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Oxidative skeletal rearrangement of 1,1′-binaphthalene-2,2′-diamines (BINAMs) *via* C–C bond cleavage and nitrogen migration: a versatile synthesis of U-shaped azaacenes†

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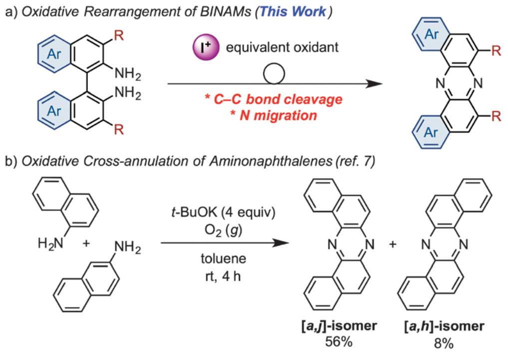
An oxidative skeletal rearrangement of 1,1′-binaphthalene-2,2′-diamines (BINAMs) that involves the cleavage of a strong C–C single bond of the binaphthalene unit and the nitrogen migration has been discovered. The unprecedented rearrangement enables access to a series of U-shaped azaacenes otherwise difficult to prepare in a selective manner by classical methods. Moreover, physicochemical properties of the unique azaacenes have been comprehensively investigated.

Azaacenes, in which parts of C═CH fragments of acenes are formally replaced with isoelectronic imine (C═N) moieties, have been emerging as promising candidates for electron-transporting (n-type) materials in organic electronics.[1] The introduction of electronegative nitrogen atoms into π-conjugated carbon frameworks allows increasing electron affinities (EAs) to lower the barriers for electron injection from metal electrodes.[2] Furthermore, owing to the decrease in the number of C–H···π contacts, azaacenes show a high propensity for adopting densely stacked packing-structures in the solid states, which favor a carrier-transporting process.[3] However, due to limited synthetic accessibility of azaacenes, the exploration of azaacene-based materials has fatally lagged behind those of acenes. Therefore, the development of novel synthetic approaches to azaacenes is fundamentally important from the viewpoints of not only synthetic chemistry but also materials science. Traditionally, syntheses of azaacenes have exclusively relied on condensation/oxidation protocols starting from *ortho*-arylenediamines and *ortho*-quinone derivatives.[4] In this context, recently, a new synthetic protocol toward the preparation of azaacenes consisting of a Pd-catalyzed double amination of activated *ortho*-dichloroarenes with *ortho*-arylenediamines and a successive oxidation leading to *linear* azaacenes in an efficient manner, has been reported.[5] On the other hand, Hiroto and Shinokubo have reported a DDQ-promoted oxidative annulation of aromatic amines to selectively give *kinked* azaacenes and aza[7]helicenes depending on the conditions applied.[6] Herein we present a new strategy to synthesize azaacenes based on the discovery of an unprecedented oxidative skeletal rearrangement of 1,1′-binaphthalene-2,2′-diamines (BINAMs) induced by an iodine-containing oxidant, which exclusively provides a series of dibenzo[*a*,*j*]phenazine-cored U-shaped azaacenes (Scheme 1a). As a relevant work, there is a single report that describes selective preparation of dibenzo[*a*,*j*]phenazine through an oxidative cross-annulation of α- and β-aminonaphthalenes mediated by a strong base (*t*-BuOK) under an O_2 atmosphere (Scheme 1b).[7] However, this known method intrinsically requires two regioisomers of aminonaphthalenes and suffers from the concomitant production of a constitutional [*a*,*h*]-isomer, thereby lacking the versatility as a synthetic approach to U-shaped azaacenes.

During our studies on the development of oxidative transformations of various amines utilizing iodine-containing oxidants,[8] we serendipitously found out that the treatment of BINAM (**1a**) with *tert*-butyl hypoiodite (*t*-BuOI)[9] produced dibenzo[*a*,*j*]phenazine (**2a**)



Scheme 1 Construction of dibenzophenazine-based U-shaped azaacenes.

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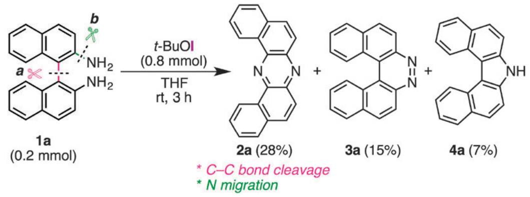
† Electronic supplementary information (ESI) available: Synthetic procedures, spectroscopic data, NMR spectra, and physicochemical properties. CCDC 1004407. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc04911j

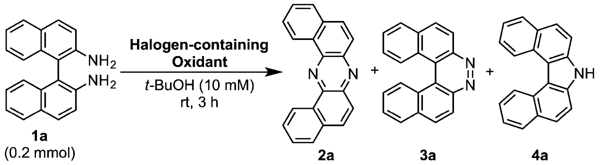
in 28% yield along with the production of reasonably expected compounds **3a**[10] (15%) and **4a**[11] (7%) [eqn (1)].

