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Selective Bromination of Perylene Diimides under Mild Conditions

Paramasivan Rajasingh,[†] Revital Cohen,[‡] Elijah Shirman,[†] Linda J. W. Shimon,[‡] and Boris Rybtchinski*,[†]

Department of Organic Chemistry and Chemical Research Support Unit, Weizmann Institute of Science, Rehovot 76100, Israel

boris.rybtchinski@weizmann.ac.il

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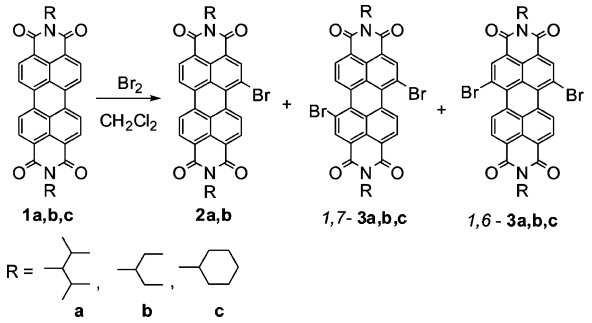

A novel method for the bromination of perylene diimides, PDI (**1**), under mild conditions is reported. Variation of the reaction conditions allows mono- and dibromination of PDIs to afford **2** and **3** (these can be separated through standard procedures) or exclusive dibromination to afford **3**. Pure 1,7 regioisomers are obtained through repetitive crystallization. The structure of 1,7-**3b** was elucidated by a single-crystal X-ray analysis. The facility of the bromination reaction, which decreases in the order **1a** > **1b** > **1c**, depends on PDI aggregation propensities. Monobrominated PDIs were utilized for the syntheses of novel unsymmetrical piperidinyl (**4a** and **4b**) and trimethylsilylethynyl derivatives (**5a** and **5b**). Computational studies (DFT) on imide substituent rotation in PDIs reveal that in the case of bulky groups there is a restricted rotation leading to isomers, in agreement with our experimental results. An aromatic core twist in PDIs bearing one and two bromine substituents was also investigated by DFT.

Introduction

Perylene diimides (PDIs) are outstandingly versatile organic chromophores.[1] They demonstrate exceptional thermal and photochemical stability, strongly absorb visible light, and show high fluorescence quantum yields.[2−4] PDIs have been utilized as industrial dyes,[1] electronic materials,[5−8] sensors,[9,10] photovoltaics,[11−15] and building blocks for light-harvesting and artificial photosynthetic systems.[16−23] Importantly, photophysical and redox properties of PDIs can be conveniently modified through substitution in the aromatic core at the positions 1, 6,

* Author to whom correspondence should be addressed. Phone: 972-8-9342172. Fax: 972-8-9344142.
[†] Department of Organic Chemistry.
[‡] Chemical Research Support Unit.

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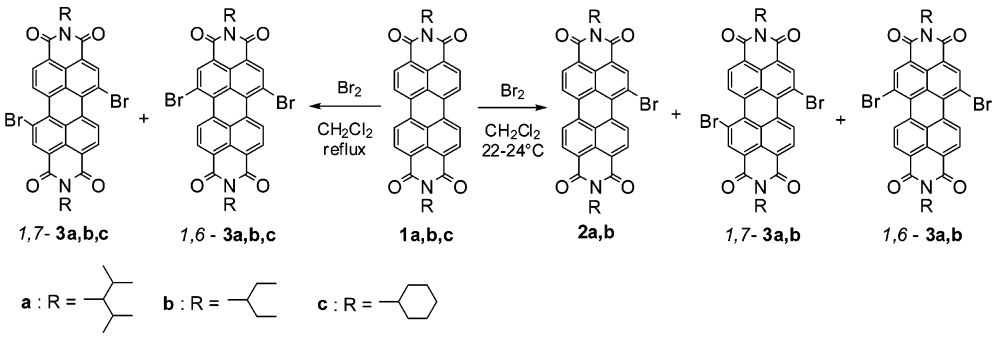
SCHEME 1. Bromination of 1a−c



