

Cascade Cyclization To Produce a Series of Fused, Aromatic Molecules

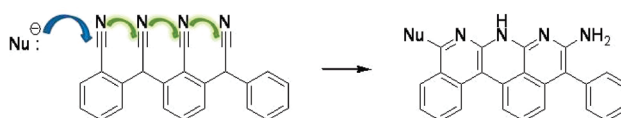
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ABSTRACT



An efficient synthesis of fully aromatic, fused-ring, monoaza-acenes through a nucleophile initiated cascading cyclization is illustrated. Photophysical properties of the resulting molecules are reported.

Fused, aromatic molecules are among the most attractive candidates for materials in organic thin layer devices. They typically form close contacts in the solid state as a result of their generally planar geometries. This behavior maximizes the electronic coupling between adjacent units. There are, however, few methods for the synthesis of fused, aromatic molecules that can be generalized to prepare molecules of various lengths. Since an increase in length generally makes these molecules easier to both oxidize and reduce, new methods for the synthesis of long fused aromatic molecules are desirable.

Nitrogen-containing oligomers have several potential applications. Unfused oligo-pyridines are widely useful as building blocks for biological applications, chelators, and metallo-organic conducting materials.¹ Molecules containing fused diaza-acene units have been prepared and extensively studied as candidates in thin film organic devices.² Fused monoaza-acenes are multipoint, hydrogen bond acceptors.³

Here, we illustrate an efficient synthesis of fused-ring, monoaza-acenes through a nucleophile initiated cascading cyclization of nitrile groups followed by spontaneous CH to NH tautomerization to give fully aromatic, fused heterocycles. The first step of this process is based on nucleophilic attack on the electrophilic cyano carbon. This is the basis for many approaches in heterocycle synthesis,⁴ and is reminiscent of the first step in the pyrolysis of poly(acrylonitrile) to form carbon fibers.⁵

Monoaza-acene oligomers containing 2–5 fused rings were synthesized by adapting a previously reported cyclization to produce amino pyridines.^{1h,6} The precursor, cyano-

(1) (a) Berry, J. F.; Cotton, F. A.; Lei, P.; Lu, T. B.; Murillo, C. A. *Inorg. Chem.* **2003**, *42* (11), 3534–3539. (b) Gaillard, S.; Elmekdem, M. K.; Fischmeister, C.; Thomas, C. M.; Renaud, J. L. *Tetrahedron Lett.* **2008**, *49* (21), 3471–3474. (c) Gong, H. Y.; Zhang, X. H.; Wang, D. X.; Ma, H. W.; Zheng, Q. Y.; Wang, M. X. *Chem.—Eur. J.* **2006**, *12* (36), 9262–9275. (d) Hancock, J. M.; Jenekhe, S. A. *Macromolecules* **2008**, *41* (19), 6864–6867. (e) Hasan, H.; Tan, U. K.; Lin, Y. S.; Lee, C. C.; Lee, G. H.; Lin, T. W.; Peng, S. M. *Inorg. Chim. Acta* **2003**, *351*, 369–378. (f) Vellis, P. D.; Mikroyannidis, J. A.; Lo, C. N.; Hsu, C. S. *J. Polym. Sci., Polym. Chem.* **2008**, *46* (23), 7702–7712. (g) Zhang, E. X.; Wang, D. X.; Zheng, Q. Y.; Wang, M. X. *Org. Lett.* **2008**, *10* (12), 2565–2568. (h) Tandel, S.; Biehl, E. R. *Heterocycles* **2000**, *53* (5), 1183–1191.

(2) (a) Bunz, U. H. F. *Chem.—Eur. J.* **2009**, *15* (28), 6780–6789. (b) Stöckner, F.; Beckert, R.; Gleich, D.; Birkner, E.; Günther, W.; Görls, H.; Vaughan, G. *Eur. J. Org. Chem.* **2007**, (8), 1237–1243. (c) Matschke, M.; Beckert, R.; Würthwein, E. U.; Görls, H. *Synlett* **2008**, (17), 2633–2636. (d) Tang, Q.; Liu, J.; Chan, H. S.; Miao, Q. *Chem.—Eur. J.* **2009**, *15* (16), 3965–3969.