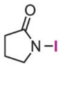


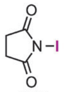
(1)

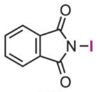
The structure of **2a** was unambiguously confirmed by the X-ray crystallographic analysis of its yellow single crystal (ESI†). Most importantly, the discovered transformation leading to **2a** formally involves the cleavage of the strong C(Ar)–C(Ar) bond [***a*** in eqn (1)] of the binaphthyl unit (*e.g.*, the bond dissociation energy (BDE) of Ph–Ph is as large as 118 kcal mol^{-1})[12] without the aid of transition metal complexes[13] and also involves the migration of a nitrogen atom [***b*** in eqn (1)] to the adjacent carbon. Encouraged by this finding, we envisioned that the utilization of this unique rearrangement reaction would offer a versatile route to U-shaped azaacenes. To establish a novel approach to synthesize U-shaped azaacenes, reaction parameters were scrutinized to identify the conditions to selectively provide **2a** (ESI†). Table 1 summarizes the effect of halogen-containing oxidants. To our delight, the use of *N*-iodolactams as oxidants like NIS, NIPy, and DIH in *t*-BuOH selectively gave **2a** in moderate yields along with trace amounts of **4a** without affording **3a**. The use of 8 mol equivalents of DIH gave **2a** in 77% yield, although the role of excess of DIH is not clear at present. In sharp contrast, when *N*-chloro-containing oxidant (*t*-BuOCl) was used, diaza[5]helicene **3a** was exclusively formed in a high yield (89%). Other types of oxidants like I_2, NBS, DDQ, PhI(OAc)$_2$, and MnO_2 failed to furnish **2a**.

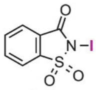
Table 1 Effect of halogen-containing oxidants[a,b]



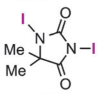


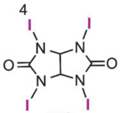




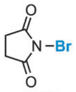


	NIPy	NIS	NIPh	NISac
2a (%)	36	47	0	0
3a (%)	0	0	0	0
4a (%)	trace	4	0	0





I_2



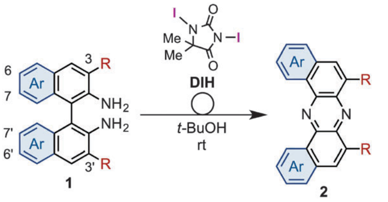
t-BuOCl

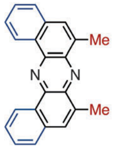
	DIH *	DIH **	TIG ***	I_2	NBS	t-BuOCl
2a (%)	49	77[c]	6	0	0	0
3a (%)	0	0	0	0	0	89
4a (%)	3	0	0	0	0	0

* 0.2 mmol of **DIH** was used.
** 1.6 mmol of **DIH** was used.
*** 0.2 mmol of **TIG** was uded.

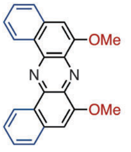
[a] Reaction conditions: **1a** (0.2 mmol) and oxidant (0.8 mmol) in *t*-BuOH (20 mL) at rt for 3 h. [b] Yields were determined by the integration of ^{1}H NMR charts of the crude products. [c] Isolated yield.

Table 2 Scope and limitation of the rearrangement of **1**[a]

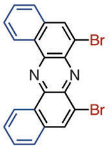




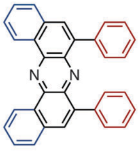
2b, 66% (5 h)



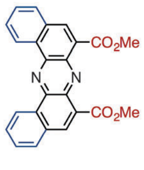
2c: 96% (2.5 h)



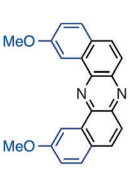
2d: 37% (24 h)



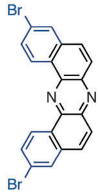
2e: 78% (6 h)



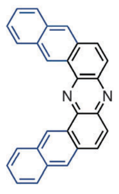
0%



2f, 62% (3 h)



2g, 50% (3 h)

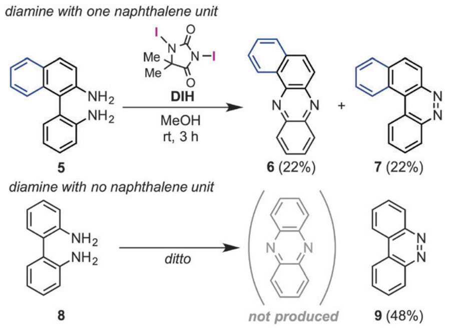


2h, 23% (3 h)[b]

[a] Reaction conditions: **1** (0.2 mmol) and **DIH** (1.6 mmol) in *t*-BuOH (20 mL) at rt for the indicated time. [b] MeOH was used as a solvent.

