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Oligoacenes

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Intermolecular Oxidative Annulation of 2-Aminoanthracenes to Diazaacenes and Aza[7]helicenes**

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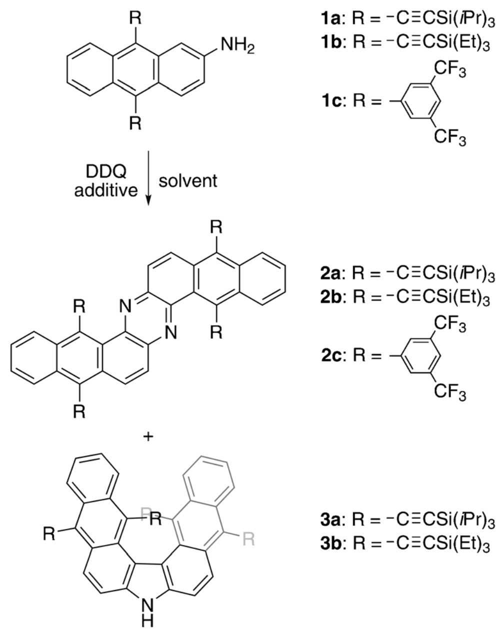
Aniline is oxidized into so-called "aniline black", well-known black pigments that are a mixture of oligomeric materials containing C=N double bonds and fused structures. Since such an oxidative fusion reaction of aniline derivatives is usually uncontrollable and provides many isomers and oligomers, it has rarely been recognized as a synthetically useful transformation.[1–3] However, the selective oxidation of aromatic amines should provide a powerful protocol to combine two aromatic units into one extended π system if the substrates and reaction conditions are carefully designed.

Recently, oligoacenes containing pyrazine units have attracted much attention as promising compounds for electron-transporting materials because of their resistance to oxidation relative to the parent oligoacenes.[4] However, the synthetic strategy for this type of azaacenes has mainly been limited to the classic condensation of *ortho*-quinone derivatives with aromatic *ortho*-diamines,[5,6] both of which are often unstable under air. Here we disclose the selective oxidative fusion of 2-aminoanthracenes mediated by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to provide pyrazine-fused bisanthracenes in high yields. Our approach, which makes use of the more-stable monoamino substrates, would be useful for the construction of various pyrazine-fused oligoacenes. Furthermore, we also found that pyrrole-fused bisanthracenes could be formed under slightly modified conditions. The pyrrole-fused dimer can be regarded as an aza[7]helicene with a stable helical conformation that exhibits circular dichroism (CD) and circularly polarized luminescence (CPL) properties.

We used 2-aminoanthracene **1a**, the two triisopropylsilylethynyl groups of which enhance the solubility of the starting material and products. We found that the oxidation of **1a** with DDQ in $CHCl_3$ (Scheme 1) afforded a pyrazine-fused dimer **2a** in 43 % yield as a single regioisomer (Table 1, entry 1). The ^{1}H NMR spectrum of **2a** was indicative of a C_{2h} symmetrical structure, thus indicating a zig-zag-type structure fused by a pyrazine linkage. Furthermore, another product **3a** was obtained as a more polar material in 48 % yield. The ^{1}H NMR spectrum showed **3a** was unsymmetrical, with one NH proton signal detected at $\delta = 9.12$ ppm. The parent mass ion peaks of **3a** at $m/z = 1087.6716$ (calcd for $(C_{72}H_{97}NSi_4)^+ = 1087.6693$) suggested a loss of one nitrogen atom from **2a**. On the basis of these data, we assigned **3a** as a pyrrole-fused dimer. Finally,



Scheme 1. Oxidation of 2-aminoanthracenes.

Table 1: Oxidation of 2-aminoanthracenes.[a]

Entry	Substrate	Additive (v/v)	t [h]	Solvent	Yield 2	Yield 3
1	**1a**	EtOH (0.5 %)[b]	1	$CHCl_3$	43	48
2	**1a**	2-methyl-2-butene (0.5 %)[b]	2.5	$CHCl_3$	70	9
3	**1a**	–	2	CH_2Cl_2	29	17
4	**1a**	TFA (0.5 %)	2.5	CH_2Cl_2	87	0
5	**1a**	EtOH (0.5 %)	2.5	CH_2Cl_2	29	58
6	**1a**	EtOH (5 %)	2.5	CH_2Cl_2	9	68
7	**1b**	TFA (0.5 %)	2.5	CH_2Cl_2	52	0
8	**1b**	EtOH (5 %)	2.5	CH_2Cl_2	4	59
9	**1c**	TFA (0.5 %)	2.5	CH_2Cl_2	57	0

[a] Reaction conditions: **1** (20.0 μmol), DDQ (2 equiv), solvent (3 mM), RT. [b] Stabilizer in commercially available $CHCl_3$.

