

Carbon Nitrides

3,6-Di(azido)-1,2,4,5-Tetrazine: A Precursor for the Preparation of Carbon Nanospheres and Nitrogen-Rich Carbon Nitrides**

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Microbead and nanophase carbon materials attract many researchers due to their unique applications,^[1] which include high-density and high-strength carbon artifacts,^[2] super-active carbon beads of high surface area,^[3] lithium storage,^[4a] lithium battery anodes,^[4b–d] spherical packing materials for HPLC,^[5]

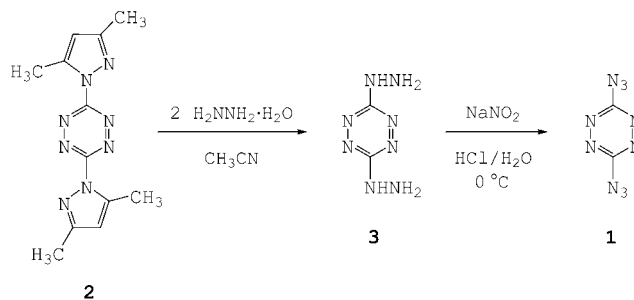
hydrogen storage applications,^[6] and catalysis.^[7] Much attention has focused on the preparation (precursors and methods) and properties of these carbon materials, because their applications significantly depend on the shape and size of the particles.

Carbon nitrides are of current interest due to their novel mechanical, optical, and tribological properties, including low density, extreme hardness, surface roughness, wear resistance, chemical inertness, and biocompatibility.^[8] These superhard diamondlike materials promise a variety of technological and biological applications. For example, they are used as biocompatible coatings on biomedical implants,^[8–9] battery electrodes,^[10] catalytic supports,^[11] gas separation systems,^[12] electronic materials,^[13] and humidity and gas sensors.^[14] Unlike carbon-based materials, applications of carbon nitrides are not only governed by the texture and size of the particles^[13] but also by the relative nitrogen content. As a consequence, an extensive effort has focused on the discovery of precursors along with the appropriate methods to increase the nitrogen content in carbon nitrides.

There is very little literature on the preparation of carbon nanospheres and nitrogen-rich carbon nitrides (> 60 wt % N). Gillan reported preparations of carbon nitrides C₃N₄ (60.9 wt % N) and C₃N₅ (66.0 wt % N) and graphitic carbon using high-nitrogen 2,4,6-tri(azido)-1,3,5-triazine as the precursor; however, the graphitic carbon consisted of irregular polygons, and no detailed description of its dimensions was provided.^[15] Lee et al. recently published a preparation of aggregate interlinked three-dimensional network of carbon nanospheres from naphthalene-derived isotropic pitch using a lengthy five-step process consisting of acidification, extraction, stabilization, oxidation, and carbonization. By mild grinding, carbon nanospheres ranging from 100 to 300 nm were individually separated.^[1]

We report here a new synthesis of the high-nitrogen compound 3,6-di(azido)-1,2,4,5-tetrazine (DiAT, **1**), from which carbon nanospheres ranging from 5 to 50 nm and nitrogen-rich carbon nitrides C₃N₄ and C₃N₅ can be prepared. Both preparation methods are simple, use mild conditions (i.e., low temperature and without applied pressure), and require no vacuum systems, extraction, carbonization and purification.

In 1963, Marcus and Remanick reported the preparation of **1** with a melting point of 130 °C, but no other physical properties or crystal structure were available.^[16] We developed an improved synthetic pathway for **1** that involves the two-step process illustrated in Scheme 1. The readily avail-



Scheme 1. Synthesis of DiAT (**1**).

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able 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**2**; 2.0 g, 7.4 mmol)^[17] rapidly reacted with hydrazine hydrate (0.78 g, 15.6 mmol) to give 3,6-di(hydrazino)-1,2,4,5-tetrazine (DHT, **3**),^[18] which underwent diazotization in 3 M HCl at 0°C to yield **1**.^[19]

The isolated sample of **1** was characterized by X-ray crystallography,^[20] differential scanning calorimetry (DSC); cyclic voltammetry; and IR, UV/Vis, and ¹³C NMR spectroscopy.^[21] The structure of **1** in the crystal, grown by slow evaporation of a solution in benzene/octane (4/1), is shown in Figure 1. Selected bond lengths and angles are listed in ref. [22].

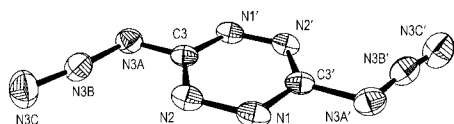


Figure 1. ORTEP diagram (25% ellipsoids) and labeling scheme for **1**.