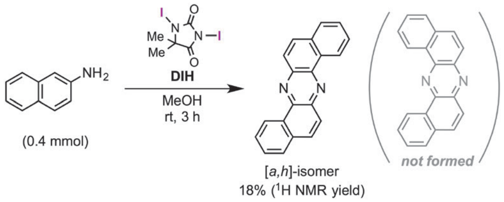
Having identified the optimal conditions for the rearrangement reaction, the scope and limitation of BINAM substrates were surveyed (Table 2). The treatment of BINAMs bearing two electron-donating substituents (Me and MeO) at the 3,3′-position with DIH successfully provided azaacenes **2b** and **2c** in 66% and 96% yields, respectively. The reaction using 3,3′-dibrominated BINAM **1d** gave desired product **2d** in a low yield, probably because of the poor solubility of the diamine in *t*-BuOH. Notably, the rearrangement of 3,3′-diphenyl diamine **1e** also efficiently proceeded to afford **2e** in a high yield, indicating that steric hindrance around the amino moieties does not affect the reaction efficiency. In sharp contrast, diamine bearing two ester groups (CO_2Me) at the 3,3′-position did not undergo the rearrangement at all. This significant lack of reactivity might be ascribed to the low nucleophilicity of amino moieties, inhibiting the formation of N–I bonds (*vide infra*). Diamines bearing the 7,7′- and 6,6′-disubstituent also underwent rearrangement to selectively provide **2f** and **2g** in moderate yields. Notably, the rearrangement of bianthracene diamine **1h** gave highly conjugated heptacyclic azaacene **2h**, which should be quite difficult to synthesize by conventional organic reactions.

Regarding mechanistic aspects, importantly, the existence of at least one naphthalene unit is indispensable for the unique rearrangement (Scheme 2): when biaryldiamines bearing one (**5**) or no (**8**) naphthyl unit were subjected to the reaction conditions, the ratios of rearranged products/benzocinnoline products were found to be positively correlated with the number (*n*) of naphthalene units. These results might indicate the involvement of dearomatization processes in the reaction pathway (*vide infra*), which would be more favorable with naphthalene units than benzene units.[14] On the other hand, a cross-over experiment applying an equimolar mixture of **1a** and **1c** resulted in no production of cross-products at



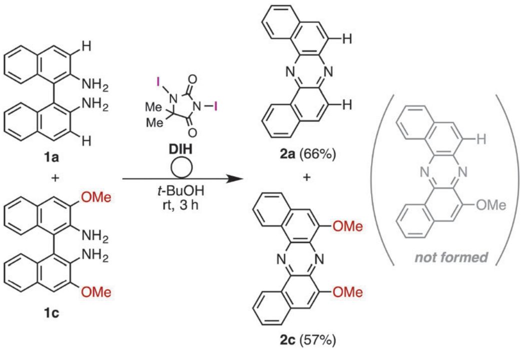
Scheme 2 Influence of a naphthalene unit.

all (Scheme 3), and a control experiment using β-naphthylamine under the optimal conditions led to the production of the [*a*,*h*]-isomer without the formation of **2a** [eqn (2)], suggesting the *intramolecularity* of the rearrangement.



(2)

Although a precise mechanism should await further investigation, in conjunction with the accumulated knowledge of the reactivities of aromatic amines toward electrophilic iodinating oxidants, a tentative reaction pathway is illustrated in Fig. 1. The reaction would start with exchange of N–H hydrogen(s) with iodine, leading to mono or di *N*-iodoamine **A**.[8] The dearomatization process to form azirine **B** could explain the indispensability of the naphthyl unit for the rearrangement.[15] Upon the formation of **B**, the highly strained intermediate would be attacked by an intramolecular amino nucleophile (Ar–NH$_2$), and the developing anion would be trapped by the extra iodinating reagent to form **C**.[16] Nitrene **D** could be generated from **C** driven by the release of its strain energy, and the subsequent insertion of nitrene to the C(Ar)–C(Ar) bond would give phenazine **2a**. Alternatively, the path from **C** to **2a** could be interpreted as a variant of Stieglitz rearrangement.[17] Carbazole **4a** might be produced through a [3,3]-sigmatropic rearrangement of the diimine that would be formed by the protonation of **1a** with generated HI, and followed by the elimination of ammonia.[11]



Scheme 3 Cross-over experiment.

