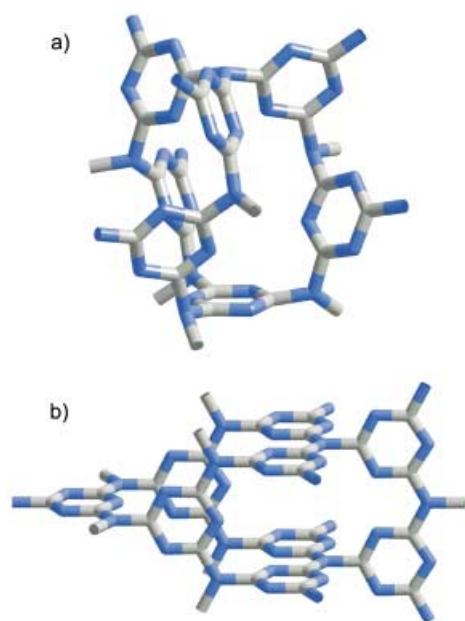


Figure 3. Proposed structures for the more energetically favored triazine-based  $C_3N_4$  networks named a) 3D-srs and b) 3D-ths. (a) and (b) are respectively derived from the Si network in the original common inorganic structures  $SrSi_2$  and  $ThSi_2$ , where the Si positions have been alternately replaced by N and  $C_3N_3$  units.

the plane of the trigonal-planar central nitrogen atom (compared to  $70.5^\circ$  in the Si network in  $SrSi_2$ ), substantially more twisted from coplanarity than experimentally determined for TDT ( $34.33(6)^\circ$ ). As in the case of the g- $C_3N_4$  polymorphs, each triazine in 3D-srs experiences contacts with two other nitrogen atoms, but in this structure the twisting of the central ring increases the distance of each contact to  $3.07 \text{ \AA}$ , considerably reducing this contribution to the energy of the system. However, the three-coordinate nitrogen atom linking the three triazine rings together is displaced by  $0.32 \text{ \AA}$  from the plane of the three adjacent carbons and  $0.22 \text{ \AA}$  from the mean plane on the triazine ring indicating substantial

strain in the network. Computation in  $P1$  does not substantially lower the energy of this form and its stability is similar to the corrugated g-AA, g-AB1, g-AB2 and g-AB3 structures (Table 1).

In searching for an alternative arrangement of an aromatic  $C_3N_4$  structure based on TDT  $C_3N_3$  core, we examined a topology based on the Si network of  $ThSi_2$  (3D-ths), a common motif in three-connected nets of inorganic compounds.<sup>[20]</sup> This structure is computed to be more stable than the corresponding 3D-srs arrangement by  $13 \text{ kcal mol}^{-1}$  in spite of the fact that it contains two coplanar adjacent triazine rings (Figure 3b). This introduces one repulsive  $N \cdots N$  interaction ( $2.43 \text{ \AA}$ ) for each triazine, whereas three such interactions are introduced by the fully planar arrangement present in the g- $C_3N_4$  structures. From the computations on the model system,  $N(C_3N_3)_3H_6$ , each such interaction can be estimated to be destabilizing by approximately  $10.7 \text{ kcal mol}^{-1}$ . However this value derived from calculations on a single molecule cannot be directly compared to the 3D-srs network since the extended structure contains a number of highly strained bonds. When compared to the planar and corrugated AA, AB1, AB2 and AB3 structures (Figure 1e), the 3D-ths is the most stable by at least  $11.4 \text{ kcal mol}^{-1}$  (Table 1).

It is important to note that the differences between the energies of the idealized and the corrugated structures reveal that the graphitic topologies become more stable through corrugation whereas the 3D-srs and 3D-ths do not. This observation indicates that the graphitic structures are experiencing destabilizing strain due to several close  $N \cdots N$  nonbonding distances (Table 1).

To quantify the factors leading to the energetic preference for the 3D-ths network over that of 3D-srs, computations on a subunit with three triazine rings attached to one central nitrogen atom, extracted from the periodic structures and capped with hydrogen atoms at optimized positions, were undertaken. This subunit of 3D-srs is destabilized by  $12.3 \text{ kcal mol}^{-1}$  relative to the analogous unit of 3D-ths indicating that avoiding close  $N \cdots N$  interactions in 3D-srs comes at the expense of introducing substantial ring strain to the overall structure. This result demonstrates that although the nitrogen–nitrogen repulsive forces are important, they are not absolute in determining the stability of the structure.

## Conclusion

A combination of experimental and theoretical methods applied to the structure type tris(1,3,5-triazine)amine have demonstrated the importance of N⋯N repulsion in determining the structure of carbon nitride extended networks. Computations on twelve triazine-based periodic C<sub>3</sub>N<sub>4</sub> models predict that planar geometries, which have long been considered to be viable, are highest in energy. Instead 3D analogues are more stable, and in particular the structure based on the Si network of ThSi<sub>2</sub> is the most stable among those computed by at least 11.4 kcal mol<sup>-1</sup>.