The X-ray analysis shows how molecules of **1** are packed densely ($d = 1.72 \text{ g cm}^{-3}$) in the crystals. Figure 2 displays a

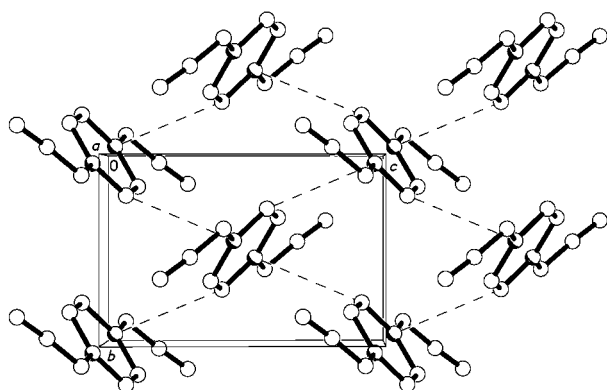


Figure 2. Packing of **1** in the crystal viewed along the *a* axis. The planar molecules are seen almost edge-on in this view, and close intermolecular C–N approaches between neighboring tetrazine rings are shown as dashed lines.

pattern formed by planar molecules that adopt two different alternating inclinations. This familiar type of packing is commonly called a herringbone pattern, and it is frequently seen in crystals of non-hydrogen-bonded planar molecules, for example, naphthalene.^[23] In **1**, the dihedral angle between the ring planes of neighboring molecules of differing tilt is 72.1°. The closest intermolecular distance in the crystal is shown as a dashed line (repeated by symmetry operations) between nearest neighbors. It is a ring C to ring N approach of 3.037 Å that is slightly shorter than the corresponding van der Waals contact distance of 3.25 Å.^[24] Parallel molecules, such as the neighbors occurring vertically or horizontally in Figure 2, have no close contacts. Each azido group is in rather close contact with four neighboring azido groups, displaying six approach distances of 3.13–3.15 Å, just slightly beyond the N···N van der Waals contact distance of 3.10 Å.

Carbon nanoparticles were prepared at two different rates of heating in the presence of air.^[25] A 0.2 g sample of **1** was loaded into a 50 mL stainless steel bomb and then heated to 150°C over 2 h to give carbon nanospheres that were characterized by IR spectroscopy, gas pycnometry, elemental analysis^[26] and by SEM (Figure 3).

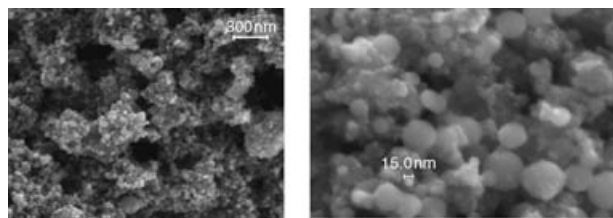


Figure 3. SEM images of carbon nanospheres at magnifications of 25 000× (left) and 150 000× (right).

When the heating time was reduced to 1 h, an audible pop occurred, and irregular carbon nanopolygons doubled in size were obtained (Figure 4). Gas pycnometry, IR spectroscopic data, and elemental analysis indicate that they are similar in composition to the carbon nanospheres.^[26]

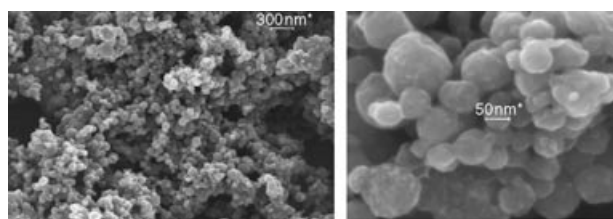


Figure 4. SEM images of irregular carbon nanopolygons at magnifications of 25 000× (left) and 150 000× (right)

In the presence of air, brown, nitrogen-rich carbon nitrides were prepared by using two different heating protocols in a 50 mL stainless steel bomb. A 0.3 g fluffy sample of **1** was heated to 100°C over 2 h and held at this temperature for an additional 4 h. The temperature was then increased to 150°C over 3 h and maintained overnight to yield leaf-like carbon nitride C₃N₄ (Figure 5, left). When **1** was heated continuously to 150°C over 5 h and then held at that temperature overnight, rope/ball-like carbon nitride C₃N₄ was obtained (Figure 5, right). Both carbon nitride products

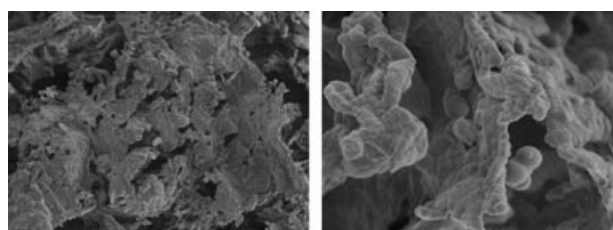


Figure 5. SEM images of leaf-like (left) and rope/ball-like (right) carbon nitride C₃N₄.

were characterized by IR spectroscopy, elemental analysis, thermal gravimetric analysis (TGA), gas pycnometry,^[27a] and SEM imaging.