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the structures of **2a** and **3a** were elucidated unambiguously by X-ray diffraction analysis (Figure 1).[7,8] As expected, **2a** has a highly planar geometry, with a mean plane deviation of 0.141 Å. On the other hand, **3a** can be regarded as an aza[7]helicene because of its helical conformation. The ethynyl groups are distorted as a result of steric repulsion between the anthracene core and the bulky silyl groups. The two naphthalene subunits (AB and CD in Figure 1c) are twisted by 46.5°. The synthesis of helicenes by intermolecular homocoupling reaction in a single step is rare.[9–11]

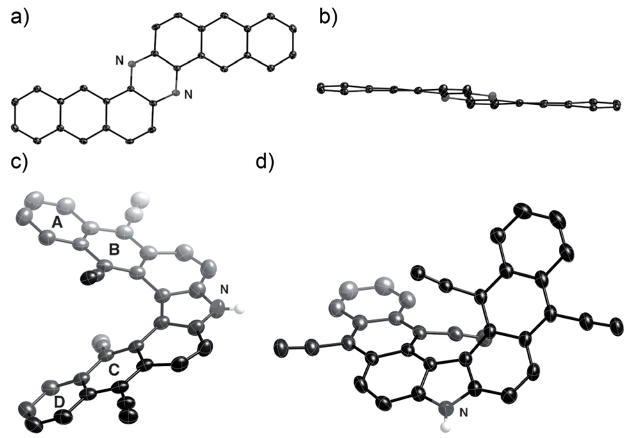
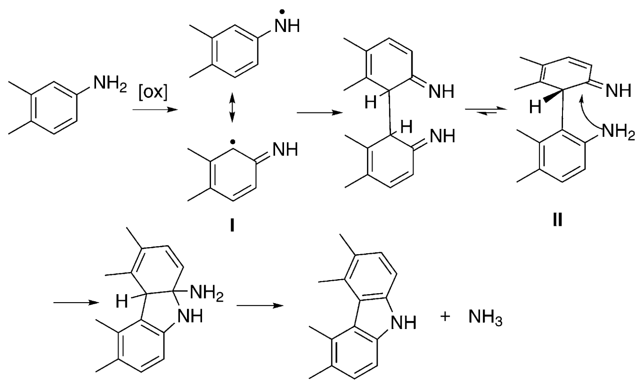


Figure 1. X-ray crystal structures of **2a** and **3a**. a) Top view and b) side view of **2a**, and c) top view and d) side view of **3a**. The thermal ellipsoids are scaled at the 50% probability level. The hydrogen atoms, alkynyl groups in (a) and (b), and silyl groups in (c) and (d) are omitted for clarity.

Interestingly, the reaction was significantly dependent on the solvent. In other solvents, such as dichloromethane, THF, and DMF, the yields were substantially lower, and the products were not formed in toluene. We found that the reaction in $CHCl_3$ with 0.5% 2-methyl-2-butene as a stabilizer predominantly produced **2a** (Table 1, entry 2). The chloroform used in entry 1 contained 0.5% ethanol instead of 2-methyl-2-butene, while a trace of hydrogen chloride may also be present in chloroform. We anticipated that the product distribution could be influenced by the presence of acid or ethanol as an additive. To eliminate other factors we chose distilled dichloromethane as a standard solvent. Eventually, the addition of 0.5% (v/v) trifluoroacetic acid (TFA, conditions A) resulted in the exclusive formation of **2a** in 87% yield. On the other hand, the reaction in dichloromethane with 5% ethanol (conditions B) predominantly afforded **3a** in 68% yield along with **2a** in 9% yield. The selective formation of **3a** over **2a** is rather remarkable, since **3a** is clearly thermodynamically unfavorable compared to **2a**. In both cases, the total yields of the reaction were considerably increased in the presence of additives, thus indicating that the additives not only accelerate the reaction but also control the product distribution.

