

Revisiting Hafner's Azapentalenes: Some Old and New Chemistry of 1,3-Bis(dimethylamino)-2-azapentalene

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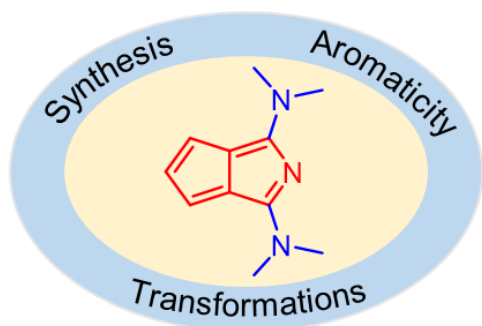
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Supporting Information Placeholder



ABSTRACT: Stable azaheterocyclic derivatives of pentalene have been reported by the group of Hafner in the 1970s, however, these structures remained of low interest until recently. Herein, we revisit the synthesis of stable azapentalene derivative 1,3-bis(dimethylamino)-2-azapentalene and further explore its properties both computationally and experimentally. Beyond the reproduction and optimization of some previously reported transformations, such as formylation and amine substitution, the available scope of reactions was expanded with azo-coupling, selective halogenations, and cross-coupling reactions.

Polycyclic π -electron systems with nonbenzenoid subunits received considerable attention recently¹ as tools for sharpening the fundamental understanding of conjugation effects and (anti)aromaticity rules.² Along with fundamental studies, they opened a new chemical space for the design of advanced organic materials for opto-electronic applications.³ Klaus Hafner,⁴ a pioneer in the development of such systems,⁵ reported on several examples including azulenes,⁶ *s*-indacenes,⁷ heptalenes,⁸ pentalenes⁹ and some of their heterocyclic derivatives.¹⁰ Among these latter examples azaazulenes received some attention,¹¹ while azapentalenes remained neglected until recently, when they started to be investigated in the context of organic light emitting diodes (OLEDs) development.^{12,13} Simple azapentalenes, like 2-azapentalene (**2**), have not been isolated so far owing to their electronic similarity to the unstable parent carbocycle, pentalene (**1**) (Figure 1). However, Hafner and co-workers reported 2-azapentalene derivatives bearing

electron donor groups (**3**) (Figure 1), which led to a strong stabilization of the 8π -electron framework.^{10,14} As only a few reports appeared on this interesting structure, we set out to further explore the chemistry of stable azapentalene derivatives including both computational and synthetic approaches. Our goal is to highlight the properties and the reactivity through some model reactions of **3**, which might inspire further studies or lead to opto-electronic applications^{12,13} of this scaffold.

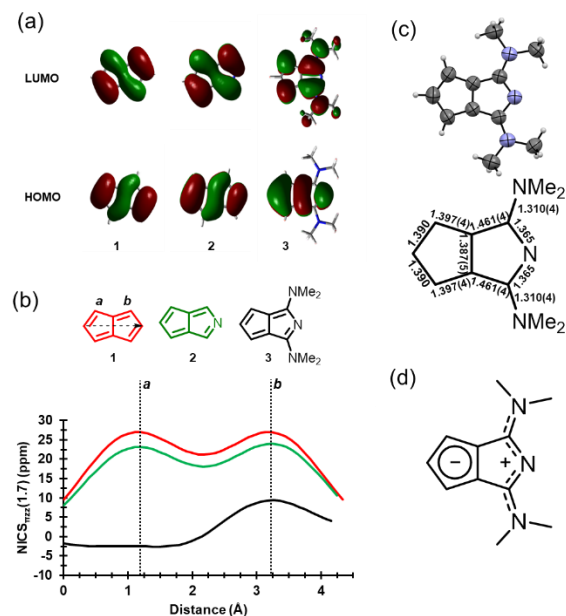


Figure 1. (a) Calculated HOMOs and LUMOs of **1**, **2**, and **3** (isosurface of 0.02 a.u. is used); (b) NICS-XY scans and (c) X-ray structure of **3** and the corresponding bond lengths (Å) (ORTEP style representation is drawn at the 50% probability level); d) Possible π -delocalized structure of **3**.

