Organic LETTERS

Letter

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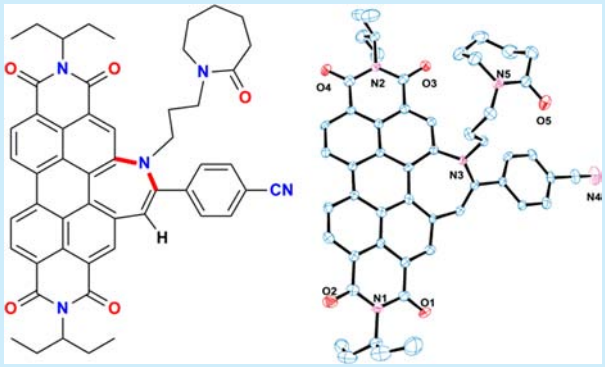
Novel Azepino-perylenebisimides: Synthesis, Structure, and Properties

Ruchika Mishra, Piyush Panini, and Jeyaraman Sankar*

Department of Chemistry, Indian Institute of Science Education and Research, Bhopal 462 066, India

Supporting Information

ABSTRACT: The first example of an azepine ring formation by counterintuitive nucleophilic participation of DBU was observed at the sterically crowded bay area of electron-deficient perylenebisimide (PBI). This is also a rare example of the formation of a seven-membered ring via two consecutive C−N bond formations in a single step. Azepino-PBIs reveal panchromatic absorption covering the whole visible region. Further novelty of these PBIs lies within the fact that their photophysical characteristics can easily be modulated by suitable substituents.



π-Conjugated materials with intense absorption and emission properties attract huge scientific interest due to their applications in various fields such as organic photovoltaics (OPV), nonlinear optics (NLO), and functional bioimaging.[1−5] Perylene-based molecular scaffolds such as perylenebisimides (PBIs) have recently been explored for such applications due to their robust and electronically tunable π-backbone.[6−13] PBIs can readily be accessed from inexpensive perylenebisanhydride (PBA) via reactions with a variety of amines.[10,14−16] The imide functionality is imparted to improve solubility and as an anchoring group for tagging applications, but the substituents on this nitrogen have little effect on the optical properties. An efficient strategy to modulate the electronic and photophysical properties of the PBIs without compromising on their solubility is through bay functionalization.[17−24] PBI core-expansion, i.e., expanding the π-conjugated circuit around the perylene core, is another plausible way to achieve molecular frameworks with tunable photophysical properties for modern applications.[25−27] There has been enormous interest in exploiting core-annulation of PBIs in order to explore new chromophores having excellent properties of both PBI and coronene.[28−35]

The formation of a coronenediimide derivative by treating bay bis-alkynylated PBIs with non-nucleophilic bases or bis-arylated PBIs with palladium complexes and a base is well-studied in the literature.[28] Langhals and co-workers[36−38] have explored another approach by introducing various heterocyclic groups fused into the PBI core. Bay-unsubstituted PBIs treated with $NaNH_2$ and arylnitrile at higher temperatures resulted in imidazolyl-fused PBIs along with bay diazepenyl-PBIs. This method provided core-expanded PBIs with remarkable spectral shifts into NIR and thus are appealing for dye-based applications. The investigations led by Xiao et al. have shown that such a bay fusion can result in interesting nonlinear optical chromophores.[22]

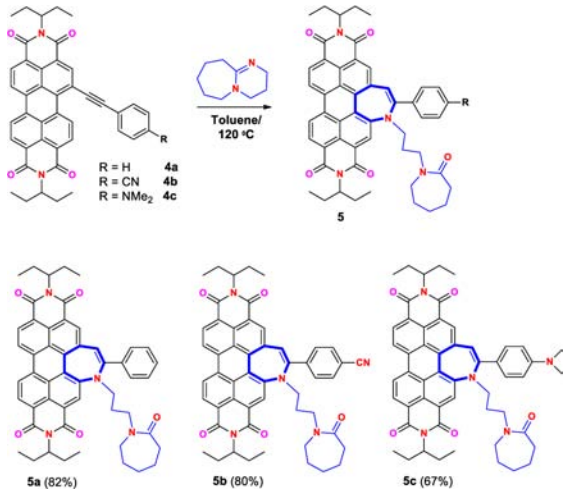
However, in most of the above investigations, the bay fusion resulted in either a five-membered or a six-membered ring appended to the PBI core. In this communication, we are excited to present the serendipitous formation and first structural characterization of a novel azepino-perylenebisimide, obtained by a simple and metal-free approach. Also, it is the first example of a cyclization reaction where DBU itself has acted as a reactant and contributed aza-nitrogen for the formation of a seven-membered ring in the sterically congested PBI bay area. Further, this reaction is a rare example where two C−N bond formations happen in a single step.