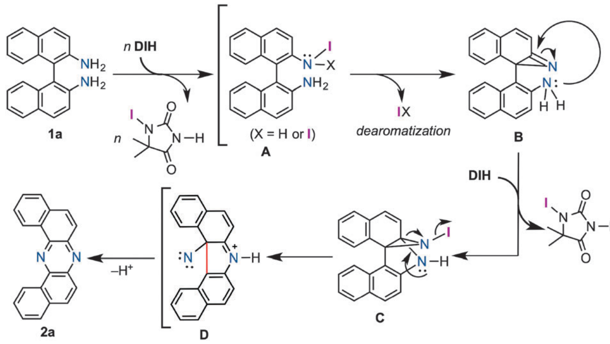
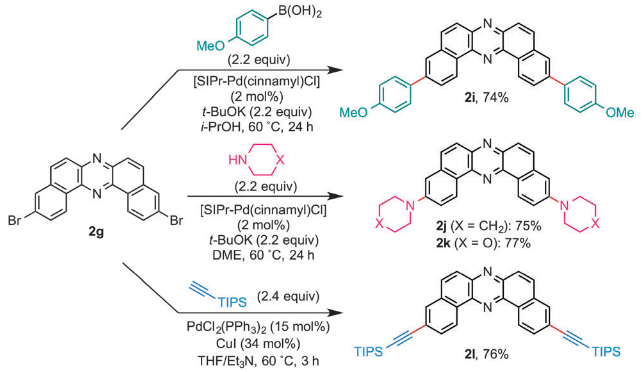


Fig. 1 A tentative pathway of the rearrangement.



Scheme 4 Pd-catalyzed functionalization of **2g**.

In light of bromo functionality of **2d** and **2g**, these compounds should serve as useful building blocks for functionalized azaacenes. Synthetic versatility of **2g** was clearly demonstrated by the preparation of **2i–2l** *via* Pd catalysis (Scheme 4). With slight modifications of the Nolan's original conditions,[18] NHC/Pd-catalyzed cross-coupling of **2g** with an arylboronic acid and cyclic amines gave the corresponding coupled products **2i–2k** in good yields. Furthermore, TIPS-acetylene was efficiently cross-coupled with **2g** to afford conjugation-extended azaacene **2l** in 76% yield.

Basic physicochemical properties of U-shaped azaacenes **2** were investigated. UV/Vis and fluorescence (FL) spectra as well as a cyclic voltammogram for **2a** are shown in Fig. 2 as a representative example (for other compounds, see the ESI†). The mirror-image type UV and FL spectra with fine vibrational structures and a small Stokes shift (9 nm) reflects the rigid structure of **2a** like typical (aza-)acenes (Fig. 2a). Likewise, diluted CH$_2$Cl$_2$ solutions of other azaacenes **2** emit fluorescence ranging from blue (λ_{em} = 425 nm) to yellow (λ_{em} = 561 nm) depending on the substituents on the conjugated core. Especially, the introduction of sterically demanding and strongly electron-donating groups like piperidino and morpholino functionalities (*i.e.*, **2j** and **2k**) resulted in significant Stokes shifts and greatly enhanced quantum yields (**2a:** λ_{em} = 425 nm, Φ_f 0.14; **2j:** λ_{em} = 561 nm, Φ_f 0.47; **2k:** λ_{em} = 543 nm, Φ_f 0.42), probably ascribed to intramolecular charge-transfer (ICT) emission. Notably, most of the azaacenes **2** showed one pair of reversible redox waves at the potentials ranging from −1.76 to −1.98 V against the Fc/Fc$^+$ redox couple, as shown in Fig. 2b, indicating the good

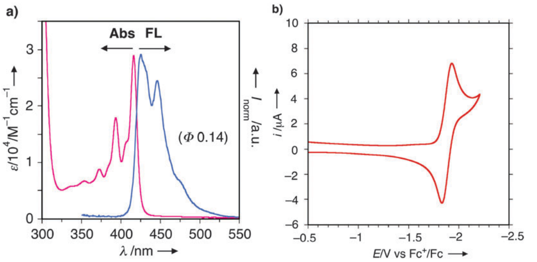


Fig. 2 (a) UV/Vis absorption and FL spectra of CH_2Cl_2 solution of **2a** (10^{-5} M order). (b) Cyclic voltammogram of CH_2Cl_2 solution of **2a** (10^{-4} M order) using $n$$Bu_4NPF_6$ as an electrolyte.

electron-accepting abilities of **2**. These values are compatible with those of n-type organic materials used for organic luminescence diode (OLED) devices like diarylanthrazolines[19] and Alq_3.[20]

In conclusion, we have discovered an unprecedented oxidative skeletal rearrangement of BINAMs and established an approach to constructing novel types of azaacenes that are otherwise difficult to synthesize by conventional methodologies. Investigation into the creation of functional conjugated materials based on these unique azaacenes are ongoing in our laboratory.

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