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## **Stringing the PDI Bow**

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**Abstract:** This study explores a new mode of contortion in perylene diimides where the molecule is bent, like a bow along its long axis. We synthesize these bowed PDIs through a facile 4-fold Suzuki macrocyclization with aromatic linkers and a tetraborylated perylene diimide that introduces strain and results in a bowed structure. By altering the strings of the bow, the degree of bending can be controlled from flat to highly bent. Through spectroscopy and quantum chemical calculations, we demonstrate that the energy of the lowest unoccupied orbital can be controlled by the degree of bending in the structures and the energy of the highest occupied orbital can be controlled to a large extent by the constitution of the aromatic linkers. The important finding is that the bowing results not only in red-shifted absorptions but also more facile reductions.

In this study, we unveil a new type of contortion in perylene-3,4,9,10-tetracarboxylic diimide (PDI, Figure 1a) that bends it like a bow along its long axis and in the process, tunes and decreases the excited state energy as the degree of bowing increases. PDI and its derivatives have been extensively investigated as electronic and optoelectronic materials in organic field effect transistors (OFETs),<sup>[1]</sup> organic photovoltaics (OPVs),<sup>[2]</sup> organic redox flow batteries,<sup>[3]</sup> organic photodetectors,<sup>[4]</sup> and in many other applications.<sup>[5]</sup> PDI plays a prominent role in such important processes as charge transport, energy transport, singlet fission, and photoinduced electron transfer at the core of these organic materials.<sup>[1d, 6]</sup> For many applications of PDI, it is beneficial to contort the core of the PDI away from planarity.[1f, 1i, <sup>2, 4]</sup> For example, a non-planar, contorted core drastically improves solar cell device performance and provides a rich design motif for non-fullerene electron acceptors in optoelectronic devices.[2]

What we describe here is an understanding of how a new type of contortion tunes the energy of PDI's electronic transitions. Contorting the PDI core helically (Figure 1b) decreases the energy of the HOMO-LUMO transition but to some extent increases the energy of the LUMO.<sup>[7]</sup> What we find here is that bowing the PDI core (Figure 1c) decreases the energy of the LUMO. The reason for this difference has to do with the overlap of the nascent  $\pi$ -bond in the LUMO of the PDI, which is enhanced by bowing the PDI and diminished by twisting (Figure

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1d). The important finding is that the bowing results not only in red-shifted absorptions but also more facile reductions. This mode of molecular contortion provides a previously unexplored tuning knob for the singlet and triplet energies of PDI<sup>[8]</sup> and its related polycyclic aromatic hydrocarbons<sup>[8-9]</sup> as demonstrated by our earlier work<sup>[8]</sup> that compound **1d** showed an increase in the singlet fission rate by 2 orders of magnitude.



Scheme 1. Synthesis of 1a-1d.



**Figure 1.** (a) PDI. (b) helically twisted PDI. (c) bowed PDI. (d) PDI showing the virtual pi-orbitals in the LUMO between the two naphthalenes, having poorer overlap in helical configuration and greater overlap in the bowed configuration.

Bent aromatic molecules, such as cycloparaphenylenes (CPPs),<sup>[10]</sup> [n]paracyclophanes,<sup>[11]</sup> [n](2,6)azulenophanes,<sup>[12]</sup> [n](2,7)pyrenophanes<sup>[13]</sup> and [n](2,11)teropyrenophanes,<sup>[14]</sup> are synthesized through multi-step cyclization strategies to introduce the high degree of strain. Here, we bend the PDI core through a four-fold Suzuki coupling between two aromatic linkers and the PDI tetraborate<sup>[15]</sup> (Scheme 1 and ESI). It's the first time that this mode of contortion has been applied to a very important class of optoelectronic materials—the PDI family. The length of the linkers, the steric repulsion between the central aromatic units

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and the PDI bay, and the repulsion of the outer aromatic units with the imide oxygen atoms together bend the PDI into a bow shape.