We next examined the scope of the substrates. The oxidation of bis(triethylsilylethynyl)anthracene **1b** under conditions A afforded pyrazine-fused dimer **2b** in 52% yield (Table 1, entry 7). On the other hand, conditions B produced **2b** and **3b** in 4% and 59% yields, respectively (entry 8).[12] Oxidation of bis(3,5-ditrifluoromethylphenyl)-anthracene **4c** under conditions A provided pyrazine-fused dimer **2c** in 57% yield (entry 9). In the case of **1c**, no pyrrole-fused dimer **3c** was obtained, even under conditions B, probably because of the steric hindrance of the aryl groups. These results suggest the versatility of the pyrazine-fusion reaction for various aminoanthracenes, while silylethynyl groups appear to be optimal to form aza[7]helicenes **3**.

We propose a possible mechanism for the formation of azahelicene **3a** in Scheme 2. The reaction begins with oxidation of the aminoanthracene **1** with DDQ to produce the plausible aminyl radical intermediate **I**.[13] Two radical intermediates **I** then couple to form a C–C single bond. Tautomerization at one side regenerates a benzene ring and one NH_2 group, which then undergoes nucleophilic addition to the imine moiety on the other side to form a five-membered ring. Finally, elimination of ammonia produces the pyrrole ring. The key intermediate **II** may allow the formation of the distorted structure of **3a**.[14] Elimination of gaseous ammonia and aromatic stabilization as a result of the formation of a benzene ring could be the driving force of the reaction.



Scheme 2. Possible mechanism for the formation of **3a**.

Figure 2 shows the UV/Vis absorption and emission spectra of **2a** and **3a** in dichloromethane. The lowest energy bands of both **2a** and **3a** exhibit bathochromic shifts compared to those of 9,10-bis(triisopropylsilylethynyl)anthracene (**4**), thus indicating effective π conjugation between the two anthracene moieties. The fluorescence of **2a** and **3a** also had moderate quantum yields ($\Phi_f = 0.45$ for **2a** and $\Phi_f = 0.36$ for **3a**). The Stokes shift of **3a** ($\Delta\nu = 2220\ cm^{-1}$) was larger than that of **2a** ($\Delta\nu = 473\ cm^{-1}$), which reflects the distorted conformation of **3a**.

To investigate the properties of **3a** as a helicene, we next carried out its optical resolution, which could be perfectly separated on a HPLC column with a chiral stationary phase to afford (*P*)-(+)-**3a** and (*M*)-(−)-**3a** (see Figure S23 in the Supporting Information). The helical chirality of these enantiomers was stable and no racemization was observed by HPLC analysis on a chiral stationary phase after three months. Figure 2c shows the circular dichromism (CD) spectra of **3a** in dichloromethane. The spectra of (*P*)-**3a** and

