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A 6π Azaelectrocyclization Strategy towards the 1,5,9-Triazacoronenes

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Abstract. We present the instance of two aromatic double bonds and an imine double bond involved thermal 6π-azaelectrocyclization and, on this basis, a one-step synthesis of triazacoronenes (TACs) from triphenylene-1,5,9-triamines and aldehydes under nonacidic conditions. This method has several advantages such as simplicity, high yields, and extensive substrate scope. A plausible reaction mechanism has been proposed with several experimental supports. A typical derivative shows a unique dimer holding together via a π-π interaction and six H-bonds and a zigzag superstructure stabilized by three centered H-bonds and Br···π interaction between the adjacent dimers.

Keywords: triazacoronenes; electrocyclic reaction; fused-ring systems; schiff bases; nitrogen heterocycles

Heterocyclic nanographenes (HNGs) constitute a unique class of two-dimensional organic materials with important physicochemical properties and have become attractive objects in modern heterocyclic chemistry.[1] 1,5,9-Triazacoronene (TAC, **1** and **2**, Figure 1) is a distinctive aza-version of coronene,[2] in which the hub ring is alternately surrounded by three pyridine rings and three benzene rings. Such a "suprabenzene-like" polyaza nanographene possess highly delocalized but highly electron-poor π-system, endowing it with some attractive properties such as stable electrogenerated chemiluminescences,[3] acid-induced spectroscopic changes,[2g] and multiple electrogenerated chemiluminescence emissions.[2h]

In 2010, we designed and realized the synthesis of nona-substituted TACs (**1**, Figure 1) from triphenylene-1,5,9-triamines and aldehydes through a TfOH-catalyzed threefold Pictet–Spengler cyclization in DMF at 100 °C. [3a] This method was recently proved to be able to conveniently access π-extending TAC derivatives with a minor modification.[3b] Very recently, Tan group synthesized trisubstituted triazacoronenes (**2**, Figure 1) and their parent via a Bischler–Napieralski cyclization of triamide precursors, which were obtained by acylation of triamine (**3**, Table 1) with acyl chlorides or anhydrides, in a molten salt ionic liquid of $AlCl_3$–NaCl at 220 °C or in $POCl_3$–P_2O_5 at 120 °C as a complementary method.[3c]

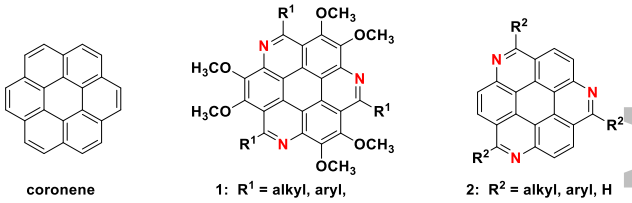

Figure 1. Coronene and its triaza derivatives

As a continuance of our interest in seeking new method to access (hetero)nanographenes, we found that the Pictet–Spengler cyclization for synthesizing TACs from the triphenylene triamine and aldehydes proceed comfortably not only under acidic, but also under neutral or even alkaline conditions. We deduce this type of nonacid-catalyzed heterocycle-forming reaction comprising a 6π-azaelectrocyclization process. A systemic literature survey by SciFinder reveals that no thermal electrocyclic reactions was reported about aza 6π-electron systems where two members of double bonds are both a part of aromatic rings.[4] Herein, we would like to report the first example of thermal electrocyclic reaction of aza 6π-system involving two aromatic C=C bonds and on this basis, a convenient and efficient method for the synthesis of TACs.

