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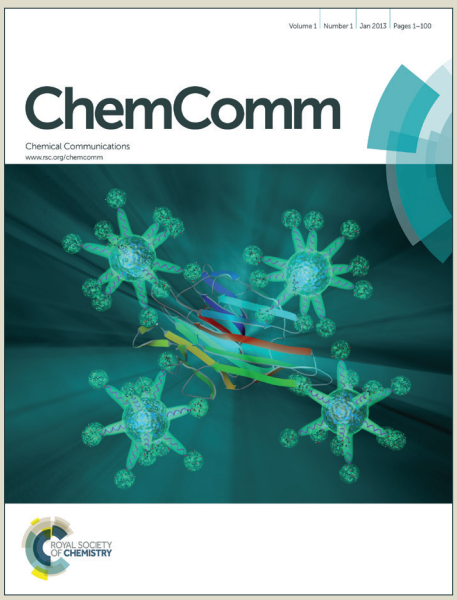

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Pentacyclic coumarin-based blue emitters - the case of bifunctional nucleophilic behavior of amidines

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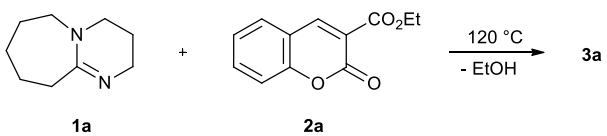
An unexpected discovery of the novel cyclocondensation reaction of 1,8-diazabicyclo[5.4.0]undec-8-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) with alkyl coumarin-3-carboxylates is described. Previously unknown skeleton is generated through the concomitant formation of new nitrogen-carbon and carbon-carbon bonds followed by the oxidation of the intermediate product by the second equivalent of starting coumarin. Pentacyclic DBN-derivatives exhibit strong fluorescence both in solutions (Φ_{fl} ~ 0.6-0.8) and in the solid state, while non-planar DBU-derivatives exhibit strong fluorescence in the solid state only.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) has been long known and utilized as non-nucleophilic strong base.[1] This is still valid today, although numerous examples have been reported, which demonstrate that both DBU and DBN can act as nucleophiles.[2] This 'controversy' was settled down by Mayr and co-workers who established nucleophilicity of DBU and DBN as stronger than DMAP.[3] Still, only a few examples of DBU as double C,N-nucleophile have been published to date.[4] The combination of suitable optical properties of coumarins such as strong light absorption, high Φ_{fl} and large Stokes shift have attracted considerable attention in various photonics applications.[5] The coumarin core is a key component in a wide range of molecular architectures serving, for example, as emitter layers in Organic Light-Emitting Diodes (OLEDs)[6] or energy- and electron-transfer systems.[7] The structure-property relationship of coumarin derivatives has recently been studied in detail.[8] Although coumarin chemistry is well developed, new synthetic methods are being continuously discovered.[9]

While studying the reactivity of esters of coumarin-3-carboxylic acid towards electron-rich aromatics,[10] we have found that additional product was formed when reaction of ester **2a** with phenol was performed in the presence of DBU (Scheme 1). Initially, we noticed that the ^{1}H NMR spectrum of the product **3a** consisted of extra signals in the upfield region. The analysis of ^{1}H NMR spectrum of the intriguing product showed that starting coumarin underwent the reaction with DBU at two positions.



Scheme 1.

The mass spectrum ([MH$^+$]=323; ESI) suggested, that this product resulted from elimination of two H atoms and one EtOH molecule between DBU and ester **2a**. An additional intriguing observation was that, the yield of the isolated product did never exceed 50% in relation to starting coumarin ester **2a**, even when initially present phenol was eliminated.

Eventually, the X-ray diffraction analysis revealed that the molecular structure of compound **3a** is comprised by unknown heterocyclic system (Figure 1).

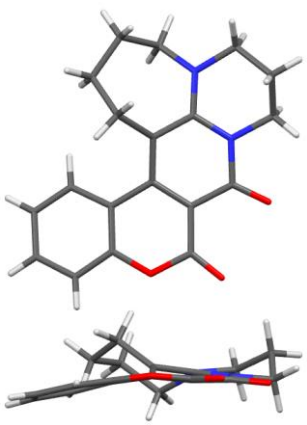


Figure 1. Molecular structure of compound **3a**.

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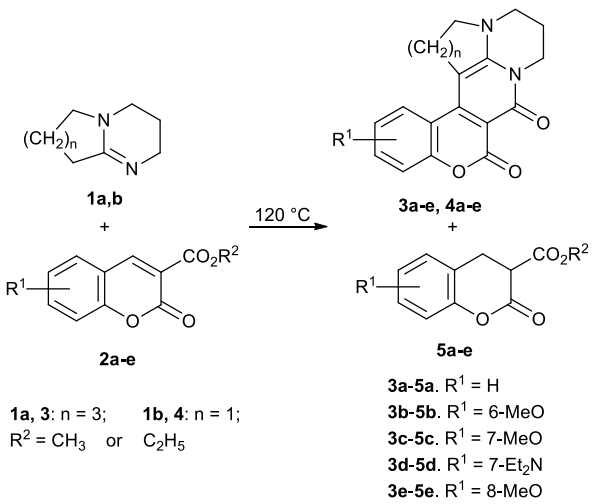
It is noteworthy, that the coumarin ring system of compound **3a** is not planar owing to the sterical hindrance imposed by the seven-membered ring (Fig. 1).