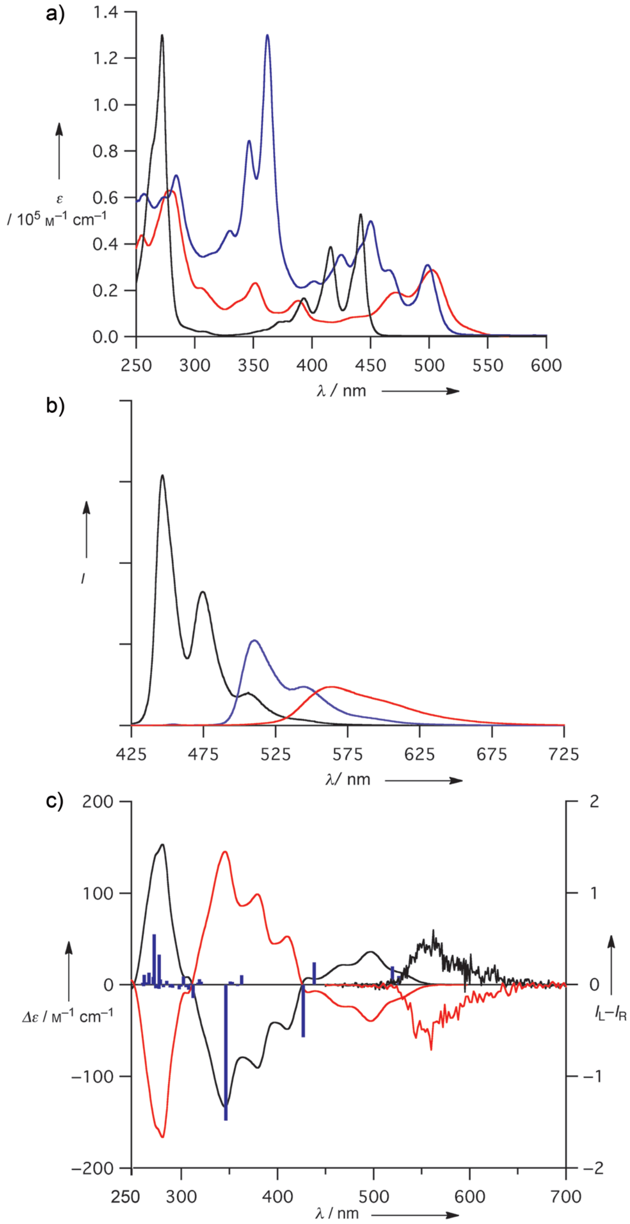


Figure 2. a) UV/Vis absorption and b) emission spectra of **2a** (blue), **3a** (red), and **4** (black) in CH_2Cl_2 with excitation at 400 nm. c) CD and CPL spectra of (*P*)-**3a** (black) and (*M*)-**3a** (red) in CH_2Cl_2. The blue lines show the CD spectrum for (*P*)-**3a** calculated by the TD-DFT method at the B3LYP/6-31G(d) level.

(*M*)-**3a** appear as mirror images. Furthermore, **3a** exhibits circular polarized luminescence (CPL) activity.[10a,15–17] The CPL anisotropy factor g_{lum} was measured to be 3×10^{-3} for both enantiomers, which is comparable to the values observed for other helicenes.

The electrochemical properties of **2a** and **3a** were determined by cyclic voltammetry (see Figure S21 in the Supporting Information). One reversible oxidation wave was observed at 0.899 V for **2a** and two reversible oxidation potentials were observed at 0.866 and 0.244 V for **3a**. The first oxidation potential of **2a** is larger than that of **4** (0.833 V), thus indicating that dimer **2a** has more tolerance to oxidation than **4**. This result is promising for the construction of air-stable larger acene derivatives.[18]

In conclusion, we have developed a facile synthetic protocol for pyrazine-fused and pyrrole-fused bisanthracenes by simple oxidation of 2-aminoanthracene derivatives. The product distribution can be effectively controlled by additives. As a result of the stable helical conformation, the pyrrole-fused dimer can be regarded as a helicene, and it exhibits CD and CPL properties. This fusion reaction is promising for the construction of oligomeric anthracenes and other functional π-conjugated molecules, which should be useful for application to optical and electronic devices. Further investigation is currently underway to expand the scope and elucidate the mechanism of this reaction.

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[8] Crystallographic data for **3a**: $C_{72}H_{97}NSi_4$, $M_r = 1088.89$, monoclinic, $a = 17.993(5)$, $b = 15.172(5)$, $c = 26.474(4)$ Å, $\beta = 111.952(13)°$, $Z = 4$, $R = 0.0596$ $(I > 2.0\sigma(I))$, $R_w = 0.1749$ (all

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[13] The plausible amynyl radical intermediate **I** can also explain the regiochemical outcome. The DFT calculations indicate no molecular orbital coefficient of the SOMO of **I** at the 3-position (see Figure S22 in the Supporting Information).

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Communications

Oligoacenes

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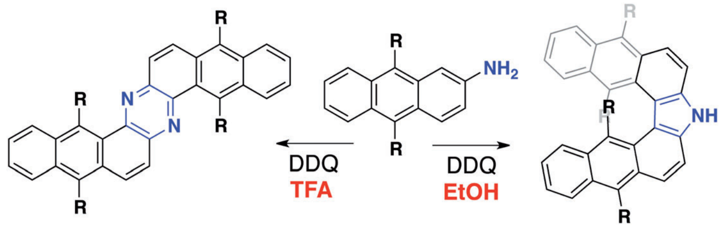
Intermolecular Oxidative Annulation of 2-Aminoanthracenes to Diazaacenes and Aza[7]helicenes



Which way to go: The product distribution in the efficient oxidation of 2-aminoanthracene derivatives to pyrazine- and pyrrole-fused bisanthracenes can be controlled by additives (see scheme; TFA = trifluoroacetic acid, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone). The pyrrole-fused dimer can be regarded as an aza[7]helicene with a stable helical conformation.

