Tetrahedron Letters 55 (2014) 4346–4349

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A concise method to prepare linear 2,3-diazaoligoacene derivatives

Junbo Li [a], Junkuo Gao [b], Wei-Wei Xiong [a], Qichun Zhang [a,*]

[a] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*
[b] *College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, China*

ARTICLE INFO

Article history:
Received 22 April 2014
Revised 21 May 2014
Accepted 5 June 2014
Available online 12 June 2014

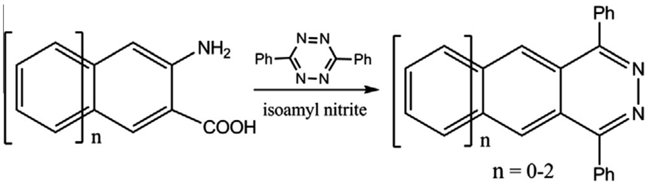
Keywords:
Azaacene
Diene
Dienophile
Cycloaddition reaction
Crystal packing

ABSTRACT

In this Letter, we demonstrate that linear 2,3-diazanaphthalene (**1**), 2,3-diazaanthracene (**2**), and 2,3-diazatetracene (**3**) can be easily prepared through [4+2] cycloaddition reaction between 3,6-diphenyl-1,2,4,5-tetrazine as the diene and arynes as dienophiles, generated in situ from *ortho*-aminoarylcarboxylic acids. The physical properties and crystal packing of the prepared compounds **1**–**3** were fully investigated. In addition, the experimental data (e.g., band gap and band position) are further confirmed by theoretical studies.

As analogs of oligoacenes,[1] oligoazaacenes have attracted significant attention, not only because of their synthetic challenges,[2] but also because of their potential application in field effect transistors,[3] phototransistors,[4] solar cells,[5] memory devices,[6] and sensing probes.[7] Although oligoazaacenes can be synthesized through S_N2 reaction between diamines and dihydroxy (or dihalo) compounds followed by oxidation, or by condensation between a diamine (or tetraamine) and a diketone (or tetraketone), these methods have posed a limitation toward the synthesis of larger azaacenes ($n > 6$)[8] because all these methods involve the formation of water as a by-product, which could modify the targeted azaacenes by changing the hybridization of the N atoms from sp^2 to sp^3. Thus, a new method to address this problem to approach large azaacenes is highly desirable.

Given our successful findings that oligoacenes can be prepared through [4+2] reactions using arynes as dienophiles,[9] we believe that this type of reaction could be a promising method to construct larger azaacenes.[7a] Herein, we demonstrate that three 2,3-diazaacenes [2,3-diazanaphthalene ($n = 0$), 2,3-diazaanthracene ($n = 1$), and 2,3-diazatetracene ($n = 2$)] can be easily prepared through [4+2] reactions between 3,6-diphenyl-1,2,4,5-tetrazine as the diene and in situ generated arynes as dienophiles (from precursor *ortho*-aminoarylcarboxylic acids) (Scheme 1). These compounds have been reported in the literature through other methods.[10] It is worth noting that all physical data [e.g., cyclic voltammetry (CV), crystal structures, and theoretical studies, except UV–vis absorption] are reported here for the first time.



Scheme 1. The synthetic method toward 2,3-diazaacenes.