In our endeavor toward developing mono-bay-substituted PBI derivatives for photophysical studies,[39] it was envisaged that an annulation selectively at one bay position should result in an unsymmetrical core. This unsymmetrical coronene-like core is interesting with respect to its aggregation-induced optical properties. On our way to verify this plan, the alkynylphenyl-substituted PBI **4a**[39] was refluxed with DBU in a sealed tube (Scheme 1). When the amount of the base was increased to an excess, a highly polar green-colored product **5a** was obtained. A brief column chromatography with 90:10 $CHCl_3$/EtOAc on basic alumina offered **5a** in 82% yield. The ^1H NMR in $CDCl_3$ also indicated the presence of a DBU framework in **5a** (see Supporting Information). It is to be noted that the unsubstituted PBI did not react with excess (30 equiv) of DBU under similar conditions even after 96 h. This corroborated the fact that alkyne substitution at the bay position was a prerequisite for the success of this reaction.

Received: June 24, 2014
Published: July 17, 2014

dx.doi.org/10.1021/ol501822c | *Org. Lett.* 2014, 16, 3994−3997

Scheme 1. Formation of Azepino-perylenebisimide 5



The versatility of this reaction was further verified with the alkynyl-PBI derivative containing a phenyl group with various electron donor (**4c**) and acceptor (**4b**) substituents. The reaction proceeded smoothly and gave the desired product in excellent yields. When **4a** was reacted with DABCO, another hindered base, the reaction did not proceed as expected. The reaction with DBN resulted in a complicated mixture having trace amount of the desired product.

There was an imminent need for a solid state structural proof to unequivocally determine the molecular structure of **5**. After repetitive trials, we were successful in growing suitable crystals for **5a** and **5b** for single crystal X-ray diffraction. Surprisingly, the solid state structures revealed the unprecedented formation of an azepine ring annulated to the PBI bay with the aza-nitrogen donated by DBU as shown in Figure 1. The ring

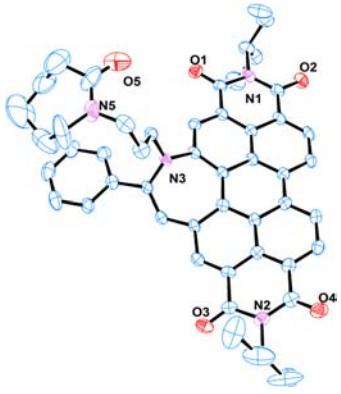


Figure 1. Single crystal X-ray diffraction structure of **5a** (CCDC 1002567) (top and side views; ORTEP 50% probability level).

rupture of the base had occurred, and the nitrogen of the azepine ring had attached to the caprolactam formed from the opened DBU ring through a propyl handle. The perylene core had been twisted along the long axis to alleviate the strain caused by the seven-membered ring formation.

In **5a** (CCDC 1002567), the torsion angle between the two naphthalene units at the azepine-bay site was 22.6° while the same for the unsubstituted bay site in the molecule was 14.4°. This fact supports the inference of an increased strain at the bay positions after annulation. The phenyl substituent that came from the starting alkynylphenyl PBI **4a** preferred to be coplanar with the PBI core, whereas the substitution on the azepine nitrogen stayed away from the core. The propyl-linked caprolactam ring assumed a chair conformation. Further, the azepine ring settled with a distorted boat conformation presumably due to the strain. The bond lengths of the azepine rings were found to be alternating and hint at minimal electronic delocalization. In **5a**, the longest bond was 1.446 Å and the shortest one was 1.337 Å; a difference (Δr) of 0.109 Å clearly indicates that the delocalization inside the azepine ring is not substantial and is perhaps a simple polyene.

Similarly, the difference Δr was 0.128 Å for **5b**. In the unit cell of **5a** and **5b**, both P and M enantiomers form racemic dimers due to strong intermolecular hydrogen bonding and C−H···π interactions (Supplementary Figures S17 and S19). In an extended packing diagram, a helical self-assembly is noticed in **5b** (Supplementary Figure S18). Though simple ring rupture of DBU had already been reported in small organic molecules,[40−42] this is the first structural elucidation of a PBI bay-annulated with a seven-membered ring.