The structure of compound **3a** clearly shows that the cyclization step is followed by the oxidation process. The first step is undoubtedly Michael addition of α,β-unsaturated lactone to C-nucleophilic site of DBU in analogy to some recently reported reactions (see Scheme S1).[11] To study the oxidation mechanism, the reaction of DBU with ester **2a** was carried out under argon atmosphere. Still, in the oxygen free atmosphere compound **3a** was formed in the exactly same yield (38%). The latter experiment suggested that the intermediate product must be oxidized by one of the substrates.

It appeared that the half amount of alkyl coumarin-3-carboxylate dehydrogenates the intermediate product, turning itself into 3,4-dihydrocoumarin derivative, which would explain why the yield of isolated product never exceeded 50%. Reduced coumarin molecules are unstable during the column chromatography and undergo air oxidation. Preparative TLC made it possible to isolate substituted dihydrocoumarin derivative **5b**. Compound **5b** is mentioned in the literature,[12] although without any analytical data. Carrying out the reaction with the ratio **2a**:**1a** = 2:1 gave rise to a twofold increase of the reaction product yield. The similar behaviour of ethyl coumarin-3-carboxylate was also reported,[12] however the reduced coumarin ester was not isolated.



Scheme 2

To demonstrate the versatility of the process the reactions were performed between diversely substituted esters of coumarin-3-carboxylic acids **2a-e** and DBU (**1a**) or DBN (**1b**) (Scheme 2). In all the cases, products **3a-e**, **4a-e** were isolated in good yields (51-76%). Notably, since the reaction center in DBN is less sterically hindered than in DBU, the reaction time for all examples with DBN is only 30 min, while the typical reaction time of esters **2a-e** with DBU is 2 hours.

The spectral characteristics of compounds **3a-e** and **4a-e** were subsequently examined and compared to those of the known esters **2a-e**. The analysis of the absorption spectra of compounds **3a-e** and **4a-e** showed that the introduction of polar substituents into new 9,10,11,12-tetrahydrochromeno[4',3':4,5]pyrido[1,2-*a*]pyrimidine-6,7-dione system, generally hardly influences the absorption properties of these heterocycles. The only exception is the position 7 of the coumarin ring system (**c** and **d** series), the addition of electron-donating substituents causes the increase of the absorption intensity (**3c**, **4c**, **3d**, **4d**, Table 1, Fig. 2). Most probably electron-rich substituents at this position interact with the amide group resulting in the growth of the contribution of the charge separated limiting form.[13]

The electronic spectra of new heterocycles differ in the shape. Due to a more rigid structure, compounds of series **4** are characterized by a well resolved structure, while the series **3** shows unstructured absorption bands.

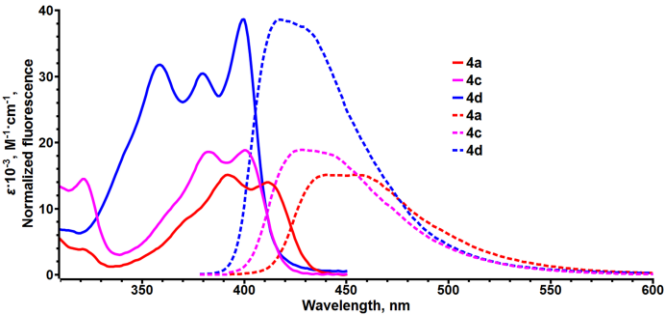


Figure 2. Absorption (solid) and emission (dashed) spectra of compounds **4a**, **4c** and **4d** in dichloromethane (DCM).

Compound synthesized are weakly sensitive to the solvent polarity. For all compounds the absorption maxima in DMSO are somewhat bathochromically shifted compared with the DCM solutions. The solutions of compounds **3a-e** and **4a-e** exposed to ambient light did not underwent significant decomposition.

