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3-Cyano-2-azaanthracene-based “push-pull” fluorophores: A one-step preparation from 5-cyano-1,2,4-triazines and 2,3-dehydronaphthalene, generated *in situ*

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ABSTRACT

A facile one-step approach towards 3-cyano-2-azaanthracenes *via* the [4+2] cycloaddition reaction between 5-cyano-1,2,4-triazines and 2,3-dehydronaphthalene, generated *in situ* from commercially available 3-amino-2-naphthoic acid, has been reported. The influence of the 1,2,4-triazine ring substituents nature on the product yield has been studied. The observed experimental results were confirmed by DFT calculations of the HOMO-LUMO energy levels of the both cycloaddends. The photophysical properties of the products have been investigated.

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Compounds, bearing the benzo[g]isoquinoline core (also known as 2-azaanthracenes)[1] are of significant interest due to their immense biological activities, in particular anti-microbial,[2] antitubercular[3] and antitumor.[4] The 2-azaanthracene moiety features in molecules which have been used as cellular stains,[5] pH sensors,[5] environmentally sensitive dyes,[6] metal cation sensors[5] and ligands.[7] Recently, some 2-azaanthracene- and 1,2-diazaanthracene-based fluorescent polymeric materials have been described.[8] Additionally, highly regioselective [4+4]-photodimerization reactions of protonated forms of 1- or 2-azaanthracenes have been reported.[9] To date, synthetic approaches toward 2-azaanthracenes, in particular those aryl-substituted on the pyridine core, are limited by the inaccessibility of the reagents or harsh reaction conditions. Thus, the most commonly used strategies for the synthesis of 2-azaanthracenes are: (i) construction of the central benzene ring by intramolecular cyclocondensation reactions of benzyl or benzoyl substituted pyridines,[10–12] (ii) intermolecular heterocyclization reactions between pyridines and substituted arenes,[13] or (iii) building-up the pyridine ring from substituted naphthalenes[14] or 1,2,3,4-tetrahydronaphthalenes[15] (Fig. 1). Modern synthetic routes to 2-azaanthracenes are based on the tandem reactions between 2-azido-3-arylacrylates and α-diazocarbonyl compounds;[16] Sonogashira cross-coupling reactions;[17,18] Ru(II)-catalyzed cyclization of ketoximes[19] or $AgSbF_6/Cp^*Co(III)$-catalyzed cyclization of O-acyloximes[20] with terminal alkynes; Rh(III)-catalyzed annulation of aminomethyl-substituted naphthalenes[21] or 3-aryl-dihydroisoxazoles with acetylenes;[22] Pd-catalyzed cascade reaction between 1,6-diynes and imidoyl chlorides;[23] Co(III)-catalized [2+2+2] cyclotrimerization between aromatic diynes and nitriles[5a] *etc.* So far, no direct synthetic approaches toward cyano-substituted aza-anthracenes have been reported.

There are few examples of synthetic approach toward 2-azaanthracenes by direct annulation of substituted pyridine rings to the naphthalene ring using Diels-Alder reactions. Representative examples include a naphtha[2,3-*c*]pyran-mediated approach[24] or approach *via* generated *in situ* pyridine-arynes[25] (*iv*, Fig. 1). On the other hand, the “1,2,4-triazine method”, the *aza*-Diels-Alder reaction between 1,2,4-triazines as dienes and various dienophiles, is a well-established tool for the construction of various pyridine

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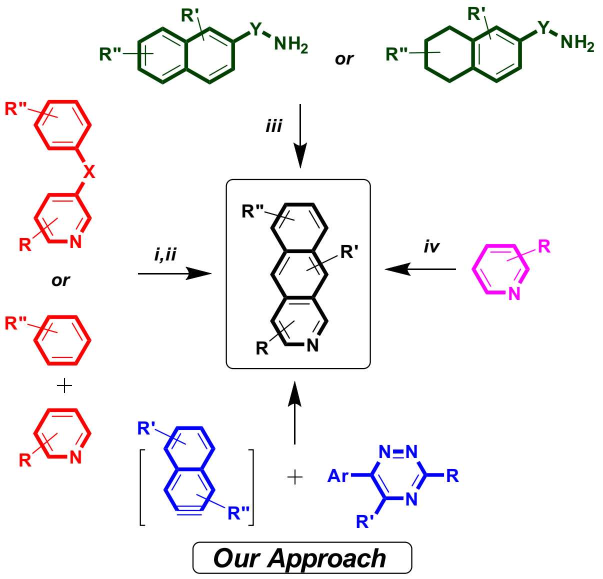
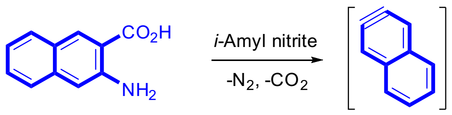