The reaction probably proceeds through the mechanism depicted in Figure 2. The first step involves an attack of DBU

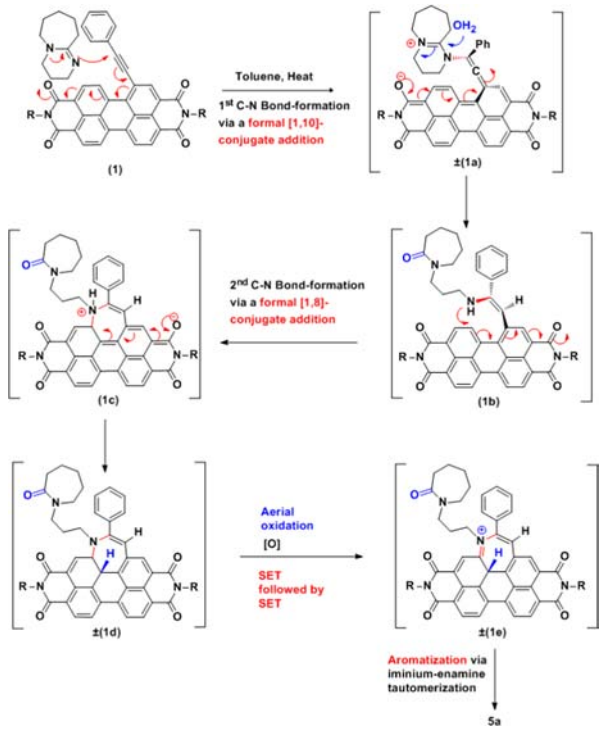


Figure 2. Proposed mechanism for the formation of **5a**.

nitrogen on to the alkyne in a [1,10]-conjugate addition fashion leading to a C−N bond formation. The intermediate carbanion is well-stabilized due to the highly electron-deficient nature of the PBI core. This is followed by the ring opening of DBU by the attack of a water molecule. A second C−N bond formation occurs via a formal 1,8-conjugate addition of the nitrogen of the secondary amine formed. Subsequently, single electron transfer leads to the formation of an iminium ion intermediate, which undergoes aromatization via an iminium-enamine tautomerization to afford the final product in excellent yields.

The synthesized molecules **5a−c** were nonfluorescent and displayed intense absorption covering the whole visible spectrum. The spectral signatures of **5a** obtained in $CHCl_3$

dx.doi.org/10.1021/ol501822c | Org. Lett. 2014, 16, 3994−3997

(Figure 3) showed a strong absorption at 472 nm along with a shoulder at 448 nm. Interestingly, the spectrum also had two

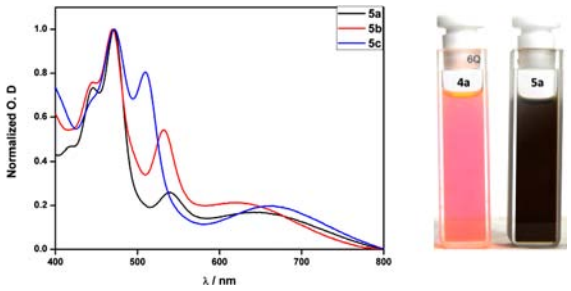


Figure 3. Absorption profiles of **5a**–**c** in chloroform (~10^{-6} M).

low energy transitions at 540 and 648 nm. The intense high-energy band at 472 nm can be attributed to π–π^* transition of the PBI backbone. This band is significantly blue-shifted compared to the π–π^* transition of the parent PBI **4a**. Further, the appearance of the two low energy bands is indicative of a charge-transfer (CT) transition. The peak centered around 648 nm is broad and covers a range from 600 to 800 nm.