Initially, we chose the reaction of the unsubstituted triamine **3** (Table 1) and 4-tert-butylbenzaldehyde under the condition we developed for the synthesis of TACs to test the adaptability of our TfOH-catalyzed threefold Pictet–Spengler cyclization. The result shows that the reaction proceeds smoothly to deliver the desired TAC **2d** in a moderate yield (65 %)

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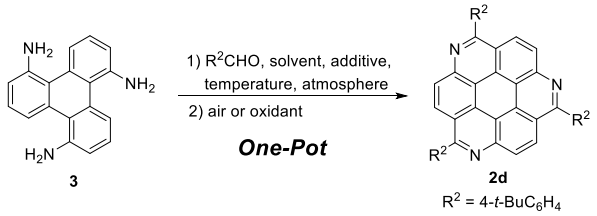
(Table 1, entry 1), suggesting that alkoxys on triamine is not indispensible to access TACs via our TfOH-catalyzed methodolgy.[3a,3c] To optimize the reaction conditions, we conducted the reaction in absence of air because we conjectured the electron-deficient nature of pyridine ring(s) preformed should retard the subsequent ring closure for this Friedel-Crafts-type heterocycle-forming reaction. As expected, the reaction under an argon atmosphere and then bubbling air gave an improved yield (84 %) (entry 2). Switching DMF to DMSO, the reaction gave the product in a comparable yield (entry 3).

Table 1. Optimization of reaction conditions [a]

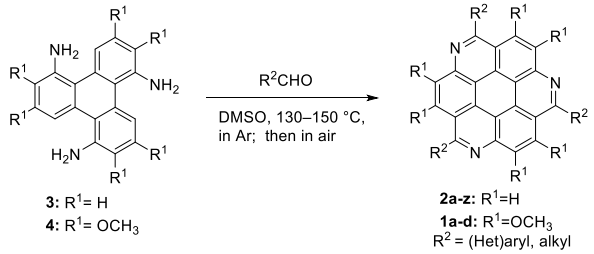


Entry	1-stage	2-stage	
	Solvent/Additive/ Atmosphere/ Temperature (°C)	Oxidant/Temperature (°C) /Time (h)	Yield[b] (%)
1[c]	DMF/TfOH/Air/120	-	65
2[c]	DMF/TfOH/Ar/120	Air/120/2	84
3[c]	DMSO/TfOH/Ar/120	Air/120/2	82
4	DMSO/None/Ar/120	Air/120/2	72
5	**DMSO/None/Ar/150**	**Air/120/2**	**90**
6[d]	DMSO/None/Ar/150	Air/120/2	88
7[e]	DMSO/Lutidine/Ar/150	Air/120/2	70
8[f]	DMSO/DMAN/Ar/150	Air/120/2	66
9[g]	DMSO/None/Ar/150	DDQ/rt/0.2	85
10[h]	DMSO/None/Ar/150	CAN/rt/0.2	83

[a] All the reactions were carried out in Schlenk tubes using 0.18 mmol of triamine **3**, 0.90 mmol of 4-*tert*-butylbenzaldehyde, and 5 mL of the solvent, 120 °C or 150 °C for 24 h in the 1-stage. [b] Isolated yields by column chromatography. [c] TfOH (1 mol %). [d] The reaction was carried out in the dark and the Schlenk tube was shielded light with silver paper. [e] 0.6 equiv of 2,6-lutidine. [f] 0.6 equiv of DMAN (1,8-bis(dimethylamino)-naphthalene). [g] 3.3 equiv of DDQ. [h] 6.0 equiv of CAN.

It was surprising that in the absence of TfOH, the reaction also proceeded to give the desired product with 72 % yield (entry 4). This unexpected result proves that such an acid-free reaction is dissimilar to the traditional Pictet–Spengler cyclization. The yield was further increased to 90 % when elevating the reaction temperature to 150 °C (entry 5). To eliminate the interference from light, we carried out the reaction in the dark and shielded light with silver paper, the reaction gives an almost indistinguishable yield (entry 6), which show that the reaction is not sensitive to light. To eliminate the interference from any acidic substances, we carried out the reaction in the presence of 2,6-lutidine or 1,8-bis(dimethyl-amino)naphthalene (DMAN) (entries 7 and 8), and found the reaction also works with yields of 70 % and 66 %. Therefore, the Pictet–Spengler cyclization is further excluded, because the formation of carbonium-ion crucial to Friedel-Crafts-like reactions cannot occur in an alkaline system. At the oxidation stage, air can be replaced by DDQ or CAN, resulting in a significantly shortened reaction time while comparable yields (entries 9 and 10).