Table 1. Optical properties of compounds synthesized.

compd	R^1	solvent	λ_{abs}, nm ($\varepsilon \cdot 10^{-3}$, $M^{-1}cm^{-1}$)	λ_{em}, nm (Φ_{fl})
3a	H	DCM	413 (16.2)	–[a]
		DMSO	415 (15.8)	–[a]
3b	6-OCH_3	DCM	415 (16.3)	–[a]
		DMSO	419 (16.1)	–[a]
3c	7-OCH_3	DCM	404 (19.6)	–[a]
		DMSO	408 (18.9)	–[a]
3d	7-NEt_2	DCM	406 (37.1)	477 (0.02)[b]
		DMSO	410 (36.7)	486 (0.02)[b]
3e	8-OCH_3	DCM	411 (17.3)	–[a]
		DMSO	415 (16.8)	–[a]
4a	H	DCM	411 (13.9), 392 (15.1)	455 (0.78)[c]
		DMSO	416 (11.8), 397 (13.7)	465 (0.79)[c]
4b	6-OCH_3	DCM	415 (13.6), 395 (14.9)	460 (0.58)[c]
		DMSO	420 (11.8), 400 (13.9)	472 (0.67)[c]
4c	7-OCH_3	DCM	400 (18.8), 384 (18.8)	430 (0.76)[c]
		DMSO	404 (16.8), 386 (17.6)	446 (0.63)[c]
4d	7-NEt_2	DCM	399 (38.6), 380 (30.7)	418 (0.14)[b]
		DMSO	403 (36.0), 384 (31.1)	425 (0.22)[b]
4e	8-OCH_3	DCM	410 (15.2), 390 (16.2)	454 (0.79)[c]
		DMSO	413 (13.8), 394 (15.7)	461 (0.75)[c]

[a] Fluorescence was not measured due to low S/N ratio
[b] standard: quinine sulfate dihydrate in 0.05 M H_2SO_4
[c] standard: 9,10-diphenylanthracene in cyclohexane

The striking difference is that while dyes **3a-e** show very weak fluorescence response, compounds of series **4** demonstrate very high emission efficiency.[14] The drastic change in fluorescence intensity between adducts with DBU and adducts with DBN can only be rationalized by combined effect of more flexible molecular structure of series **3** and distortion of chromen-2-one moiety (Fig. 1). Typically, coumarins lacking electron-donating group at position 7 possess negligible Φ_{fl}.[15] In contrast, in

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tetrahydrochromeno[4',3':4,5]pyrido[1,2-*a*]pyrimidine-6,7-diones **4a-e**, very high fluorescence quantum yield is almost independent on substituent orientation in benzene ring (Table 1). Intriguingly, compounds from both series (**3** and **4**) show strong fluorescence in the solid state. Given antiparallel arrangement in crystal packing of compound **3a** (Fig. S1) it can be assumed that dyes **3a-e** represent new case of aggregation-induced emission enhancement (AIEE).[16] In contrast to many other ultraviolet-light excitable fluorophores,[15] dyes **4a-e** have the advantage of being easily fine-tuned and functionalized, due to the variety of commercially available (or easily synthesizable) 2-hydroxybenzaldehydes. At the same time our studies have proven that Φ_{fl} remains almost constant regardless these structural modifications.

Conclusions

In conclusion, alkyl coumarin-3-carboxylates undergo unusual, oxidative double addition to cyclic amidines (DBU or DBN). Our serendipitous discovery directly led to the development of a first method for the construction of 3H-chromeno[3,4-*c*]pyridine-4,5-diones, while delivering new example for DBU reactivity as C- and N-nucleophile. This reaction is sensitive to the structure of cyclic amidine, with the shortest reaction times achieved for DBN. In this transformation esters of coumarin-3-carboxylic acid play dual role, the second equivalent oxidizes the intermediate reaction product. The difference in rigidity between DBN-adducts and DBU-adducts as well as distortion from planarity for the latter ones, are responsible for huge difference in emission intensity (~0 vs. ~0.8). All polyheterocyclic compounds, bearing coumarino[3,4-*c*]pyridine skeleton display fluorescent properties in the solid state, as a result of AIEE.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details for compounds **3a-e**, **4a-e** and **5b**, ^{1}H NMR and ^{13}C NMR spectra, mechanistic proposition, X-ray crystallographic data for **3a**. CCDC 984996. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

‡ X-ray crystallographic data for **3a**: formula: $C_{19}H_{18}N_2O_3$, M_w = 322.35; orthorhombic, *Pbca*; a = 14.9390(16) Å, b = 9.9164(11) Å, c = 19.963(2) Å; V = 2957.3(6) Å^3, Z = 8; D_c = 1.448 g cm^{-3}; R_1 = 0.0393 ($I > 2\sigma(I)$), wR_2 = 0.1101 (all data), GOF = 1.058.

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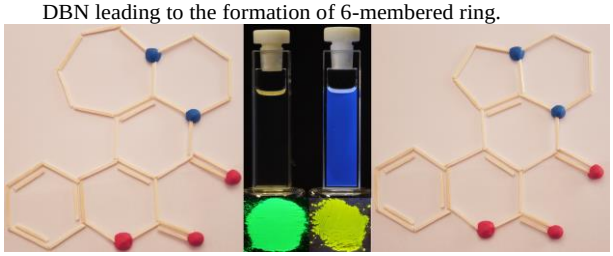
Table of contents graphic and text:

Esters of coumarin-3-carboxylic acids undergo addition to DBU and DBN leading to the formation of 6-membered ring.



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