This observation is in line with expected absorption characteristics of PBI derivatives with strong electron donors having CT behavior.[21,39] The absorption features including CT band intensity heavily depend on the nature of the substituent present on the phenyl moiety in addition to the azepine nitrogen. This is clearly reflected in the case of **5c** where the presence of an additional electron-donating *N*,*N*-dimethylamino- substituent significantly enhances the absorption intensity. The charge transfer bands in the bathochromic region disappeared when a chloroform solution containing 10^{-6} M **5a** was protonated with trifluoroacetic acid (Figure 4). The

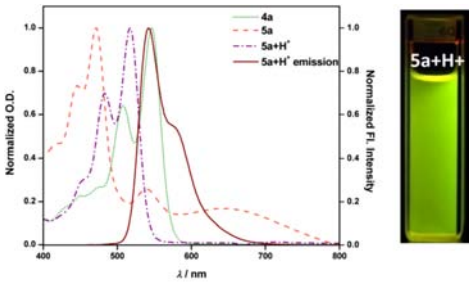


Figure 4. UV–vis absorption spectra of **4a** and **5a** along with the emission spectra of protonated **5a**.

protonation resulted in a red-shift of the π–π^* transition of the PBI core to 519 nm. This further confirms that **5a** has a provision for an intramolecular CT behavior. As expected, the fluorescence that was quenched in neutral **5a** was regained after protonation.

To gain further insights into the delocalization of HOMO and LUMO and the effect of substituents on them, DFT calculations were performed at the CAM-B3LYP/6-311g** level using the Gaussian 09 suite of programs.[43] HOMO is delocalized over the whole PBI core with slightly more contribution from the azepine ring fragment (Supplementary Figure S27). The LUMO is predominantly spread over the main PBI framework, leaving little contribution from the seven-membered heterocyclic ring. In case of **5c**, the contribution of *N*,*N*-dimethylaminophenyl moiety toward the HOMO is significant compared to other substituents. Hence, the broad band around 650 nm can be attributed to HOMO → LUMO transition that appears to be of CT in origin.

The structural rigidity was further confirmed by cyclic voltammetric studies. All three molecules **5a**–**c** showed two reversible reductions in the range −0.7 and −0.9 V in dichloromethane containing 0.1 M tetrabutylammonium-hexafluorophosphate (Table 1 and Supplementary Figure

Table 1. Absorption and Electrochemical Details in $CHCl_3$

compd	λ_{max} (nm)/ε (M^{-1} cm^{-1})	E_{red} (V)	HOMO (eV)[a]	LUMO (eV)[a]
5a	472 (27600), 540 (8000), 648 (CT, 5500)	−0.71, −0.85	−6.70	−2.52
5b	470 (21700), 533 (11900), 621 (CT, 4900)	−0.69, −0.83	−6.99	−2.57
5c	472 (45000), 510 (37500), 667 (CT,12700)	−0.78, −0.91	−6.47	−2.36

[a]From TDDFT/CAM-B3LYP 6-311g(d,p).

S15), with respect to saturated calomel electrode (SCE). Compared to that of alkynyl linked **4a**–**c**, these values were considerably cathodic. This fact further substantiates that the alkyl groups present on the azepine nitrogen act as donor moieties, thereby making the PBI core less electron-deficient.

The reductions of **5c** become increasingly difficult due to the presence of two electron-donating moieties on its periphery reflecting the trend observed in absorption studies. The redox properties thus demonstrate the effective electronic tunability offered by various phenyl substituents, which is highly desirable for various molecular electronic applications.

In summary, we have succeeded in obtaining a novel panchromatic absorbing chromophore via a DBU-mediated specific azepine ring formation at the sterically congested PBI bay position. This turned out to be a straightforward and amenable method for the construction of a new class of azepino-based PBI chromophores without the use of any metals. The photophysical, electrochemical, and computational studies on these PBI derivatives provide important insights into the modulation of optoelectronic properties of these novel dyes. The solid-state structures of the chromophores reveal a distorted boat-shaped azepine ring, which leads to a distinctive core-conjugation resulting in exceptional photophysical characteristics. Most importantly, the tunability of the absorption as well as redox behavior via the substituents on the attached phenyl ring hints at the possible application of these molecules as promising next generation panchromatic dyes. Collectively, the photophysical and redox versatility of azepino-perylene-bisimide derivatives presented here can well be exploited for various futuristic applications where a precise tunability is required at the molecular level.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic and spectroscopic characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sankar@iiserb.ac.in.

dx.doi.org/10.1021/ol501822c | *Org. Lett.* 2014, 16, 3994–3997

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors sincerely thank Dr. Alakesh Bisai, IISER Bhopal for thoughtful comments on mechanistic details; IISER Bhopal for the infrastructure; and DST, New Delhi for funding. R.M. and P.P. thank UGC, New Delhi for their SRF.

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