Table 2. Scope of the 6π azaelectrocyclization reactions [a]



Entry	R^1	R^2	Product	Yield[d] (%)
1	H	C_6H_5	**2a**	82[e]
2	H	4-Me-C_6H_4	**2b**	78[e]
3	H	2-Me-C_6H_4	**2c**	94
4	H	4-*t*-Bu-C_6H_4	**2d**	90
5	H	4-CH_3O-C_6H_4	**2e**	88[e]
6	H	2-CH_3O-C_6H_4	**2f**	91
7	H	3,4-$(CH_3O)_2C_6H_3$	**2g**	81
8	H	2-(C_6H_5)-C_6H_4	**2h**	84
9	H	2-F-C_6H_4	**2i**	85
10	H	4-Cl-C_6H_4	**2j**	86[e]
11[b]	H	2-Cl-C_6H_4	**2k**	87
12	H	4-Br-C_6H_4	**2l**	84[e]
13[b]	H	2-Br-C_6H_4	**2m**	82
14	H	3-Br-C_6H_4	**2n**	86
15[b]	H	6-Br-3,4-$(CH_3O)_2C_6H_2$	**2o**	92
16	H	6-F-3,4-$(CH_3O)_2C_6H_2$	**2p**	78
17	H	4-NO_2-C_6H_4	**2q**	90[e]
18[b]	H	4-CN-C_6H_4	**2r**	89[e]
19	H	4-CF_3-C_6H_4	**2s**	81[e]
20	H	4-pyridinyl	**2t**	87[e]
21	H	2-thiophenyl	**2u**	82[e]
22[c]	H	*n*-propyl	**2v**	62
23[c]	H	*n*-hexyl	**2w**	55
24[c]	H	cyclohexyl	**2x**	64
25[c]	H	CO_2Et	**2y**	42
26[c]	H	CF_3	**2z**	25
27	OMe	4-*t*-Bu-C_6H_4	**1a**	67
28	OMe	4-Br-C_6H_4	**1b**	62
29[b]	OMe	4-CN-C_6H_4	**1c**	80
30	OMe	4-NO_2-C_6H_4	**1d**	76

[a] Reaction conditions: triamine **3** or **4** (0.18 mmol or 0.11 mmol, 1 equiv), aldehyde (0.90 mmol or 0.55 mmol, 5 equiv), in DMSO (5 mL) was stirred at 150 °C for 24 h under argon atmosphere, then bubbling air. [b] The reaction was carried out at 130 °C. [c] The reaction was carried out at 80 °C for 12 h, then at 150 °C for 12 h. [d] Isolated yields by column chromatography, unless otherwise noted. [e] Yields by filtration and washing with water and acetone, products are pure enough for NMR analysis.

