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Reactions of HDDA-Derived Benzyne with Perylenes: Rapid Construction of Polycyclic Aromatic Compounds

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Abstract

Benzyne produced by the thermal cycloisomerization of tetrayne substrates [i.e., by the hexadehydro-Diels–Alder (HDDA) reaction] react with perylenes to produce novel naphthoperylene derivatives. Cyclic voltammetry and absorption and emission properties of these compounds are described. DFT studies shed additional light on the dearomatization that accompanies the reaction as well as some of the spectroscopic behavior.

Polycyclic aromatic compounds (PACs) have long been important from not only fundamental theoretical and structural perspectives but also because of their biological and environmental impact, especially with respect to their carcinogenicity.¹ More recently, PACs have attracted considerable attention due to their promising applications in optoelectronic materials such as organic light-emitting diodes (OLED), organic field effect transistors (OFET), and organic photovoltaic cells (OPV).² Development of facile and efficient strategies for creating novel PACs remains of significance in the fields of both chemistry and materials.³

Strategies for synthesis of π -extended PACs based on *de novo* construction of the aromatic cores often leads to lengthy and/or inefficient routes. One way to circumvent this limitation is by starting from a building block already containing multiple aromatic rings. Perylene (**1**) has been employed in this role to good advantage.⁴ Examples particularly relevant to the work we report here are shown in Scheme 1a. *o*-Benzyne (**2**) adds in [4+2] fashion to **1** to

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Supporting Information

Experimental procedures for the synthesis, spectroscopic characterization data, and ¹H- and ¹³C NMR spectra for new compounds; DFT computational methods; and CV and UV and fluorescence spectral data for **10a-c** and **10e-g** (66 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Notes

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give naphtho[1,2,3,4-ghi]perylene (**4**) following thermal extrusion of dihydrogen from the intermediate adduct **3**.^{5,6} The bis-benzyne precursor **5** was recently used to capture **1** under conditions where **6** precipitated from solution, mitigating its further conversion to the second benzyne. Subsequent treatment with fluoride ion, now in the presence of a Pd(0) catalyst led to the insoluble trimer **7**, which was characterized at atomic resolution by scanning probe microscopy.⁷

The thermal cycloisomerization of a 1,3,-diyne bearing a tethered alkyne diynophile (see **8**) leads to formation of a carbocyclic benzyne moiety (see **9**),⁸ a process we have termed as the hexadehydro-Diels–Alder (HDDA) reaction (Scheme 1b).⁹ Recently, we have turned our attention to exploring the application of the HDDA reaction to the synthesis of compounds of potential utility in various photonic or electronic materials. One avenue has been to examine the reactions of **9** with **1**. If these were to proceed by way of the precedent in Scheme 1a, multiple substituents and functionality could readily be incorporated into the naphtho[1,2,3,4-ghi]perylene products **10**. We report the results of some of our studies here.

One of the first reactions we explored was that between perylene (**1**) and the tetrayne precursor **8a** (Scheme 2), which contains a dipropargylated malonate ester linker. This HDDA cascade, effected simply by heating a CHCl₃ solution of **8a** and (only) 1.5 equiv of **1** at 85 °C for 10 h, provided an air-stable yellow powder that could be purified by column chromatography to remove excess perylene followed by addition of methanol to a dichloromethane (DCM) solution of this material to precipitate the pure product. Analysis of the 1D and 2D ¹H-NMR spectra allowed us to assign the structure as **10a**. Resonances corresponding to H5, H6, and H10, each of which resides in a bay region of the naphtho[1,2,3,4-ghi]perylene moiety, were observed at ca. δ 8.9 ppm (Figure 1). In contrast the resonance for H1, the fourth bay region proton, as well as that of H2 resided significantly farther upfield, a reflection of the shielding provided by the adjacent aryl group of the biaryl moiety. No alkyl methine protons were observed, suggesting that two hydrogen atoms had been lost from the presumed initial Diels–Alder adduct between **9a** and **1** (cf. Scheme 1a) to rearomatize the perylene subunit. The ESI mass spectrum confirmed that fact.