The π -electron perimeter of azapentelene derivatives is isoelectronic with the parent carbocyclic pentalene.¹⁵ Indeed, looking at the calculated frontier orbitals of azapentelene **2** (Figure 1a), the replacement of a C atom to a N heteroatom does not considerably influence the electronic system. Unlike to pentalene (**1**) and 2-azapentelene (**2**), there is a cyclopentadienyl anion-type contribution to the HOMO of **3**, which influences not only its stability, but also affects the reactivity of the system. The different electron distribution in **3** contributes to a larger calculated HOMO-LUMO gap (2.46 eV) compared to pentalene (1.62 eV) and 2-azapentelene (1.77 eV) (B3LYP/6-311+G(d,p) in CH₂Cl₂ solvent model; for further details, see section S4 in the Supporting Information). Notably, a similar substitution strategy renders pentalene itself stable as well, which was prepared by the group of Hafner,¹⁶ and recently new insights were reported on this structure¹⁷ (see also section S4.3 in the Supporting Information). The electronic differences that underlie the stability and reactivity differences within the series are also reflected in the calculated (anti)aromaticity features of the molecules. In contrast to the strong global antiaromatic character of **1** and **2**, NICS-XY¹⁸ scan reveals that in **3** the 5-membered carbocycle is weakly aromatic and the heterocyclic 5-membered ring shows a weak antiaromatic character (Figure 1b). The calculated ACID¹⁹ plots support these findings (see section S4 in the Supporting Information). Furthermore, the harmonic oscillator model of aromaticity (HOMA)²⁰ indicated a more preserved local aromaticity in the carbocyclic ring (0.837) compared to the heterocyclic ring (0.634) in **3**. For the π -electron perimeter of **3** a HOMA value of 0.736 was obtained, which also supports the overall stability of the molecule (the HOMA perimeter value for pentalene is -0.346, which is attributed to its antiaromatic character).

Following one of the original reports^{14b} for the synthesis of **3**, we initially attempted to perform the reaction between **6** and **7**, however, the solubility of **6** in THF at -20°C was poor and no

product could be isolated in this way. Alternatively, the formation of cyanin **6** was carried out from (dichloromethylene)dimethylammonium chloride (**4**) and dimethylcyanamide (**5**) and instead of isolation, it was reacted immediately with **7** (Figure 2a). By performing the sequence in CH₂Cl₂ at room temperature in the second step to improve the solubility of **6**, compound **3** was isolated as a bench-stable red solid in a moderate, 34% yield. In the ¹H NMR spectrum (500 MHz) of **3**, the chemical shifts of the Hs attached to the carbocyclic ring appeared at 6.19 and 6.05 ppm in CDCl₃, 6.02 and 5.78 ppm in CD₃CN and 5.98 and 5.68 ppm in DMSO-*d*₆. As a comparison, the chemical shifts of lithium cyclopentadienide²¹ are 5.51 and 5.32 ppm in CD₃CN and DMSO-*d*₆, respectively. The ¹H NMR spectrum of **3** was also calculated, and among the different methods the M11L functional²² provided the closest fit with the measured data (Table S3 in the Supporting Information). In the X-ray crystallographic structure of **3** considerable bond-length equalization is found in the carbocycle (Figure 1c) that points toward a cyclopentadienyl (aromatic) character (Figure 1d). The equal bond lengths around the heterocyclic N supports the presence of a charge-delocalized azacyanine unit (Figure 1d).

The absorption spectrum of **3** was not substantially affected by the solvent used (Figure 2b). The spectrum displays maxima around 500 nm, 375 nm and 300 nm in each solvent. These absorptions could be assigned using time-dependent density functional theory (TD-DFT, CH₂Cl₂ solvent model, for further details, see section S4 in the Supporting Information) calculations as the HOMO → LUMO ($f = 0.0049$), the HOMO-1 → LUMO ($f = 0.2491$) and the HOMO-2 → LUMO ($f = 0.5756$) transitions. The obtained maximum at 499 nm in CH₂Cl₂ corresponds to an optical HOMO-LUMO gap of 2.48 eV, which agrees well with the calculated energy difference in the same solvent (2.46 eV). Azapentelene **3** can be protonated by the addition of acids such as HCl and AcOH, which results in the appearance of a band at 465 nm in the UV-vis spectrum (Figure 2c). Our attempt to characterize the redox properties of **3** using cyclic voltammetry (CV) was unsuccessful, as the compound quickly degraded/polymerized under the measurement conditions.