Under a nitrogen atmosphere, a 0.3 g consolidated sample of **1** was again heated to 150 °C with the two different heating protocols (see above). The sheet-like and rope/ball-like carbon nitrides C₃N₅ were characterized by IR spectroscopy, elemental analysis, TGA, gas pycnometry,^[27b] and SEM imaging (Figure 6).

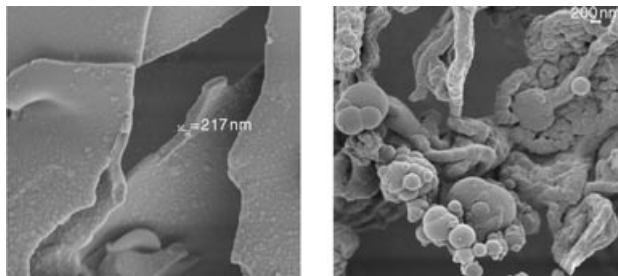


Figure 6. SEM images of sheet-like (left) and rope/ball-like (right) carbon nitride C₃N₅.

Unlike many other organic compounds, for example, meso-carbon microbeads,^[28] mesophase pitch-based carbon fibers,^[29] and non-azido-substituted triazines^[30] and heptazines,^[31] **1**^[16] and other polyazido compounds containing only C and N atoms^[32] are ideal precursors for nitrogen-rich carbon nitrides because of their clean and thermodynamically favorable decompositions, which presumably extrude nitrogen gas as the only by-product [Eqs. (1) and (2)].



More importantly, the conversion processes to nitrogen-rich carbon nitrides from these polyazido compounds generate no environmental waste or pollution.

The reproducible results in this study are novel and important in demonstrating that **1** undergoes decomposition in a single-step heating process to give 1) the first carbon nanospheres ranging from 5 to 50 nm at low temperature and without applied pressure and 2) three novel morphologies of nitrogen-rich carbon nitrides. Remarkably, since the texture, size, and nitrogen content of carbon nitrides ($\rho = 0.58\text{--}1.32 \text{ g cm}^{-3}$) are highly dependent on the heating protocols, they can be tailored for particular applications.

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[1] S.-I. Lee, S.-H. Yoon, C. W. Park, Y. Korai, I. Mochida, *Carbon* **2003**, *41*, 1652–1654.

[2] a) M. Inagaki, Y. Tamai, S. Naka, K. Kamiya, *Carbon* **1974**, *12*, 639–643; b) Y. Yamada, T. Imamura, H. Kakiyama, H. Honda, S. Oi, K. Fukuda, *Carbon* **1974**, *12*, 307–319.