With this result in hand, we explored some aspects of the substrate scope for this reaction (Scheme 2). Tetraynes **8a–c** demonstrate that arenes having both electron-poor and –rich character are well tolerated. The three-atom tether in the tetrayne can include a sulfonamide (**8d**) and ether (**8e**) functionality as the central linking atom. The electron-deficient perylene derivative containing ester groups in the 3, 4, 9, and 10 positions was also an effective benzyne trapping agent, even when used in near stoichiometric quantities (1.2 equiv). It is noteworthy that each of the tetraynes **8a–e** can be prepared in just two steps from commercially available alkyne precursors (alkyne bromination and Cadiot-Chodkiewicz cross-coupling; see Supporting Information).

In the reaction giving **10g**, a small amount (5%) of the bis-adducts **11-syn** and **11-anti** were also formed. These could be chromatographically separated from **10g**, but coeluted as a 2:1 mixture, an orange powder upon solvent removal. These arise from subsequent head-to-tail and head-to-head addition of the benzyne from **8c** to the product **10g**, which indicates that dihydrogen was being lost during the course of the HDDA cascade reaction time and

temperature. Trace amounts of analogous double adducts were observed in the crude NMR spectra of most of the product mixtures leading to **10a-f**, but in those other instances solubility issues made isolation of pure material challenging. Experiments using an excess of tetrayne substrate over the amount of perylene (or perylene tetraester) did not allow for efficient production of any of the expected bis-adducts. It is worth noting that perylene has been converted by dienophiles into double addition adducts in a single operation in only a few instances and never in high yield.¹⁰

DFT [SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)//B3LYP/6-31G(d)] calculations were performed on a model system to further probe mechanistic aspects of these reactions. We calculated the energy profile (Figure 2) for the reaction between benzyne itself (**2**) and perylene (**1**). The Diels–Alder (DA) reaction is computed to have a free energy of activation (cf. **TS1**) of ca. 11 kcal•mol^{−1}. That step is highly exergonic because, in addition to the usual driving force for π - to σ -bond change accompanying a DA event, the high degree of strain energy in benzyne more than compensates for the lowering of the perylene aromatic resonance stabilization. We also located a transition structure, **TS2**, (27.4 kcal•mol^{−1} uphill) that directly connects the DA adduct **3** and product **4**. **TS2** was computed to have a symmetrical structure, suggesting a concerted loss of dihydrogen. In comparison to the activation energy required for similar concerted dehydrogenation of dihydronaphthalene derivatives (ca. 31 kcal•mol^{−1}, computed)⁶ and dihydrobenzene (42.7 kcal•mol^{−1}, experimental),¹¹ we suggest that the activation energy for the conversion of **3** to **4** would be even lower for the 3c,13a-dihydro adducts leading to products **10** because of the additional π -substituents present in **10**. In other words, the DA adduct of the HDDA benzyne and perylene may require an activation energy even less than 27.4 kcal•mol^{−1} for the release of dihydrogen, consistent with the fact that we never detected an intermediate dihydro adduct in any of the reactions we report here.

We measured the cyclic voltammograms of dichloromethane (DCM) solutions of all of the adducts **10a-g** (see SI) with the exception of **10d**, which showed only limited solubility in all common solvents, including DCM. Two representative voltammograms (those of **10c** and **10g**) are shown in Figure 4. The PAC **10c** showed a reversible oxidation wave (at 0.69 eV) but no reduction was observed before the onset of solvent decomposition. All four of the PACs derived from the parent perylene compound (i.e., **10a**, **10b**, **10c**, and **10e**) showed very similar behavior [^{ox}E_{1/2s} between 0.68–0.71 eV and no reduction half wave]. The oxidation potentials of the core structures present in this subset of PACs, each an unsubstituted perylene subunit, were insensitive to the electronic character of the remote substituents R present on the phenyl rings.