The electron density distribution induced by the N(CH₃)₂ groups determines the reactivity of **3**. Specifically, reactivity towards electrophiles is expected at the carbocyclic region, while towards nucleophiles at the heterocyclic region.

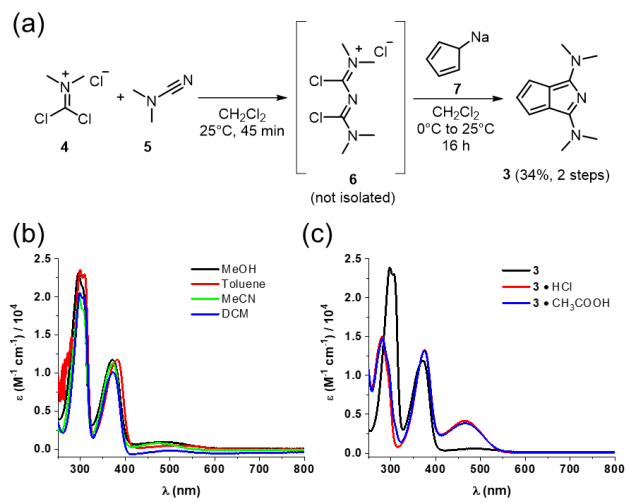


Figure 2. (a) Optimized one-pot synthesis of **3**; (b) UV-vis spectra of **3** in different solvents at rt; (c) UV-vis spectra of **3** (MeCN, rt) in the presence of acids.

Nucleophilic substitution at the heterocyclic ring to exchange the NMe₂ groups have been described,^{14c} which we could reproduce under slightly modified conditions that facilitated purification (Scheme 1a) by reducing the amount of the amine reagent. Instead of heating compound **3** in piperidine at 110°C to obtain compound **8**, using toluene as a solvent and an excess (30 equiv.) of piperidine relative to **3**, compound **8** could be isolated in a moderate yield (33%).

We attempted the extension of this chemistry to other amines with moderate success. Indoline, having an aniline-type nitrogen, was reactive under similar conditions leading to a mixture of di- (**10**) and mono-substituted (**11**) derivatives. Upon purification, the disubstituted derivative repeatedly decomposed, while the monoindoline derivative **11** was isolated and characterized. To optimize the synthesis of **11**, the reaction was repeated with only 10 equiv. indoline that led to the isolation of **11** as a dark purple solid in 29% yield. The syntheses of compounds **8** and **11** were also carried out under microwave conditions with similar results in shorter reaction times (6 h) (see Supporting Information). Upon using morpholine or piperazine and its derivatives (1-phenylpiperazine, 1-methylpiperazine, 1-(2-hydroxyethyl)piperazine) as the amine reagent, while the products could be detected (LC-MS), their isolation was not feasible due to decomposition.

By addressing the reactivity of the carbocycle having aromatic character in **3** towards electrophiles, several new derivatives could be isolated, and the scope of tolerated reactions could be expanded compared to the initial work by Hafner and co-workers. The previously reported formyl azapentalene **12**^{14c,14d} could be prepared (Scheme 1b) using a modified Vilsmeier-Haack formylation²³ in an excellent yield (95%) as a bench-stable brownish-yellow solid, and its crystal structure could also be determined (Scheme 1g).