- [3] a) T. Nitta, M. Nozawa, S. Kida, *J. Chem. Eng. Jpn.* **1992**, *25*, 176–182; b) J. Economy, L. Dominguez, C. L. Mangun, *Ind. Eng. Chem. Res.* **2002**, *41*, 6436–6442.
- [4] a) X. Huang, H. Li, Q. Wang, W. Liu, L. Shi, L. Chen, *Wuli* **2002**, *31*, 444–449; b) A. Mabuchi, K. Tokumitsu, H. Fujimoto, T. Kasuh, *J. Electrochem. Soc.* **1995**, *142*, 1041–1046; c) H.-Y. Lee, S.-M. Lee, *Electrochem. Commun.* **2004**, *6*, 465–469; d) S. Dasgupta, R. Bhola, R. Jacobs, K. James, US 6261722, **2001**.
- [5] a) H. Honda, *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 97–108; b) T. Yokono, M. Nakahara, K. Makino, Y. Sanada, *J. Mater. Sci. Lett.* **1988**, *7*, 864–866.
- [6] S. Isobe, T. Ichikawa, J. I. Gottwald, E. Gomibuchi, H. Fujii, *J. Phys. Chem. Solids* **2004**, *65*, 535–539.
- [7] a) Z. C. Kang, Z. L. Wang, *J. Phys. Chem.* **1996**, *100*, 5163–5165; b) H. Shioyama, *Carbon* **2003**, *41*, 2882–2884.
- [8] a) E. K. Wilson, *Chem. Eng. News* **2004**, *82*, 34–35, and references therein; b) F. Z. Cui, D. J. Li, *Surf. Coat. Technol.* **2000**, *131*, 481–487, and references therein.
- [9] a) D. J. Li, L. F. Niu, *Bull. Mater. Sci.* **2003**, *26*, 371–375; b) D. J. Li, S. J. Zhang, L. F. Niu, *Appl. Surf. Sci.* **2001**, *180*, 270–279.
- [10] a) D. Y. Zhong, G. Y. Zhang, S. Liu, E. G. Wang, Q. Wang, H. Li, X. J. Huang, *Appl. Phys. Lett.* **2001**, *79*, 3500–3502; b) M. Kawaguchi, *Adv. Mater.* **1997**, *9*, 615–625.
- [11] H. L. Chang, C. M. Hsu, C. T. Kuo, *Appl. Phys. Lett.* **2002**, *80*, 4638–4640.
- [12] J. N. Armor in *Materials Chemistry, An Emerging Discipline* (Eds.: L. V. Interrante, L. A. Caspar, A. B. Ellis), Advances in Chemistry Series, American Chemical Society, Washington, DC, **1995**, Ch. 13, p. 245.
- [13] I. Widlow, Y. W. Chung, *Braz. J. Phys.* **2000**, *30*, 490–498.
- [14] W. Kulisch, C. Popov, L. Zambov, *New Diamond Front. Carbon Technol.* **2001**, *11*, 53–76.
- [15] a) E. G. Gillan, *Chem. Mater.* **2000**, *12*, 3906–3912; b) W. Long, Y. Shun, Y. Bing, *Rare Met. Mater. Eng.* **2002**, *31*, 96–100, and references therein; c) A. K. Pal, *Curr. Sci.* **2002**, *83*, 225–236.
- [16] J. H. Marcus, A. Remanick, *J. Org. Chem.* **1963**, *28*, 2372–2375.
- [17] M. D. Coburn, G. A. Buntain, B. W. Harris, M. A. Hiskey, K.-Y. Lee, D. G. Ott, *J. Heterocycl. Chem.* **1991**, *28*, 2049–2050.
- [18] D. E. Chavez, M. A. Hiskey, *J. Heterocycl. Chem.* **1998**, *35*, 1329–1332.
- [19] a) Since **1** is extremely sensitive to friction, impact, and electrostatic discharge, one should always handle **1** wet with thick gloves behind a glass shield and limit the amount to less than 300 mg; b) For an explanation of methods for characterizing explosive sensitivity, see R. T. Paine, W. Koestle, T. T. Borek, E. Duesler, M. A. Hiskey, *Inorg. Chem.* **1999**, *38*, 3738–3743; c) 10 mL of a solution of NaNO₂ (0.61 g, 8.84 mmol) was added dropwise to a 35 mL of 3 M HCl containing **3** (0.5 g, 3.52 mmol) at 0 °C. The bright orange precipitated solid was collected by filtration and washed thoroughly with cold water. The sample was mounted for drying above a stainless steel bomb in a hood behind a glass shield overnight. **1** was then washed into the bomb with CH₂Cl₂ that was gradually evaporated. The lid of the bomb was secured tightly before the assembled apparatus was moved.
- [20] CCDC-238514 (**1**) 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 (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [21] Characterization of **1**: DSC: fast decomposition at 130 °C. Cyclic voltammetry in 0.2 M Bu₄NPF₆/CHCl₃ (vs SSCE): $E_{1/2} = +0.44$, -0.09 V. IR (Nujol mull): $\tilde{\nu}(\text{N}_3) = 2169$ (vs), 2142 cm^{-1} (vs); $\tilde{\nu}(\text{tetrazine}) = 1460$ (vs), 1193 (vs), 1065 (vs), 927 (vs), 817 (vs), 546 cm^{-1} (vs). UV/Vis (CHCl₃): $\lambda_{\text{max}}(\epsilon)$: 541 sh (4.64×10^2), 521 (6.50×10^2), 373 (1.79×10^3), 268 nm ($1.94 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ¹³C NMR (300 MHz, CDCl₃, 25 °C): $\delta = 164.2$ ppm.