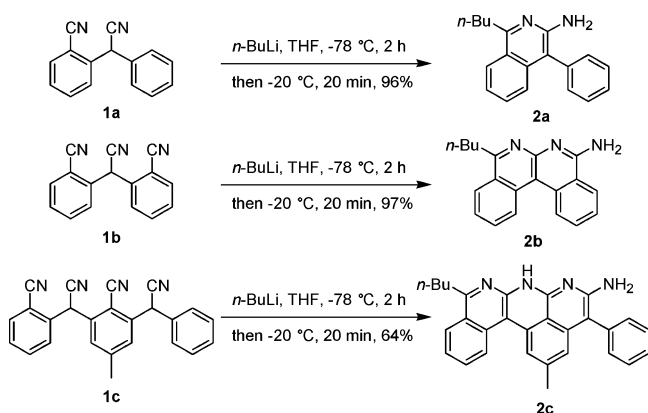
(3) (a) Murray, T. J.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1992**, *114* (10), 4010–4011. (b) Djurdjevic, S.; Leigh, D. A.; McNab, H.; Parsons, S.; Teobaldi, G.; Zerbetto, F. *J. Am. Chem. Soc.* **2007**, *129* (3), 476–477. (c) Blight, B. A.; Camara-Campos, A.; Djurdjevic, S.; Kaller, M.; Leigh, D. A.; McMillan, F. M.; McNab, H.; Slawin, A. M. Z. *J. Am. Chem. Soc.* **2009**, *131* (39), 14116–14122.

(4) Collier, S. J.; Langer, P. *Sci. Synth.* **2004**, *19*, 403–425.

(5) (a) Grassie, N.; Hay, J. N. *J. Polym. Sci.* **1962**, *56*, 189–202. (b) Grassie, N.; McNeill, I. C. *J. Polym. Sci.* **1958**, *27*, 207–218. (c) Coleman, M. M.; Petcavich, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 821–832. (d) Peebles, L. H., Jr.; Peyser, P.; Snow, A. W.; Peters, W. C. *Carbon* **1990**, *28* (5), 707–715. (e) Zhu, Y.; Wilding, M. A.; Mukhopadhyay, S. K. *J. Mater. Sci.* **1996**, *31*, 3831–3837. (f) Surianarayanan, M.; Vijayaraghavan, R.; Raghavan, K. V. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2503–2512.

containing oligomers (**1a–c**) were synthesized (see the Supporting Information) through both nucleophilic aromatic substitution and palladium mediated pathways. The reaction of **1a–c** with *n*-BuLi (Scheme 1) afforded cyclized derivatives **2a–c** in acceptable to excellent yields. In each case the benzylic hydrogens tautomerized to nitrogen to form a completely aromatic heterocycle. To our knowledge, this is the first example of a cascading cyclization reaction to form fused, completely aromatic molecules. Note that only the terminal cyano group is attacked by the nucleophile. Products of the attack at internal cyano groups were not observed. Furthermore, only one regioisomer was observed in each case where the starting oligomer was not symmetric.

Scheme 1



The synthesis of oligonitriles (e.g., molecules with a $-\text{CR}=\text{N}-$ repeating unit) has been accomplished by using several approaches including stepwise construction⁷ and ring-opening methods.⁸ Open-chained examples assume a helical conformation.⁹ Saturated heterocycles have been prepared via nucleophile-initiated attack of one cyano group on another.¹⁰ This latter approach is reminiscent of the first step shown here.

Photophysical behaviors of cyclized oligomers **2a**, **2b**, and **2c** are shown in Figure 1. Molecules **2a** and **2b** have similar absorption spectra indicating that a fused and pendant phenyl group have a similar electronic effect here. This trend has been observed in other types of fused and conjugated systems.¹¹ As expected molecule **2c** shows a characteristic red-shift due to extended conjugation as compared to **2a** and **2b**. All molecules fluoresce with quantum yields (ϕ_F) of 0.63, 0.16, and 0.58 for molecules **2a**, **2b**, and **2c** respectively.

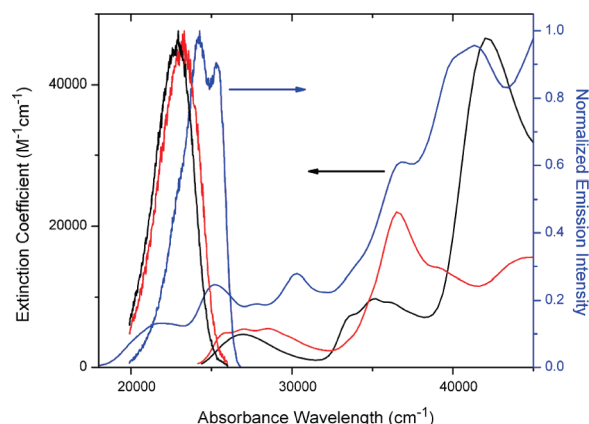


Figure 1. Absorbance and emission spectra of **2a** (black), **2b** (red), and **2c** (blue) taken in CH_3CN solvent.