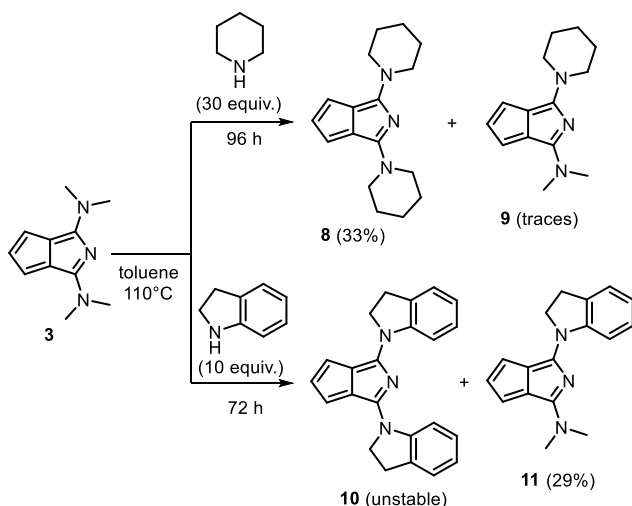
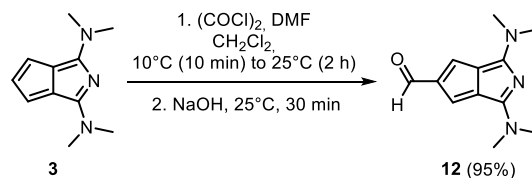
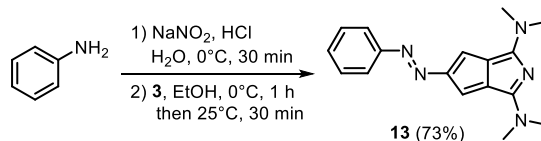
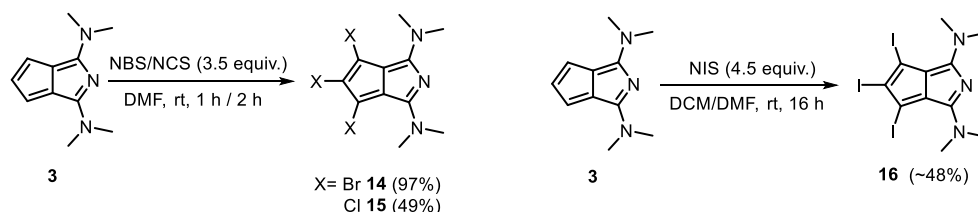
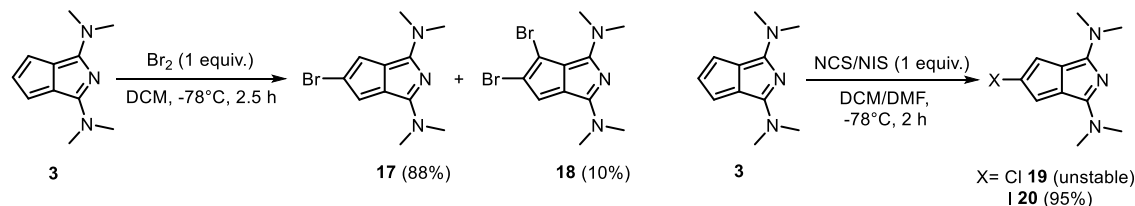
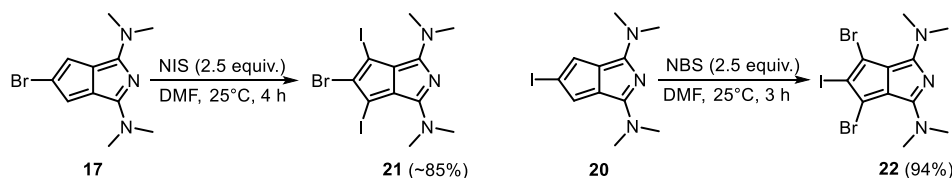
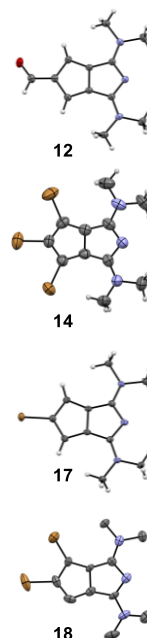
The reaction of **3** with benzenediazonium chloride provided the novel azoazapentalene **13** in good yield (73%) (Scheme 1c) as an orange-colored product, which slowly degrades at ambient conditions but can be stored at low temperature under inert atmosphere.