- [22] Selected bond lengths [\AA] and angles [$^\circ$] for **1**: N1–N2 1.310(3), N2–C3 1.328(3), C3–N3A 1.376(4); N2–C3–N3A 119.9(2), N1'–C3–N3A 113.9(2), N1'–C3–N2 126.2(3).
- [23] C. P. Brock, J. D. Dunitz, *Acta Crystallogr. Sect. B* **1982**, *38*, 2218–2228.
- [24] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384–7391.
- [25] Los Alamos is at an elevation of 7500 feet with a typical atmospheric pressure of 580 torr (11.2 psi or 0.76 atm). The relative humidity is normally below 20% for most of the year.
- [26] Characterization of carbon nanospheres and irregular carbon nanopolygons: IR (Nujol mull): $\tilde{\nu}$ = 1112 (vs), 475 cm^{-1} (vs). Elemental analysis (found): C 98.06, H 0.00, N 0.34, O 0.26 %. Gas pycnometry: ρ = $1.35 \pm 0.05 \text{ g cm}^{-3}$.
- [27] a) Characterization of leaf-like and rope/ball-like carbon nitride C_3N_4 : IR (Nujol mull): $\tilde{\nu}$ = 1088 (vs), 974 (s), 890 (s), 811 (s), 775 (vs), 467 cm^{-1} (vs). Elemental analysis (found): C 38.76, H 1.68, N 59.52 %. TGA: robust up to about 650 $^\circ\text{C}$. Gas pycnometry: ρ = $0.58 \pm 0.02 \text{ g cm}^{-3}$ for the leaf-like and $1.03 \pm 0.03 \text{ g cm}^{-3}$ for the rope/ball-like form. b) Characterization of sheet-like and rope/ball-like carbon nitride C_3N_5 : IR (Nujol mull): $\tilde{\nu}$ = 1261 (vs), 1099 (vs), 1027 (s), 890 (s), 801 (s), 778 (vs), 482 cm^{-1} (vs). Elemental analysis (found): C 35.60, H 1.86, N 66.31 %. TGA: robust up to about 650 $^\circ\text{C}$. Gas pycnometry: ρ = $1.32 \pm 0.02 \text{ g cm}^{-3}$ for the sheetlike and $1.23 \pm 0.02 \text{ g cm}^{-3}$ for the rope/ball-like form.
- [28] a) Y. G. Wang, Y. Korai, I. Mochida, K. Nagayama, H. Hatano, N. Fukuda, *Carbon* **2001**, *39*, 1627–1634; b) Y. C. Chang, H. J. Sohn, C. H. Ku, Y. G. Wang, Y. Korai, I. Mochida, *Carbon* **1999**, *37*, 1285–1297.
- [29] a) H. Yang, S. H. Yoon, Y. Korai, I. Mochida, O. Katou, *Carbon* **2003**, *41*, 397–403; b) E. Mora, C. Blanco, R. Santamaria, M. Granda, R. Menendez, *Carbon* **2003**, *41*, 445–452; c) I. Mochida, S. H. Yoon, Y. Korai, *Chem. Rec.* **2002**, *2*, 81–101, and references therein.
- [30] a) T. Sekine, H. Kanda, Y. Bando, M. Yokoyama, K. Hojou, *J. Mater. Sci. Lett.* **1990**, *9*, 1376–1378; b) M. R. Wixom, *J. Am. Ceram. Soc.* **1990**, *73*, 1973–1978; c) H. Montigaud, B. Tanguy, G. Demazeau, S. Courjault, M. Birot, J. Dunogues, *C. R. Seances Acad. Sci. Ser. 2* **1997**, *325*, 229–234; d) M. Todd, J. Kouvetakis, T. L. Groy, D. Chandrasekar, D. J. Smith, P. W. Deal, *Chem. Mater.* **1995**, *7*, 1422–1426; e) B. L. Ivanov, L. M. Zambov, G. T. Georgiev, C. Popov, M. F. Plass, W. Kulisch, *Chem. Vap. Deposition* **1999**, *5*, 265–273.
- [31] a) B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, W. Schnick, *J. Am. Chem. Soc.* **2003**, *125*, 10288–10300; b) W. Zheng, N.-B. Wong, W. Wang, G. Zhou, A. Tian, *J. Phys. Chem. A* **2004**, *108*, 97–106; c) T. Komatsu, *J. Mater. Chem.* **2001**, *11*, 802–805; d) E. Kroke, M. Schwarz, *Coord. Chem. Rev.* **2004**, *248*, 493–532; e) E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll, A. D. Norman, *New J. Chem.* **2002**, *26*, 508–512.
- [32] a) D. R. Miller, D. C. Swenson, E. G. Gillan, *J. Am. Chem. Soc.* **2004**, *126*, 5372–5373; b) M. H. V. Huynh, M. A. Hiskey, R. Gilardi, E. L. Hartline, D. P. Montoya, *Angew. Chem./Angew. Chem. Int. Ed.* **2004**, accepted.