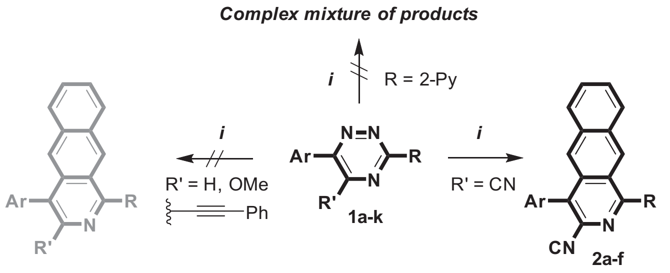
Fig. 1. Selected synthetic approaches toward 2-azaanthracenes.

systems,[26] including benzo-annulated (using *in situ* generated benzyne[27]), or α-cyano-substituted (using 5-cyano-1,2,4-triazines as dienes[26d]). To our surprise, except for the recent synthesis of 3,4-diazaanthracene[28] this methodology has not been used for the one-step preparation of 2-azaanthracenes, especially cyano-substituted derivatives. Herein, we report an aryne-based approach to the synthesis of aryl-substituted 3-cyano-2-azaanthracenes. Due to possessing of "push-pull" fluorophore system, one may expect both the improved photophysical properties and/or environment sensitivity for these compounds.

Commercially available 3-amino-2-naphthoic acid was used for the *in situ* generation of 2,3-dehydronaphthalene (Scheme 1). The starting 1,2,4-triazines **1a**–**k** were prepared as reported previously.[29–33] Next, the reaction between 2,3-dehydronaphthalene and 1,2,4-triazines **1a**–**k** was investigated. It was found that the reaction rate depends strongly on the strength of the electron-withdrawing group in the C5 position of the 1,2,4-triazine ring. Thus, in the case of 1,2,4-triazines **1a**–**e** the presence of a hydrogen atom, electron-donating methoxy-group, phenyl group, or weakly electron withdrawing phenyl-acetylene group in the C5 position of the 1,2,4-triazine ring did not promote the reaction with 2,3-dehydronaphthalene. According to a literature, the introduction of strongly electron-withdrawing cyanogroup into 1,2,4-triazines increases their reactivity in aza-Diels-Alder reactions. For instance, reaction of 5-cyano-1,2,4-triazines with 2,5-nonbornadiene afforded the corresponding aza-Diels-Alder products, *i.e.* pyridines, in shorter reaction times and under smoother reaction conditions (several hours refluxing in toluene),[32] while for other 5-R-1,2,4-triazines the same reaction required harsh conditions (several days refluxing in *o*-xylene).[34] As we expected, the reaction of 5-cyano-1,2,4-triazines **1f**–**k** with 2,3-dehydronaphthalene resulted in the corresponding aza-Diels-Alder products, namely 2-azaanthracenes **2a**–**f**, in up to 60% yields (Scheme 2, Table 1).[35]



Scheme 1. 3-Amino-2-naphthoic acid-based approach for the *in situ* generation of 2,3-dehydronaphthalene.



Scheme 2. Reaction of 1,2,4-triazines **1a**–**h** with 2,3-dehydronaphthalene. *Reagents and conditions*: 3-Amino-2-naphthoic acid (1.5 eq.), *i*-amyl nitrite (1.5 eq.), toluene-1,4-dioxane (8:1), reflux, 1.5 h.

Table 1
Scope and limitations.

	R	R′	Ar	Product	Yield[a] [%]
1a	C_6H_5	H	C_6H_5	–	0
1b	C_6H_5	OCH_3	C_6H_5	–	0
1c	C_6H_5	$-C{\equiv}CC_6H_5$	C_6H_5	–	0
1d	2-Py	C_6H_5	C_6H_5	Traces	–[b]
1e	2-Py	CN	C_6H_5	Traces	–[b]
1f	4-F-C_6H_4	CN	4-$CH_3C_6H_4$	**2a**	55
1g	C_6H_5	CN	C_6H_5	**2b**	51
1h	Me	CN	4-$CH_3C_6H_4$	**2c**	32
1i	*i*-Pr	CN	C_6H_5	**2d**	49
1j	Thienyl-2	CN	C_6H_5	**2e**	60
1k	2-F-C_6H_4	CN	4-F-C_6H_4	**2f**	50

[a] Isolated yield.
[b] A complex mixture of several products was detected.