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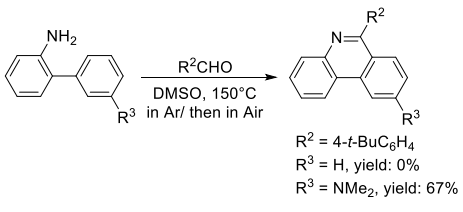
Under the optimized conditions (Table 1, entry 5), the scope of such a non-acid catalyzed reaction was then examined using a variety of (hetero)aromatic and aliphatic aldehydes (Table 2).As shown in Table 2, the reaction was found to be not significantly affected by the substituents on the aromatic aldehydes. The aromatic aldehydes bearing an electron-donating group (**2b-2g**) or electron-withdrawing group (**2i-2n**, **2q-2s**), sterically hindered aldehydes (**2h**) and heteroaromatic aldehydes (**2t-2u**), give the corresponding TACs in good yields. It is noteworthy that aliphatic aldehydes (**2v-2x**) give the desired TACs in satisfying yields, perhaps due to that the side-reactions, i. e., aldol condensation of aliphatic aldehyde and tautomerization of imine intermediate to enamine are weakened under neutral conditions. So, this reaction provides a much better tool for the synthesis of TACs bearing aliphatic arms.[3a,3c] More remarkably, aliphatic aldehydes bearing with strongly electron-withdrawing group, such as ethyl glyoxylate and trifluoroacetaldehyde, furnished the desired product (**2y-2z**) in 42 % and 25 % yields, respectively. A control experiment shows that trifluoroacetaldehyde gave a complex mixture without any detectable product using our TfOH-catalyzed threefold Pictet–Spengler cyclization in DMF at 120 °C. The hexamethoxy triamine **4** works well to deliver the desired products (**1a-1d**) in good yields, indicating the extensive scope of this non-acidic concerted reaction.

Since [1,1'-biphenyl]-2-amine can be regard as the substructure of triamine **3**, it could be envisaged to proceed this aza 6π-electrocyclization with aldehydes such as 4-*tert*-butylbenzaldehyde. However, no desired phenanthridine was detected in the reaction mixture other than the Schiff base. In contrast, the reaction works well when using $N^{3'}$,$N^{3'}$-dimethyl-[1,1'-biphenyl]-2,3'-diamine as the substrate to deliver the wanted substituted phenanthridine in the yield of 67 % (Scheme 1 and Figures S85, S86, S125, SI). It seems that the sluggish azaelectrocyclization of biphenyl 6π-systems involving an imine double bond and two aromatic double bonds were promoted by placing proper substituents. Similar trends are found in the normal 6π-electrocyclization reactions of 1,3,5-(hetero)hexatrienes. [4d, 5]



Scheme 1. The synthesis of 6-(4-(tert-butyl)phenyl)-N,N-dimethylphenanthridin-9-amine

The X-ray study reveals that in crystal of **2o**[6] (Figure 2), two crystallographically distinct molecules form a face-to-face dimer in a cross-embedded manner. In the dimer, two aromatic planes, with mean plane deviations (MPDs) of 0.037Å and 0.042Å from the least-squares plane defined by 18 atoms of core, parallel virtually to each other with a trifling dihedral of 1.17 ° and an average interplanar distance of 3.63 Å. All veratryl rings are twisted from the core plane in the range of 67.24–93.06° while the bromine atoms position out of the dimer. Most interestingly, two aromatic cores are overlapped greatly with a tiny slippage of 0.46 Å; the pyridine rings of one molecule are superimposed oppositely to those of the dimerized partner. These structural features should be attributed to the strong π-π interaction between two aromatic cores and especially, six C–H···N interactions between each nitrogen atom of one molecule and each 2-hydrogen atom of the veratryl groups of another molecule. The length of the six hydrogen bonds ranges from 2.40-2.87 Å (Figure 2, b) and Figure S1, SI).