Note that the pendant phenyl group has a large effect on the quantum yield of these molecules. This behavior is observed when the quantum yields of anthracene and phenyl anthracene are compared.¹² In that case, the pendant phenyl group affects the relative energies of the first excited singlet and triplet states, reducing the rate of intersystem crossing substantially and thus increasing the quantum yield for fluorescence. A similar mechanism may be in operation here.

Packing, intermolecular distance, and self-assembly are extremely important properties in organic conducting materials and can be determined through the crystal structures. Analysis of the crystal structures for molecules **2b** (Figure 2) and **2c** (Figure 3) indicates two structural features in these molecules that influence organization. First, all form multipoint hydrogen bonding interactions via the intermolecular interaction of the nitrogen as the hydrogen bond acceptor and $\text{N}-\text{H}$ as the hydrogen bond donor. This type of organizational motif has been illustrated previously.^{3b,13} Molecule **2b** has two nonbonded $\text{N}-\text{N}$ distances of 3.05 Å and molecule **2c** has an average $\text{N}-\text{N}$ distance of 3.04 Å. These values are comparable to those found for $\text{N}-\text{N}$ distances in nucleic acids.¹⁴

Second, molecule **2b** forms tubular 2D close-packed layers uncharacteristic of most tetracene derivatives.¹⁵ Here, hy-

(12) Nijegorodov, N. I.; Downey, W. S. *J. Phys. Chem.* **1994**, 98 (22), 5639–5643.

(13) (a) Zimmerman, S. C.; Corbin, F. S. In *Molecular Self-Assembly*; Springer-Verlag: Berlin, Germany, 2000; pp 63–94. (b) Brunsfeld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, 101 (12), 4071–4097. (c) Sontjens, S. H. M.; Meijer, J. T.; Kooijman, H.; Spek, A. L.; van Genderen, M. H. P.; Sijbesma, R. P.; Meijer, E. W. *Org. Lett.* **2001**, 3 (24), 3887–3889. (d) Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2003**, (1), 5–16.

(14) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(15) (a) Robertson, J.; Trotter, J.; Sinclair, V. C. *Acta Crystallogr.* **1961**, 14 (7), 697. (b) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, 19 (7), 222–228. (c) Moon, H.; Zeis, R.; Borkent, E. J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. N. *J. Am. Chem. Soc.* **2004**, 126 (47), 15322–15323. (d) Miao, Q.; Lefenfeld, M.; Nguyen, T. Q.; Siegrist, T.; Kloc, C.; Nuckolls, C. *Adv. Mater.* **2005**, 17 (4), 407–412. (e) Chen, Z. H.; Muller, P.; Swager, T. M. *Org. Lett.* **2006**, 8 (2), 273–276. (f) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, 128 (9), 3044–3050.

(6) Rao, U. N.; Biehl, E. R. *Heterocycles* **2002**, 56 (1–2), 443–455.

(7) Heße, N.; Fröhlich, R.; Wibbeling, B.; Würthwein, E. U. *Eur. J. Org. Chem.* **2006**, (17), 3923–3937.

(8) Möllers, C.; Prigge, J.; Wibbeling, B.; Fröhlich, R.; Brockmeyer, A.; Schäfer, H. J.; Schmälzlin, E.; Bräuchle, C.; Meerholz, K.; Würthwein, E. U. *Eur. J. Org. Chem.* **2003**, (7), 1198–1208.

(9) Buhmann, M.; Möller, M. H.; Rodewald, U.; Würthwein, E. U. *Angew. Chem., Int. Ed.* **1994**, 33 (22), 2337–2339.

(10) Marhart, E. A.; Greving, J. B.; Fröhlich, R.; Würthwein, E. U. *Eur. J. Org. Chem.* **2007**, 507, 1–5081.

(11) Zhang, X. N.; Cote, A. P.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, 127 (30), 10502–10503.