In contrast, the PAC **10g** gave rise to a CV in which both oxidation (1.15 eV) as well as reduction (−1.50 and −1.75 eV) half waves were observable. The four carboethoxy groups present on the pyrene-derived core in **10g** lowered the reduction potential, a feature that was also seen for **10f** (+0.93, −1.68, and −1.92 eV, respectively). In this pair, each having an electron deficient perylene core, the redox potentials were responsive to the nature of the substituents on the two phenyl rings—OMe for the more easily oxidized and difficultly reduced **10f** vs. CO₂Me for **10g**.

Absorption and fluorescence spectra were also recorded for each of **10a-c** and **10e-g** (see SI). Again, representative examples are shown here for **10c** and **10g** (Figure 5a). The lowest energy absorption, reflective of the HOMO-LUMO gap, is red-shifted ca. 25 nm in the UV-visible spectrum of the naphthoperylenetetraester **10g** relative to **10c**. The emission spectra for both compounds mirror the absorption bands¹² and, again, the maximum is red-shifted ca. 25 nm in the spectrum for **10g**.

The HOMO and LUMO energies and molecular orbital maps were computed for each of **10a-c/e-g** [(TD)DFT, B3LYP/6-31G(d)]. In two instances only, the HOMO and LUMO were seen to be located in two significantly different portions of the molecule (Figure 5c). Namely, the HOMO in **10a** resided principally on the naphthoperylene core while the LUMO was largely localized on the alkynyl *p*-carbomethoxyphenyl substituents. The reverse was true for **10f**, the naphthoperylenetetraester that bears *p*-methoxyphenyl substituents. It might be expected, then, that emission from the excited state singlets for each of these compounds would reflect the intramolecular charge transfer character in each. Indeed (and uniquely among all of the compounds **10**), the emission spectra for both **10a** and **10f** (Figure 5b) are noticeably broader and red-shifted in comparison to those of their counterparts **10b-e** (see, for example, **10c** in panel a) and **10g** (panel a), respectively. It is notable that the redistribution of orbital density in both of these molecules involved, principally, the arene substituent on the alkyne (rather than the biaryl) since the former can (and does in the DFT optimization) adopt co-planarity with the naphthoperylene polycycle.

In conclusion, we have described a series of new polycyclic aromatic compounds that can be readily accessed through reaction between HDDA-generated benzyne **9** and perylene (**1**) or its 3,4,9,10-tetraethyl ester derivative. The reaction is accompanied by in situ aromatization of the initial Diels–Alder adduct, presumably by spontaneous ejection of dihydrogen. Novel bis-adducts **11** were observed. CVs showed an interesting lack of sensitivity to electronic substitution for the derivatives of the parent perylene (i.e., **10a-e**) but a significant responsiveness to MeO- vs. MeO₂C-substituents in the electron-deficient perylenes **10f** vs. **10g**. Finally, absorption and emission spectra revealed a behavior that was consistent with the differences in the computed HOMO and LUMO maps.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
 ^1H -NMR spectrum of **10a** (500 MHz, CDCl_3).

Figure 2.
Double adducts from benzyne addition to **10f**.

Figure 3. Computed free energy changes for the reaction of benzyne (**2**) with perylene (**1**) to give the naphthoperylene **4** via extrusion of dihydrogen from the primary Diels–Alder adduct **3**.

Figure 4.
Cyclic voltammograms for **10c** (blue) and **10g** (orange).

Figure 5.

Absorption (unnormalized) and fluorescence (normalized) spectra for (a) **10c** (blue) and the tetraester-substituted perylene **10g** (orange) and (b) **10a** (green) and the electron deficient perylene **10f** (red). (c) Computed (DFT) HOMO and LUMO for **10a** and **10f** showing the orbital density on the phenyl substituents for the LUMO of **10a** and the HOMO of **10f**.

Scheme 1.

(a) Synthetic strategies based on perylene for the synthesis of some polycyclic aromatic compounds (PAC).^{5b} (b) Possible routes to PACs through HDDA cascade reactions.

Scheme 2.

Synthesis of polycyclic aromatic compounds 10a-g through reactions of tetraynes 8a-e with perylene 1

^aIn the reactions leading to **10f** and **10g**, (1.2 equiv) of tetraethyl 3,4,9,10-perylene tetracarboxylate was used in place of perylene (**1**).