Stringing the Perylene Diimide 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. These bowed PDIs were synthesized through a facile fourfold 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, it is demonstrated that the energy of the lowest unoccupied orbital can be controlled by the degree of bending in the structures and that 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), organic photovoltaics (OPVs), organic redox-flow batteries, and organic photodetectors, and in many other applications. 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.

For many applications of PDI, it is beneficial to contort the core of the PDI away from planarity. For example, a nonplanar, contorted core drastically improves solar cell device performance and provides a rich design motif for nonfullerene electron acceptors in optoelectronic devices.

What we describe here is an understanding of how a new type of contortion tunes the energy of the electronic transitions of PDI. 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. 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 n-bond in the LUMO of the PDI, which is enhanced by bowing of the PDI and diminished by twisting (Figure 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 dial for the singlet and triplet energies of PDI and its related polycyclic aromatic hydrocarbons, as demonstrated by our earlier work that found that 1d showed an increase in the singlet fission rate by two orders of magnitude.

Bent aromatic molecules, such as cyclopentaphenylene (CPPs), [2]paracyclophanes,[11] [n](2,6)azulenophanes,[12] [n](2,7)pyrenophanes,[13] and [n](2,11)teropyrenophanes,[14] are synthesized through multistep cyclization strategies to introduce the high degree of strain. Here, we bend the PDI core through a fourfold Suzuki coupling between two aromatic linkers and the PDI tetraborate (Scheme 1, see also the Supporting Information). This is 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 and the PDI bay, and the repulsion between

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Figure 1. a) PDI. b) Helically twisted PDI. c) Bowed PDI. d) PDI showing the virtual π-orbitals in the LUMO between the two naphthalene moieties, with poorer overlap in the helical configuration and greater overlap in the bowed configuration.
the outer aromatic units and 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 determined by single-crystal X-ray diffraction (SCXRD). The important finding is that altering the strings (the aromatic linkers) changed the degree of bending in the bow (the PDI core). X-ray diffraction analysis shows that 1a is essentially flat, with a slight twist in its PDI core. The bowing in 1b–1d suggests that their strings are under significant tension. Homodesmotic calculations reveal that the strain indeed increases through this series, with 1a being the least strained and 1d being the most strained (see the Supporting Information, 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 as those obtained from 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 unit, which increases as the degree of bowing increases: 34° for 1b, 44° for 1c, and 45° for 1d. Similarly, the distance between the two nitrogen atoms of the PDI also decreases as the degree of bowing increases (Table 1).

Variable-temperature (VT) 1H NMR studies (Figures 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 quickly on the NMR timescale at all the temperatures tested. This finding is in good agreement with our DFT calculations on the energies of the syn/anti isomers of 1a–1d (Table S6). The energy differences for 1a and 1b are as small as 1.7 kcal mol⁻¹, while the values for 1c and 1d are as large as 11.9 kcal mol⁻¹. For 1c and 1d, even though the syn/anti isomer conversions were not detected between 230 K and 400 K (Figures S3 and S4, for detailed explanations see also the Supporting Information), the rotation and waggling behaviors of the 2,5-thienyl moieties in 1c and the p-phenyl groups in 1d are very different. For 1c, the fast rotation of the 2,5-thienyl units is frozen below 260 K (Figure S3) and converts into the waggling mode. In contrast the p-phenyl groups in 1d can only wagg at temperatures below 340 K and then start to rotate freely when the temperature is raised above 375 K.

We first examined the effect 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 a red shift.

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

<table>
<thead>
<tr>
<th></th>
<th>N to N distance [Å]</th>
<th>Bend angle [°]</th>
<th>Strain energy [kcal mol⁻¹]</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>11.36</td>
<td>–</td>
<td>30</td>
</tr>
<tr>
<td>1b</td>
<td>10.90</td>
<td>11.04</td>
<td>37.57</td>
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<tr>
<td>1c</td>
<td>10.42</td>
<td>10.49</td>
<td>42.96</td>
</tr>
<tr>
<td>1d</td>
<td>10.25</td>
<td>10.31</td>
<td>44.67</td>
</tr>
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shift of about 50 nm. Although it is difficult to compare across the set in detail (for example, the thiophene-containing bridges are chemically quite different from the phenyl-containing bridges, and charge transfer between the thienyl moiety and the PDI is also a factor in the UV/Vis spectra for 1b and 1c), a 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 maxima at λ = 625, 612, 668, and 617 nm with quantum yields of 0.6%, 0.9%, 0.8%, and 31.6%, respectively (Figure S5).

Cyclic voltammetry was used to probe the effect that bowing has on the reduction potential of PDI and to estimate the LUMO energies of the bowed PDIs. Figure 3b contains the cyclic voltammograms for 1a–1d. The trend is clear: it is easier to reduce the PDI to PDI/C0 as the degree of bowing in the molecular structures increases. It is worth noting that 1b has a smaller bend angle than 1c, but showed a similar reduction potential because of the additional influence of a stronger charge transfer than that in 1c (Figures S13, S14, and 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–LUMO transitions.[7] 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.

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 π-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 π-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, with σ-bonds accomplishing this fusion. In the ground state, the π-interaction between the two halves is repulsive, but in the HOMO–LUMO excited state the repulsive π-interaction becomes 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–LUMO transitions and affects their LUMOs in very different ways. As PDI twists along its
These are not the final page numbers!


[16] Deposition Numbers 1991412 (for 1a), 1991413 (for 1b), 1991414 (for 1c) and 2006155 (for 1d) 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.
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**Bow to demands:** A new mode of contortion in perylene diimides has been investigated, where the molecule is bent along its long axis like a bow. By adjusting the tension in the strings of the bow, the degree of bending can be controlled from flat to highly bowed. The important finding is that the bowing results not only in red-shifted absorptions but also in more facile reductions.