Halogenation of the carbocycle of **3** could be an entry to its arylated and alkynylated derivatives through cross-coupling chemistries and could facilitate its integration into extended π -systems. Interestingly, maybe due to the less widespread applications of transition metal catalyzed coupling reactions in the early 1980s, Kläs and Hafner paid little attention to the halogenation of **3**. Their only attempt of bromination using Br₂ led to a product mixture containing mono-, di- and tribrominated derivatives, where the structure of the dibromo derivative could not be determined.^{14c} We systematically studied the selective halogenations of **3** (Scheme 1d-f). Initially, we used N-halosuccinimides (NXS) as halogenating agents. The reaction of **3** with NXS (1 equiv.) in all cases (X= Br, Cl, I) led to the formation of product mixtures, while with excess reagent, the reactions could be driven towards the trihalogenated products (Scheme 1d). In case of NBS, the tribrominated derivative **14** could be obtained in excellent yield (97%). Trichlorination was less

efficient (49% yield), but the selectivity of the trisubstituted product **15** remained high while the conversion of **3** was lower. Additionally, under the basic work-up, we observed some loss of product due to decomposition. Notably, under the conditions similar to the bromination/chlorination triiodinated product (**16**) was not detected. When the reaction was carried out in CH₂Cl₂/DMF solvent mixture, in which both NIS and the diiodinated product was soluble, triiodinated derivative **16** could be obtained. Unfortunately, **16** decomposed over time. Following trihalogenations, we turned to the synthesis of monohalogenated derivatives (Scheme 1e). As 1 equiv. of NXS at rt led to product mixtures, we first adjusted the temperature to tune selectivity. The reaction of **3** with NBS (0.7 equiv.) in DMF at -35°C (lower temperature led to the precipitation of **3**) provided a product mixture, similar as in the rt reaction. However, using Br₂ and adjusting the reaction conditions (CH₂Cl₂, -78°C), the monobrominated product **17** could be isolated in high yield (88%) along with some dibrominated derivative **18** (10%). The structures of **17** and **18** could be determined crystallographically (Scheme 1g). The likely reason of this selectivity is the precipitation of the HBr salt of **17** upon the use of Br₂, which prevents further incorporation of bromine. Further monohalogenated products could be obtained using NCS and NIS under low temperature in CH₂Cl₂/DMF solvent mixture. Notably, the iodinated derivative **20** was isolable in excellent yield, while the chlorinated compound **19** degraded during the work-up and purification steps. The successful trihalogenation and monohalogenation processes provided the interesting perspective of the synthesis of derivatives containing different halogen atoms (Scheme 1f). The reactions, using NIS and NBS, respectively, for the transformations of **17** and **20**, were successful, leading to products **21** and **22** in high yields, although we observed the degradation of **21** over time.

With the halogenated derivatives in hand, we probed their reactivity in model Suzuki and Sonogashira cross coupling reactions (Scheme 2). Both the tribrominated (**14**) and the monobrominated (**17**) scaffolds were reactive in Suzuki coupling with phenylboronic acid in the presence of Pd catalyst (Scheme 2a,b). In the former case the triphenyl azapentalene **23** was obtained as a stable material in low yield (13%). Under the applied conditions disubstituted and dehalogenated products were also detected (by LC-MS) during the reaction. Monophenyl azapentalene **24** could be detected under similar reaction conditions, however, its isolation was not feasible due to rapid decomposition of the product.

The Sonogashira coupling of tribromo azapentalene **14** and monobromo azapentalene **17** with phenylacetylene were unsuccessful. The reaction of **14** with TIPS-acetylene (10 equiv.) led to stable mono- (**25**) and disubstituted (**26**) derivatives in low to moderate yields, while the triacetylene product was not detected (Scheme 2c). By decreasing the TIPS-acetylene excess (6 equiv.), compound **25** could be obtained in higher isolated yield (56%). The increased stability of the TIPS-acetylene derivatives compared to the phenylacetylene derivatives could be due to the steric shielding of the acetylene moiety by the large TIPS group that could prevent side-reactions.