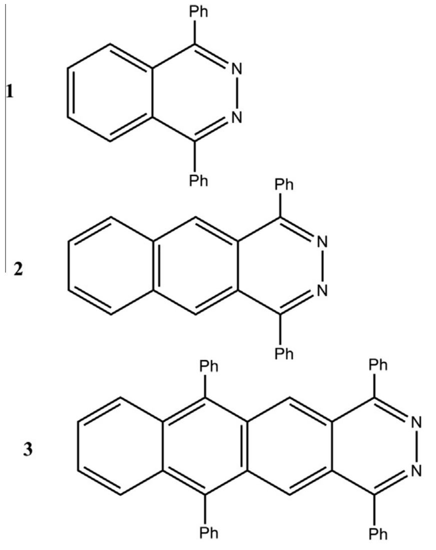
1,4-Diphenyl-2,3-diazanaphthalene (**1**), 1,4-diphenyl-2,3-diazaanthracene (**2**), and 1,4,6,11-tetraphenyl-2,3-diazatetracene (**3**) (Scheme 2) have been synthesized through [4+2] reactions between 3,6-diphenyl-1,2,4,5-tetrazine and the corresponding aryne precursors [2-aminobenzoic acid (for **1**, yield 58%), 3-amino-2-naphthoic acid (for **2**, yield 63%), and 3-amino-9,10-diphenylanthracene-2-carboxylic acid[11] (for **3**, yield 40%)]. The compounds prepared were fully characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry (HRMS). Moreover, the structures of compounds **1**–**3** were further confirmed by single crystal structure analysis (CCDC numbers for **1**–**3** are 998769, 998770 and 993356, respectively).

The crystal structures and the crystal packing arrangements of compounds **1**–**3** are shown in Figure 1. Compound **1** possesses an orthorhombic space group, $Cmc2_1$ (36), and its unit cell data are as follows: $a = 20.1791(10)$ Å, $b = 10.7017(6)$ Å, $c = 8.2409(3)$ Å, $\alpha = \beta = \gamma = 90(0)°$. The molecules of compound **1** are stacked with an offset head-to-head mode due to the spatial hindrance of the phenyl

---

[*] Corresponding author. Tel.: +65 67904705; fax: +65 67909081.
E-mail address: qczhang@ntu.edu.sg (Q. Zhang).

http://dx.doi.org/10.1016/j.tetlet.2014.06.033
0040-4039/



Scheme 2. Molecular structures of compounds **1–3**.

groups. There are weak π–π stacking interactions (∼3.75 Å)between the pyridazine unit and benzene groups. Compound **2** has a monoclinic space group, C12/c1 (15), and its unit cell data are: $a = 20.4657(5)$ Å, $b = 10.6386(3)$ Å, $c = 7.6951(2)$ Å, $\beta = 96.16(0)^\circ$. Being different from compound **1**, compound **2** shows an offset head-to-tail stacking and the distance between the two naphthalene units is nearly 3.86 Å, indicating a very weak π–π stacking interactions between the molecules. Compound **3** possesses a triclinic space group, p1 (2), with unit cell data of $a = 10.0261(4)$ Å, $b = 13.2546(4)$ Å,

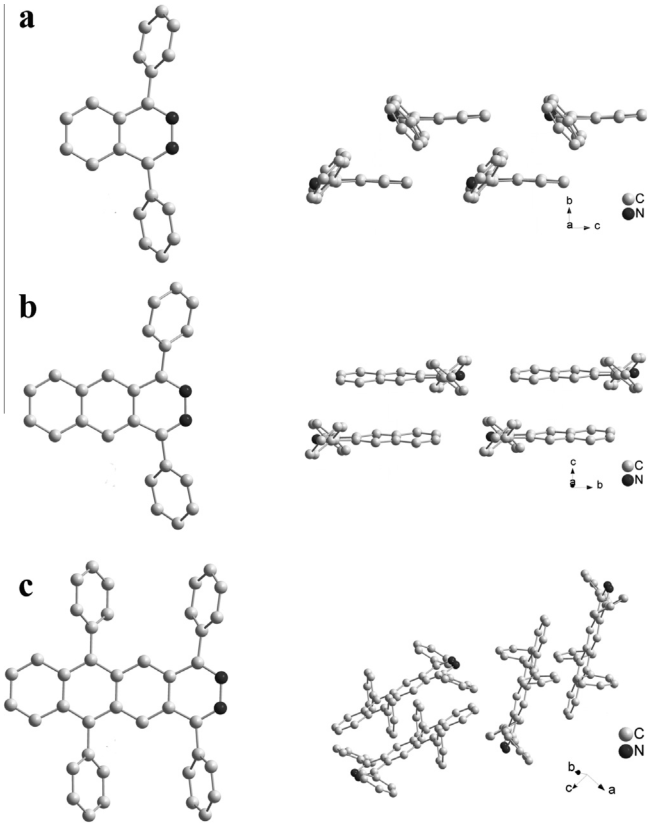


Figure 1. Crystal structures of compounds **1–3** (hydrogen atoms are omitted) and Crystal packing arrangements.