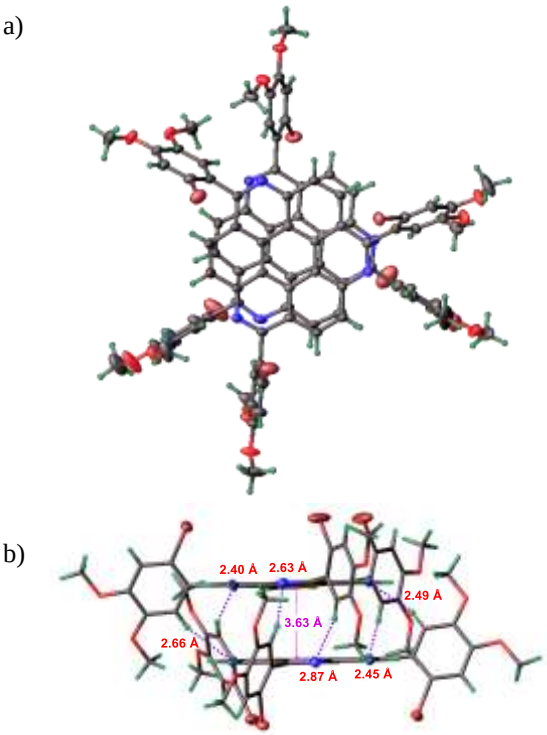


Figure 2. Molecular structure of **2o**: (a) top view and (b) side view

The unit cell comprises two dimers, which link with each other centrosymmetrically via two sets of intermolecular three centered $(C–O)_2\cdots H(C)$ hydrogen bonds between a rim H atom of one molecule and two OCH_3 units of another (bond length 2.53 and 2.80 Å); two adjacent dimers between two neighboring cells associate reciprocally in a similar manner (bond length 2.49 and 2.76 Å) (Figure S2, SI). The dimers pack into zigzag stacking geometry along c-axis and slipped π-stacked columns along a-axis by two intermolecular Br···π interactions between the Br atom and the aromatic plane of an adjacent molecule with the atom-plane distances of 3.19 and 3.55Å (Figure S3-6, SI).

A plausible mechanism is shown in Scheme 2 though an exact mechanism of the reaction requires

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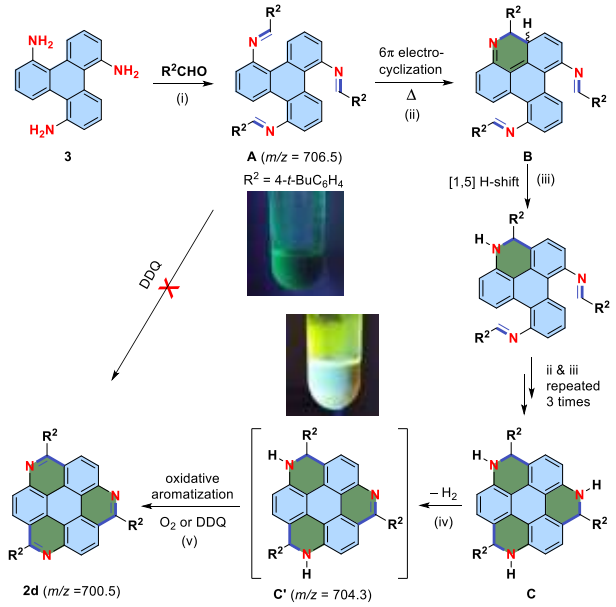
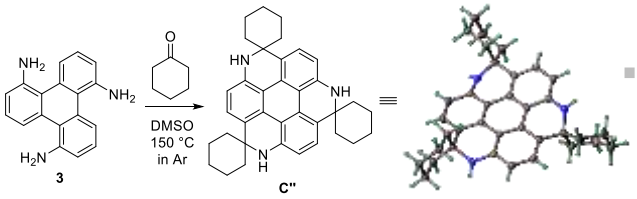
further investigation. Initially, triamine **3** condenses with an aldehyde to produce the tri-Schiff base, i. e., triimine **A**. Then, the triimine undergoes a thermal 6π-azaelectrocyclization with the formation of the intermediate **B**, followed by a rapid [1,5]-H shift to recover the aromaticity of the triphenylene framework,
This process repeated three times to generate the intermediate **C**, which is dehydrogenated to achieve the aromatization of three dihydropyridine moieties, delivering the product **2d** by oxidant or air.



Scheme 2. Proposed pathway of the reaction (R = 4-t-BuC_6H_4). The photographs were taken under the irradiation of 365 nm UV lamp.