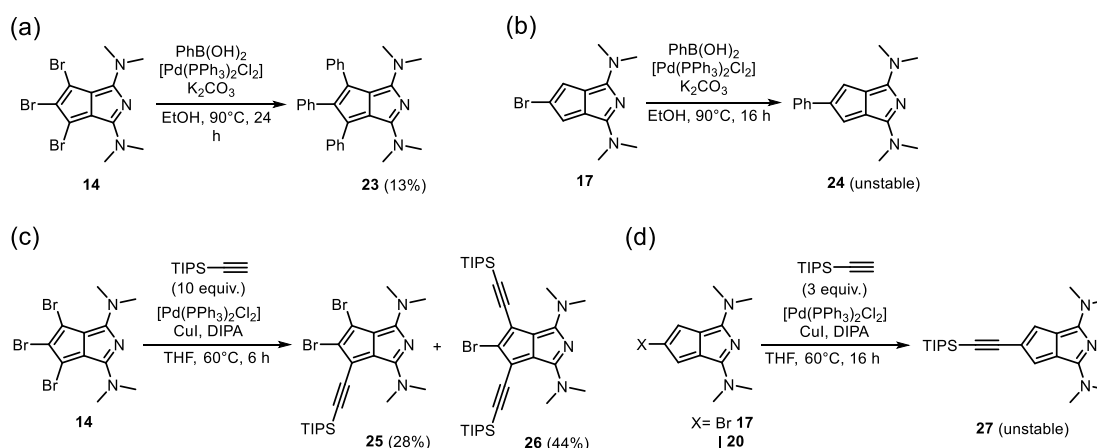
a. Nucleophilic substitution of the NMe₂-groups**b. Vilsmeier–Haack reaction****c. Azo-coupling****d. Trihalogenation reactions****e. Monohalogenation reactions****f. "Mixed" halogenation reactions****g. X-Ray structures**

Scheme 1. Reactivity mapping of compound **3** (ORTEP style representations are drawn at the 50% probability level, disordered H atoms are omitted for clarity).

The corresponding monofunctionalization, using either **17** or **20**, was not successful (Scheme 2d). Although the desired product (**27**) was detected in both cases (by LC-MS) during the reaction along with considerable amount of dehalogenated starting material, following the work-up it disappeared from the mixture. From the cross-coupling attempts it seems that the monofunctionalized products are challenging substrates due to comparably low stability in most of the cases. In these derivatives the remaining two reactive positions in the carbocyclic ring could be responsible for the decomposition. It is likely that protecting these positions will lead to further stable derivatives. In summary, we synthesized 1,3-bis(dimethylamino)-2-azapentalene **3** and characterized its structure and basic opto-

electronic properties using both experimental techniques (¹H NMR, X-ray crystallography, UV-vis spectroscopy) and computed aromaticity indices (NICS, ACID, HOMA). These revealed that the donor NMe₂ groups have a key role in stabilizing the azapentalene π-system that otherwise has an antiaromatic character. Due to this electron donation the heterocyclic ring of **3** become relatively electron poor, while its carbocyclic ring relatively electron rich that is also reflected in its reactivity, which we explored through model reactions. These included the reproduction and optimization of some previously reported transformations such as formylation and amine substitution, and also the expansion of the previously known scope of reactions with azo-coupling, selective halogenations and cross coupling

reactions. In future research we plan to further expand the scope of stable derivatives of **3** and to incorporate it into π -extended frameworks and photoresponsive structures.



Scheme 2. (a, b) Suzuki reactions of bromoazapentalenes; (c, d) Sonogashira reactions of different haloazapentalenes.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed synthetic procedures, crystallographic data, computational details and analyses, copies of ^1H NMR, ^{13}C NMR and HRMS spectra. (PDF)

CCDC 2295069–2295072 (for **3**, **12**, **14**, **18**, respectively) as well as 2296808 and 2296809 (for **12** and **17**, respectively) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

A data set collection of computational results is available in the ioChem-BD repository and can be accessed via <https://doi.org/10.19061/iochem-bd-6-284>

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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