Figure 2 displays both the chemical structures we prepared for this study (**1a-1d**) and the corresponding molecular structures from single crystal X-ray diffraction (SCXRD). The important finding is that by altering the strings (the aromatic linkers), the degree of bending in the bow (the PDI core) was changed. From the X-ray diffraction analysis, **1a** is essentially flat, having a slight twist to its PDI core. The bowing in **1b-1d** suggests that their strings are under significant tension. Homodesmotic calculations reveal that indeed the strain increases through this series with **1a** being the least strained

and **1d** being the most strained (ESI, homodesmotic calculations). Table 1 tabulates the strain energy from these calculations and other structural metrics. The structures we obtained from single crystal X-ray diffraction are essentially the same values as those obtained from the density functional theory (DFT) calculations (Figure S6). Table 1 also summarizes the structural parameters. One measure of the degree of bowing in these structures is the angle between the two naphthalene units in the perylene, which increases as the degree of bowing increases:  $34^{\circ}$  for **1b**,  $44^{\circ}$  for **1c** and  $45^{\circ}$  for **1d**. Similarly, the distance between the two nitrogen atoms of the PDI also decreases as the degree of bowing increases (Table1).



Figure 2. (a) chemical structures of 1a-1d. (b) SCXRD structures of 1a-1d. (ShelXT<sup>3</sup> was used for single-crystal analysis.)

Table 1. Structural parameters and calculations of the strain for 1a-1d.

	N to N distance [Å]		Bend angle [°]			Strain energy [kcal/mol]
	crystal	calc.	crystal	Calc.	-	
1a	11.36	11.35				30
1b	10.90	11.04	37.57	34.09		32
1c	10.42	10.49	42.96	43.66		33
1d	10.25	10.31	42.95	44.67		42

Variable temperature (VT) <sup>1</sup>H NMR studies (Figure S1-S4) reveal these compounds have a much more complex but interesting behavior in solution. The anti/syn (anti/syn denotes the two strings are on the opposite/same side of the PDI core) isomers and their interconversions were detected for **1a** and **1b**, but not for **1c** and **1d**, which are conformationally locked.

Furthermore, the *p*-phenyl and the 2,5-thienyl linkers in **1a** and **1b** are rotating fast on the NMR timescale at all temperatures tested. It is in good agreement with our DFT calculations on the energies of the syn/anti isomers of **1a-1d** (Table S6). For **1a** and **1b**, the energy differences are as small as 1.7 kcal/mol, while for **1c** and **1d** the values are as large as 11.9 kcal/mol. For **1c** and **1d**, even though the syn/anti isomer conversions were not detected between 230 K to 400 K (Figure S3 and S4, see ESI for detailed explanations), the rotation and waggling behaviors of the 2,5-thienyls in **1c** and the *p*-phenyls in **1d** are very different. For **1c**, the fast rotation of the 2,5-thienyls is frozen below 260 K (Figure S3) and converts to the waggling mode. While in **1d**, the *p*-phenyls can only waggle at temperature below 340 K and then start to rotate freely when the temperature is raised above 375 K.

We first examined the consequences of bowing the PDI on its optical absorbance. Figure 3a displays the UV-vis spectra for 1a-1d. Bowed PDIs show red-shifted optical absorptions relative to both flat and helically twisted PDI. For example, a comparison of slightly bent 1a and the strongly bowed 1d reveals an ~50 nm red shift. While it is difficult to compare across the set in detail (for example, the thiophene-containing bridges are chemically quite different than the phenyl-containing bridges, and charge transfer between thienyl moiety and the PDI is also a factor in the UV-vis spectra for 1b and 1c), the more general conclusion is that a greater degree of bowing leads to greater red-shifted absorbances. In the simplest approximation, this suggests that bowing either raises the HOMO energy or lowers the LUMO energy (or effects some combination of the two). 1a-1d showed fluorescent maximum at 625, 612, 668 and 617 nm with quantum yields of 0.6%, 0.9%, 0.8% and 31.6%, respectively (Figure S5).



**Figure 3.** UV/vis absorption (a) in DCM (1 x  $10^{-5}$  M) and cyclic voltammetry (b) of **1a-1d** with Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as supporting electrolyte, Ag/AgCl as reference electrode and the Fc/Fc<sup>+</sup> redox couple as an internal standard. (The two pink dashed lines indicate the first redox peaks of **1b**).