To gain insights into this mechanism, we tried to isolate the related intermediates for spectroscopic identification. Unfortunately, attempts to get the intermediate **A** in pure form failed since it is labile during purification. The triimine **A** was observed via MS spectrometry in the reaction mixture of **3** with 4-tert-butylbenzaldehyde in the presence of activated 4A Molecular Sieve in DMSO at room temperature (Scheme S7 and Figure S9, SI). Noticeably, direct oxidation of **A** formed in situ in DMSO by DDQ gave a complex mixture without any detectable product (Scheme S7 and Figure S10, SI). In sharp contrast, after **A** formed in situ in DMSO was simply preheated under an Ar atmosphere, the similar oxidation delivered the wanted product **2d** rapidly (Scheme S8 and Figure S12, SI). It was noteworthy that the fluorescence of **A** showed significantly variation after simple heating treatment, which was observed under the irradiation of 365 nm UV lamp. Moreover, a monodehydrogenated species **C′** was observed via MS in the reaction mixture before oxidation (Scheme S8 and Figure S11, SI). These results suggest that intermediate **C**, derived from triimine **A** via the thermal 6π electrocyclization and the subsequent [1,5]-H shift, should be a key intermediate in such a transformation.

A more solid evidence for this mechanism was obtained from the reaction of triamine **3** with cyclohexanone in which a triannulated product **C″** (Scheme 3), a close analogue of immediate **C**, was achieved in 45 % yield under the argon atmosphere. The structure of **C″** was fully confirmed by spectroscopic characterization and X-ray crystallographic analysis (Figures S7, S87, S88, S126, SI).[6] In this case, the dehydrogenative aromatization after the 6π-electrocyclization and [1,5]-H migration is forbidden as no hydrogen atom exists on the spiro-quaternary centers derived from the carbonyl carbon of cyclohexanone. Thus, we suggest that the key step of this transformation involve a mechanism containing the 6π-azaelectrocyclization.



Scheme 3. The synthesis of triannulated product C″

In summary, we report an efficient synthetic approach for trisubstituted triazacoronenes using a 6π azaelectrocyclization strategy as the heterocycle-forming reaction. This method shows several advantages such as simplicity, high yields, and extensive substrate scope, and thus provides a new tool for the synthesis of heteroatom-doped nanographenes. Compared to Bischler–Napieralski cyclization, this non-acid catalyzed cyclization furnishes directly TACs in a single step from aldehydes and triamine precursors. A plausible reaction mechanism involving a 6π azaelectrocyclization, a [1,5]-H migration and an oxidative aromatization for the formation of TACs has been proposed with some experimental supports. X-ray structural study for a typical derivative shows a dimer holding together via a π-π interaction and unique six H-bonds and a zigzag superstructure stabilized by three centered H-bonds and Br···π interaction between the adjacent dimers.

Experimental Section

General Procedure for 6π-Azaelectro-cyclization Reaction of Triamine with Aldehydes

To a dried 25mL Schlenk tube, were added: triamine **3** or **4** (50.0 mg, 0.18 mmol or 0.11 mmol), aldehyde (5.0 equiv, 0.90 mmol or 0.55 mmol). The content was purged with Argon. DMSO (5mL) was then added, and the reaction mixture was heated at 130-150°C for 24 h. Then bubbling air to the resulting mixture by air pump at 120°C (checked by TLC). After the reaction was complete, cooled to rt. and water (15 mL) was added, extracted with CH_2Cl_2 (2 × 30mL), washed with brine (2 × 30 mL). The organic layer

was dried by anhydrous $MgSO_4$ and concentrated under reduced pressure to give crude product which was purified by silica gel column chromatography. Some compounds were purified by filtration due to its poor solubility, washed with water and acetone (2 × 5 ml), and dried under vacuum to afford pure products.

Acknowledgements

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[6] CCDC-1836906 (**2o**) and 1836907 (**C''**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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COMMUNICATION

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