It was previously reported that 3-(2-pyridyl)-substituted 1,2,4-triazines reacted with arynes to afford the 1,2,4-triazine ring transformation products, *i.e.* 10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles,[36] rather than 1-(2-pyridyl)-3-isoquinolines as classical aza-Diels-Alder products. Upon introduction of the cyano-group to the C5 position of 3-(2-pyridyl)-1,2,4-triazines, the reaction with benzyne mainly led to 1-(2-pyridyl)-3-cyanoisoquinolines.[37] However, in the case of 3-(2-pyridyl)-1,2,4-triazines **1d**–**e** the reaction with 2,3-dehydronaphthalene resulted in a complex mixture of products. In the reaction of 3-(2-pyridyl)-1,2,4-triazine **1d** with 2,3-dehydronaphthalene the reaction mixture was analyzed using GC-MS (Fig. S1, ESI).

The structures of the products **2a**–**f** were confirmed based on ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. Thus, in the ^1H NMR spectra of **2a**–**f**, the resonance signals of two protons in the C5 and C10 positions of the 2-azaanthracene ring were distinguished as one-proton singlets in the region of 8.30–8.83 ppm along with the ABCD-benzene ring system signals, which fully correlated with the previously published spectral data for 2-azaanthracenes.[18] Additionally, the signals of the corresponding substituents in the C3 and C6 positions of the pyridine cycle were observed. In case of compound **2f** the proton signal corresponding to the C10 position of the 2-azaanthracene moiety was observed as a doublet with a coupling constant $J = 3.0$ Hz, possibly due to the interaction with the fluorine atom in the *ortho*-position of the adjacent aromatic substituent. At least one example of such interaction was previously reported.[38]

In Diels–Alder reactions two new bonds are simultaneously formed between the diene and dienophile in a [$\pi4s+\pi2s$] fashion. The reaction kinetics are governed by the energy difference between the HOMO and LUMO; the smaller the energy difference between the Frontier Molecular Orbitals (FMO), the faster the reaction.[39]

The herein reported inverse electron demand aza-Diels–Alder reactions were governed by the $HOMO_{dienophile}$–$LUMO_{diene}$ gap.[40]

Table 2
Frontier Molecular Orbital Energies and HOMO-LUMO Gap for Compounds **1a**,**c**,**e**,**g** in comparison to 2,3-dehydronaphthalene.[a]

	1a	1c	1e	1g	2,3-Dehydro-naphthalene
E_{LUMO}, eV	−2.23	−2.51	−2.93	**−2.97**	−2.12
E_{HOMO}, eV	−6.59	−6.55	−7.00	**−6.99**	−6.49
ΔE, eV ($E_{HOMOdienophile}-E_{LUMOdiene}$)	4.26	3.98	3.56	**3.52**	–

[a] Best energy match is indicated in bold.

In order to analyze the above experimental results theoretical calculations of the HOMO and LUMO energies and the HOMO-LUMO gap for 2,3-dehydronaphthalene (dienophile) and 1,2,4-triazines **1a**–**h** (dienes) were carried out (Table 2).

All calculations were performed using the Gaussian 09[42] suite of programs and employed density functional theoretical method with Austin-Frisch-Petersson functional with dispersion corrections[43] and the balanced polarized triple zeta basis set of Ahlrichs and co-workers.[44] After each geometry optimization, frequency calculations were performed to ensure the local energy minimum structures. The same level of theory was used to determine the HOMO and LUMO energies for the optimized structures. To assign the molecular orbitals, the GaussView[45] suite of programs was employed. The solute-solvent interactions are described by the polarizable continuum model using an integral equation formalism variant[46] and SMD[47] solvation model of Cramer and Truhlar. All HOMO and LUMO orbitals are shown using the SMD solvation model. Compared to the HOMO of benzyne (−9.58 eV)[48] the calculated HOMO value for 2,3-dehydronaphthalene is much lower (-6.49 eV), therefore it reacts only with "activated" dienes. According to Table 2 the introduction of a strong electron-withdrawing group, *i.e.* a cyano-group, in the 1,2,4-triazine core reduces the LUMO level of the molecule, decreasing the $\text{HOMO}_{2,3\text{-dehydronaphthalene}}$–$\text{LUMO}_{1,2,4\text{-triazine}}$ gap. Thus, based on the lowest values for the HOMO-LUMO gap, the Diels-Alder reaction between 1,2,4-triazines **1e** and **1g** with 2,3-dehydronaphthalene was most favored (Fig. 2).