We can use cyclic voltammetry to probe the effect that bowing has on the reduction potential of PDI and use this to estimate the LUMO energies of the bowed PDIs. Figure 3b contains the CVs for **1a-1d**. The trend is clear: it is easier to reduce the PDI to PDI<sup>-</sup> as the degree of bowing in the molecular structures increases. It's worth noting that **1b** has a smaller bend angle than that of **1c**, but showed similar reduction potential due to additional influence of a stronger charge transfer than that of **1c** (Figure S13-14 and Figure S16). With these data in hand, we draw the simple conclusion that destabilization of the PDI nucleus by this longitudinal bowing reduces the LUMO energy.

These results for the longitudinally bowed PDIs stand in contrast to the behavior of helically twisted PDIs. Destabilizing the PDI nucleus by helical twisting generally yields more energetically demanding reductions despite the similar red-shifted HOMO-to-LUMO transitions.<sup>[7]</sup> We used DFT calculations to learn more about these trends. In each of the distortions, the two naphthalene imide moieties remain largely unaffected, therefore we dissected PDI into its constituent halves.



Figure 4. The HOMO and LUMO orbitals of: (a) the naphthalene imide and (b) the PDI.

In Figure 4 we show the HOMO and LUMO of naphthalene imide and compare these to the HOMO and LUMO of the parent, planar PDI. The first item of note is that the HOMO of PDI is a linear combination (appropriately normalized) of the HOMO on the upper naphthalene imide and the negative of the HOMO on the lower naphthalene imide. The change of phase between the two halves (upper and lower) of the orbital indicate that there is a planar node bisecting this orbital, and this planar node raises the energy of this orbital. In short, the HOMO of PDI is  $\pi$ -antibonding with respect to the upper and lower naphthalene imide fragments.

The second item to note is that the LUMO of PDI is similarly a linear combination of the LUMO of the upper naphthalene imide and that of the lower naphthalene imide, however in this case the two are combined with the same phase (sign). This LUMO is  $\pi$ -bonding with respect to the upper and lower fragments, and this is underscored by the significant decrease in its orbital energy relative to that of the naphthalene imide LUMO (-3.5 eV versus -2.4 eV). Our heuristic conclusion

is that PDI can be viewed as the fusion of two naphthalene imides, and  $\sigma$ -bonds accomplish this fusion. In the ground state the  $\pi$ -interaction between the two halves is repulsive, but in the HOMO-to-LUMO excited state the repulsive  $\pi$ -interaction become attractive.

This coupling between the two halves of the molecule in the PDI system and particularly its effect on the LUMO system rationalizes why twisting or bending the PDI lowers the energies of the HOMO-to-LUMO transitions and affects their LUMOs in very different ways. As PDI twists along its long axis the energy of its HOMO is affected because this axis is perpendicular to the central nodal plane of the orbital, however the energy of the LUMO should increase since the twist is disturbing the smooth continuity between the two halves of the LUMO. While the energies of both orbitals may increase, the HOMO is affected more than is the LUMO. In the case of bowing the situation is reversed: the energy of the HOMO is raised because orbital density is forced closer to the central node, while the energy of the LUMO is lowered because its inter-naphthyl π-bonding is enhanced. In this case as well, the energies of both orbitals may be affected with bowing, but that of the HOMO will increase more than that of the LUMO.

We show here a means to control the degree of bowing in PDI. We synthesize these bowed PDI structures by a 4-fold Suzuki macrocyclization. By tuning the groups that bridge the PDIs we can adjust the degree of bowing and therefore the energy of the orbitals. We use quantum chemical calculations to understand the red-shifted absorptions in the bowed structures. PDI is best viewed as two naphthalene-1,8-imides  $\sigma$ -bonded to one another. The excited states, and therefore the practical utility of PDIs, can be rationally manipulated by controlling how the two naphthalene-1,8-imides interact. The bowed structures provide better overlap between the nascent pi-bond of the LUMO and also more facile reductions. These structures also provide a means to tune the singlet and triplet energy levels, which will be important in using these molecules as building blocks for materials exhibiting efficient singlet fission.

#### **Experimental Section**

For experimental and calculation details, see the Supporting Information. The crystallographic information files (CIFs) are deposited at the Cambridge Crystallographic Data Centre (CCDC, http://www.ccdc.cam.ac.uk) with CCDC numbers: 1991412 for **1a**, 1991413 for **1b**, 1991414 for **1c** and 2006155 for **1d**.

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#### COMMUNICATION

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