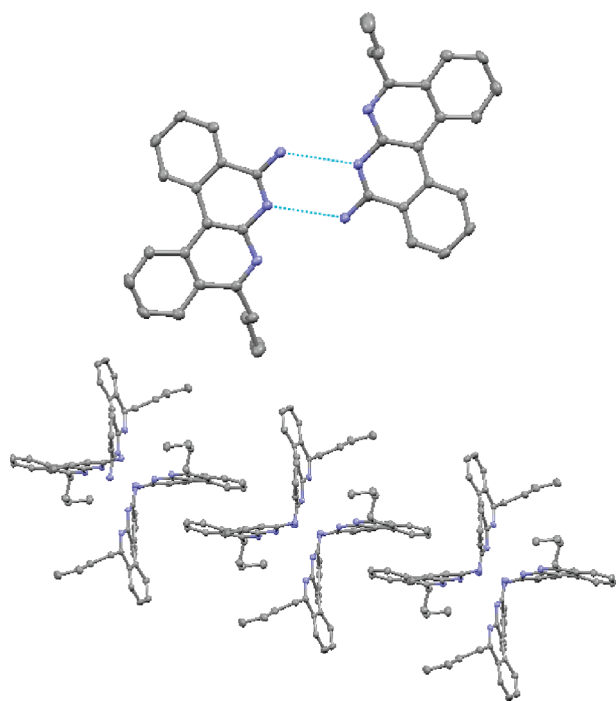


Figure 2. Hydrogen bonding interactions (top) and packing (bottom) of molecule **2b**.

hydrogen bonding appears to dominate over the face-to-face packing found in hydrocarbons. Thus, at most two molecules stack face-to-face with an average 4.0 ± 0.1 Å distance between them. The longer molecule **2c** forms relatively flat, although slipped, 2D close-stacked layers with an average 3.8 ± 0.2 Å distance between molecules in the stacking direction. The slipped, 2D packing motif is typical of substituted pentacenes,^{15d,16} and is the packing motif that offers the highest performance in thin film devices.¹⁷ It is

(16) (a) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4* (1), 15–18. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127* (14), 4986–4987. (c) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7* (15), 3163–3166.

(17) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106* (12), 5028–5048. (b) Sheraw, C. D.; Jackson, T. N.; Eaton, D. L.; Anthony, J. E. *Adv. Mater.* **2003**, *15* (23), 2009–2011.

(18) Chong, Y. S.; Carroll, W. R.; Burns, W. G.; Smith, M. D.; Shimizu, K. D. *Chem.—Eur. J.* **2009**, *15* (36), 9117–9126.

intuitive¹⁸ that longer, fused, aromatic molecules should face-to-face stack more readily. This nicely illustrates the minimum size at which this packing motif is found in this series of molecules.

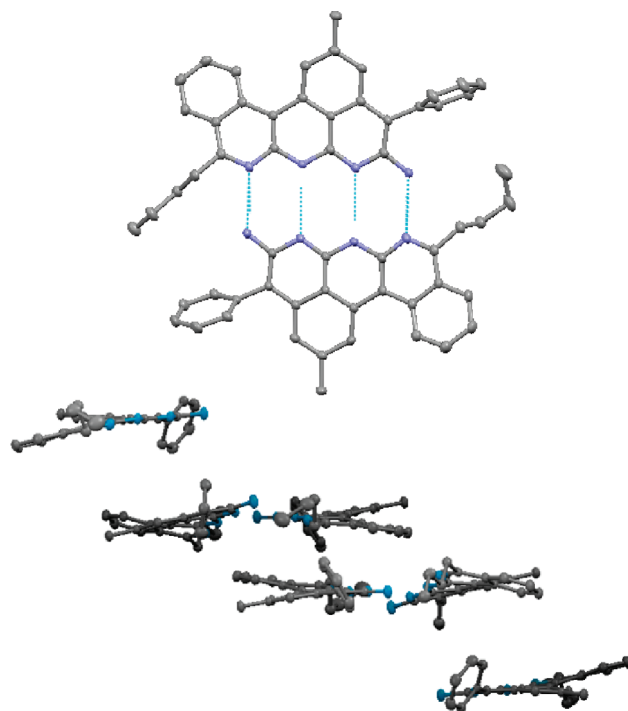


Figure 3. Hydrogen bonding interactions (top) and packing (bottom) of molecule **2c**.

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Supporting Information Available: Experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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