The introduction of a cyano-group to the 2-azaanthracene core is beneficial in terms of the possibility for further transformation, for instance into the carboxylic[49] or aminomethyl[50] groups. Additionally, *vide supra*, we expected improved photophysical properties. As expected, in both the emission and absorption spectra of 2-azaanthracenes **2a**–**f** (except compound **2e**) separated vibrational bands were observed which was probably caused by the influence of the cyanogroup in the C3 position of the 2-azaanthracene core on the *n*-π* and π-π* energy levels (Figs. 3a, S3–S4, ESI).[51,52] Depending on the substituent nature the quantum yield values were 14.9% (**2a**), 0.86% (**2b**), 30.3% (**2c**), 28.4% (**2d**), 4.5% (**2e**) and 15.3% (**2f**) with fluorescence maxima at approximately 400, 430, 450 and 500 nm (Table 3, Figs. 3a, S3–S4, ESI).

Representative compound **2a** did not show any significant changes in its fluorescence emission in the presence of selected metal cations (Figs. S5–S6, ESI), however drastic changes were visually observed by changing the solvent polarity. Thus, in UV–Vis absorption spectra of compound **2a** the change in a solvent polarity did not affect much the shape and the position of the absorption maxima (Fig. S7, ESI), while in the emission spectra the most polar solvents, such as CH_3CN or DMSO, cause a bathochromic shift of the emission maxima for compound **2a** (Figs. 3b, S8, ESI). According to a literature[53,54] compound **2a** manifests a positive solvatochromism. That means that the excited state dipole moment for compound **2a** is larger than the ground state dipole moment, and upon the photoexcitation the solvent relaxation can occur to stabilize the excited state and destabilize the Franck-Condon ground state.

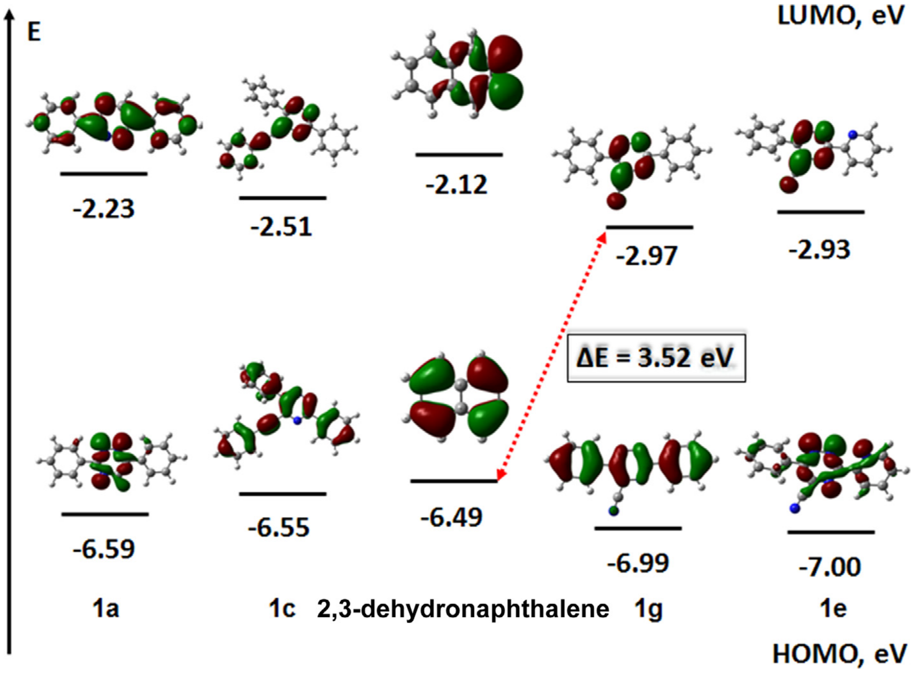


Fig. 2. The HOMO-LUMO energy level diagram for 2,3-dehydronapthalene and the most representative 1,2,4-triazines **1a**, **1c**, **1e**, **1g**. The most favorable orbital interaction of 2,3-dehydronaphthalene and 1,2,4-triazine **1g** is indicated.