## Experimental Section

**TDT was prepared under an atmosphere of N<sub>2</sub>:** Cyanuric chloride (0.50 g, 2.7 mmol) and lithium nitride (0.10 g, 2.7 mmol) were placed in a Pyrex tube (o.d. × i.d. = 11 × 9 mm<sup>2</sup>). The tube was evacuated (10<sup>-3</sup> Torr) and subsequently sealed. The reaction proceeded over 48 h at 250 °C in a Fisher Isotemp oven and was slowly cooled to room temperature (0.1 °C min<sup>-1</sup>). The product was collected by vacuum filtration and washed with water and ethanol to remove LiCl and cyanuric chloride impurities, respectively. The clear needles were mechanically separated from a tan, amorphous powder. Needles of TDT were recovered in low yield (<10% based on cyanuric chloride, C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub>). FTIR (KBr):  $\tilde{\nu}$  = 1546.0 (m), 1510.3 (vs), 1408.4 (w), 1303.7 (w), 1296.4 (w), 1260.7 (m), 1093.5 (w), 864.7 (w), 859.1 (vw), 808.5 (vw), 797.3 (w), 756.5 (w), 668.2 cm<sup>-1</sup> (vw); X-ray powder diffraction pattern *d* spacings (Å) and *hkl* indices of the most prominent diffraction lines: 9.697 (110), 4.854 (211), 3.956 (31–1), 3.656 (410), 3.446 (321), 3.246 (122), 2.932 (42–1), 2.846 (312), 2.790 (600), 2.681 (250), 2.218 (710). EIMS (70 eV) *m/z*: [M<sup>+</sup>] 458 (23), 459 (3), 460 (41), 461 (6), 462 (34), 463 (5), 464 (16), (3), 465 (4). This isotope distribution is in excellent agreement with the predicted pattern for C<sub>9</sub>N<sub>10</sub>Cl<sub>6</sub>. EDS determined qualitatively that the needles were composed of carbon, nitrogen, and chlorine atoms, with no other elements detected. We note that TDT was proposed, without structural evidence, for a product resulting from a multi-step organic synthesis.<sup>[21]</sup> However, the reported solubility and the FT-IR spectrum of this material is different from what we observed in the one-step synthesis described in this report.

**Crystal data for TDT:** crystal dimensions 0.06 × 0.06 × 0.40 mm<sup>3</sup>, crystal system rhombohedral, space group *R* $\bar{3}$ , *a* = 19.278(2), *c* = 7.438(1) Å, *V* = 2393.9(5) Å<sup>3</sup>, *Z* = 6,  $\rho_{\text{calcd}}$  = 1.918 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  = 52.72°, *T* = 158(2) K, 7257 reflections collected, 1095 independent, 950 observed [*I* > 2σ(*I*)],  $\mu$  = 1.095 mm<sup>-1</sup>,  $T_{\text{max/min}}$  = 0.965/0.767, 76 parameters, final *R* indices [*I* > 2σ(*I*)]: *R*1 = 0.0223, *wR*2 = 0.0608, max/min residual electron density 0.22/–0.29 e Å<sup>-3</sup>. CCDC-413138 (TDT) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Computational studies:** Computations on all extended N(C<sub>3</sub>N<sub>3</sub>)<sub>3</sub> based C<sub>3</sub>N<sub>4</sub> structures were carried out using CASTEP<sup>[22]</sup> as implemented in version 4.2 of the Cerius<sup>2</sup> package from Accelrys. DFT calculations using the GGA-PW91 functional with an ultrasoft pseudopotential and precise basis set were chosen based on its performance in the following model calculations. The experimental difference between the aromatic and nonaromatic allotropes of carbon, graphite and diamond is experimentally observed to be 0.45 kcal mol<sup>-1</sup> favoring graphite.<sup>[23]</sup> The calculation predicts this difference to be 3.84 kcal mol<sup>-1</sup>, which demonstrates the propensity of this basis set to overestimate aromatic stabilization. However, the recently determined energy 0.25 ± 7.43 kcal mol<sup>-1</sup> preference for α-Si<sub>3</sub>N<sub>4</sub> over the β-Si<sub>3</sub>N<sub>4</sub> polymorph is computed to be 0.99 kcal mol<sup>-1</sup> suggesting that these calculations can differentiate accurately within a given structure type.<sup>[24]</sup> Corrugation (deplanarization) of graphitic structures was studied in *P1* by

manually displacing atoms from symmetry-enforced positions and carrying out energy minimization.

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