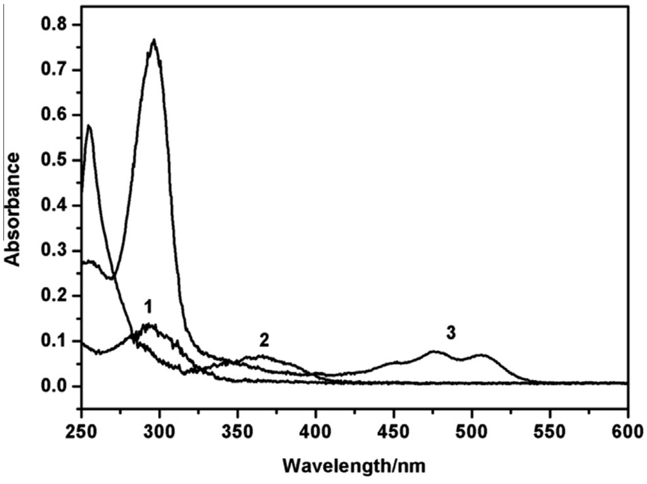


Figure 2. UV–vis spectra of compounds **1–3** (1×10^{-5} M) in CH_2Cl_2.

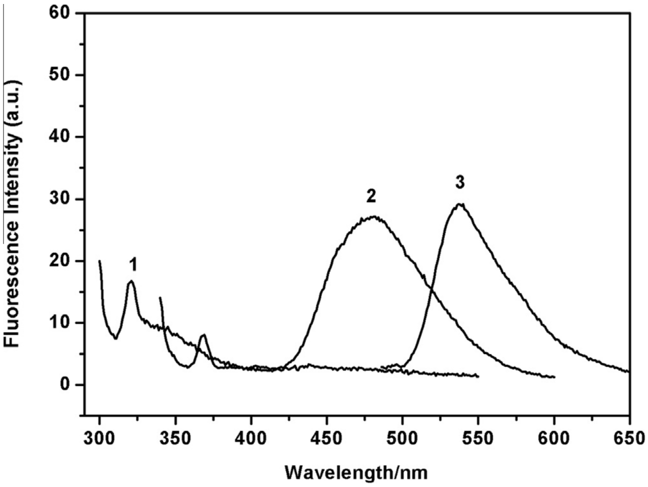


Figure 3. Fluorescence spectra of compounds **1–3** (1×10^{-5} M) in CH_2Cl_2.

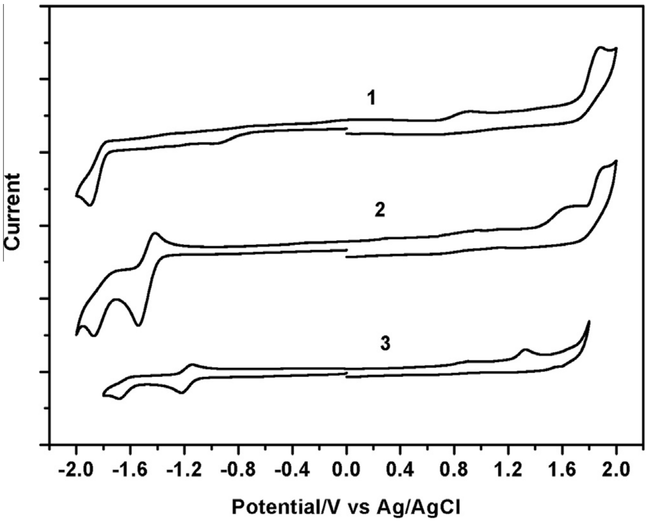


Figure 4. Cyclic voltammetry curves of compounds **1–3** in CH_2Cl_2 solution containing 0.1 M TBAP electrolyte. Scanning rate: 100 mV/s.