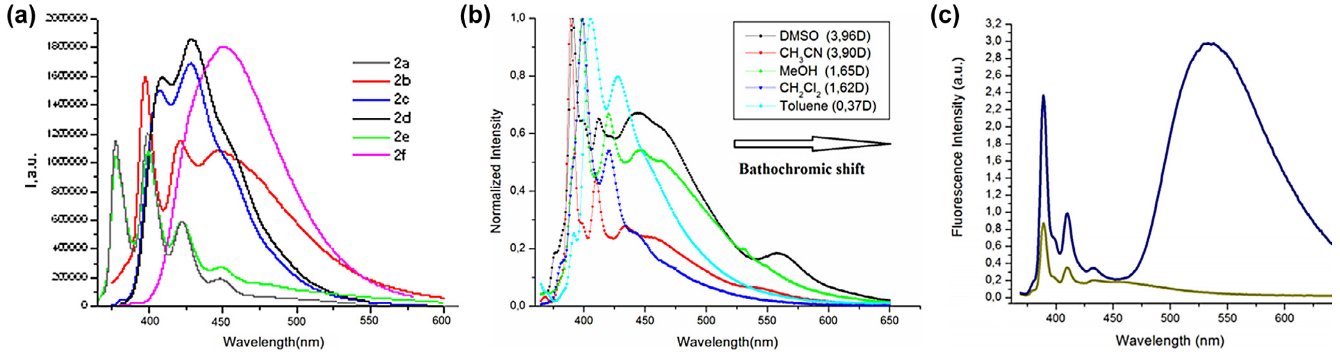


Fig. 3. (a) Emission spectra of compounds **2a–f** in CH_3CN; (b): Emission spectra of compound **2a** in DMSO (black), CH_3CN (red), MeOH (green), CH_2Cl_2 (sky blue), Toluene (blue); (c) Emission spectra of compound **2a** in CH_3CN before and after (sky blue) the addition of TFA (*ca.* 10 eq).

Table 3

Photophysical properties of 3-cyano-2-azaanthracenes **2a–f**.

Product	λ_{abs}[a] (nm)	λ_{em}[b] (nm)	Stokes shift (nm)	Φ[c] (%)
2a	340, 357, 376, 404	377, 399, 422, 448	44	14.9
2b	370, 382, 402	398, 420, 447, $500_{sh.}$	45	0.86
2c	356, 372, 393	407, 428, $455_{sh.}$	35	30.31
2d	356, 373, 393	409, 429	36	28.44
2e	$338_{sh.}$, 356, 376, 398, $418_{sh.}$	378, 400, 423, 449	51	4.57
2f	$371_{sh.}$, 381, 401	449	48	15.37

[a] Absorption maxima in CH_3CN at room temperature.

[b] Emission maxima in CH_3CN at room temperature.

[c] Absolute fluorescence quantum yields were measured in CH_3CN according to a reported procedure41 by using Horiba-Fluoromax-4 spectrofluorimeter equipped with integrated sphere.

Finally, in trifluoroacetic acid it was found that protonation of 2-azaanthracene **2a** led to a strong bathochromic shift (up to 550 nm) (Figs. 3c, S9, ESI) in its fluorescence emission spectra along with strong fluorescence enhancement, due to quarternization of the pyridine nitrogen atom, and, possibly, excimer formation due to cation-π interactions.[9] It was previously confirmed, that the protonation of the pyridine moiety favors the preorganization of 1- or 2-azanthracenes[9] or structurally related acridines[55] *via* head-to-tail orientation through cation-π interactions. The possible preorganization model for **2a** is suggested (Fig. S10, ESI).

In summary, we have studied the possibility of using 2,3-dehydronaphthalene, *in situ* generated from commercially available 2-amino-3-naphthoic acid, as a dienophile in the reaction with substituted 1,2,4-triazines to afford benzo[*g*]isoquinolines (2-azaanthracenes). Only 1,2,4-triazines activated by the electron-withdrawing cyano-group at the C5 position were successfully involved as dienes in this reaction, affording the corresponding cyano- and aryl-substituted 2-azaanthracenes, which were isolated in moderate yields. In all other cases the reaction of 1,2,4-triazines with 2,3-dehydronaphthalene was either not observed or resulted in an inseparable complex mixture of products. Due to unique photochemical properties the reported 2-azaanthracenes could possibly be utilized as environmentally sensitive dyes and *pH* indicators.

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.11.008.

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35. The corresponding 5-cyano-1,2,4-triazine **1** (1 mmol) was suspended in dry toluene (80 mL). Isoamyl nitrite (0.2 mL, 1.5 mmol) was added and the resulting mixture was stirred at reflux, while a solution of 3-amino-2-napthtoic acid (280 mg, 1.5 mmol) in dry 1,4-dioxane (10 mL) was added a dropping funnel over 30 min. The reaction mixture was heated at reflux for an additional 1 h, then cooled to room temperature. The resulting mixture was washed with a potassium hydroxide solution (3 M, 3 x 50 mL) and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. Products **2a**–**f** were separated by column chromatography (SiO_2, DCM as eluent). Analytically pure samples were obtained by recrystallization from MeCN.
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