7, and 12 (bay region).[2] Substitutions at bay positions and expansion of the PDI core are usually carried out starting from the halogenated derivatives, particularly brominated PDIs.[2,4] These are almost exclusively synthesized through bromination of perylene dianhydride (PDA) in concentrated H_2SO_4 upon heating, followed by imidation with amines.[24] Usually this bromination procedure affords a mixture of di-, tri-, and tetrabrominated PDIs. The dibromoperylene diimides contain 1,7 (major) and 1,6 (minor) regioisomers. Recently, purification of the 1,7 regioisomer by repetitive recrystalization has been reported.[25] Among the brominated perylene diimides, 1,7-dibrominated PDIs are the most widely used as starting materials for a broad variety of PDI derivatives.[2,4]

Herein we report on PDI bromination methodology that employs mild conditions (organic solvent, room temperature) resulting in facile formation of mono- and dibrominated perylene diimides. The selectivity of the reaction toward exclusive dibromination can be controlled through variation of the reaction conditions. To the best of our knowledge, our method is the first reported procedure allowing exclusive dibromination of PDIs. Computational studies on the imide group rotation and PDI aromatic core twist are also reported, providing insight into the inherent dynamics of PDI molecules.

Results and Discussion

Our approach to bromination of PDIs was based on the following observation. When we performed literature procedures to obtain PDI derivatives functionalized in the bay region,[2] the reactions appeared to be significantly more facile in the case of PDIs bearing bulkier imide substituents, apparently because of the reduced aggregation. Thus, we chose for our studies on bromination three known PDI derivatives bearing dimethylpentyl, ethylpropyl, and cyclohexyl substituents (compounds **1a**,[26] **1b**,[27] and **1c**,[28] respectively, see Scheme 1). The solubility of the compounds decreases in the order **1a** > **1b** > **1c**,[3] reflecting the decrease of the imide substituent bulk and the increase of PDI aggregation propensity, which is controlled by $\pi-\pi$ stacking.[2−4] Notably, compound **1a** has been reported to demonstrate very interesting solid-state properties (strong, anisotropic fluorescence, small Stokes shifts);[26] hence, bromination of **1a** would be highly desirable and can lead to novel photonic materials.

High resolution ^{1}H and ^{13}C NMR spectra of compound **1a**[26] (starting material in bromination reaction) suggested that two very similar isomers in a 1:1 ratio are present, see Figure S1 (Supporting Information). This phenomenon was addressed by computational studies (see below), revealing that the isomers are due to restricted rotation (kinetic barrier of ∼32 kcal/mol) of the bulky dimethylpentyl group around the N−C bond; see Figure 3 for the structures of the rotational isomers. Restricted rotation of bulky PDI imide substituents (2,5-di-*tert*-butylphenyls) leading to two isomers has been reported.[29−31] All dimethylpentyl PDI derivatives described below contain two rotational isomers in 1:1 ratio. Clear observation of the two isomers in the NMR spectra of dimethylpentyl PDIs was possible only using 500 MHz NMR.

In order to accomplish bromination, dimethylpentyl PDI, compound **1a**, was stirred with excess of bromine (68 equiv) in dichloromethane at 22−24 °C for 2 days (Scheme 1), resulting in dibrominated PDI **3a** (26%), monobrominated PDI **2a** (57%), and unreacted starting material **1a** (15%). Compounds **2a** and **3a** were separated by column chromatography. They were characterized by multinuclear NMR spectroscopy, mass spectroscopy, elemental analysis, UV−vis and fluorescence spectroscopy, and electrochemistry; see Table 1. Mass spectroscopy and elemental analysis of **2a** indicated that it is a monobrominated derivative, while NMR spectra showed that two very similar isomers in a 1:1 ratio were present (both of them corresponded to the PDI brominated in the bay region) because of restricted rotation of the bulky dimethylpentyl group around the N−C bond. Notably, in the ^{13}C NMR spectrum of **2a** the carbonyl groups give rise to eight signals of equal

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TABLE 1. Absorption and Emission Properties of Compounds 2a,b−5a,b in Chloroform, and Redox Potentials in Dichloromethane (in V vs SCE)[a]

compound	absorption λ_{max}[b] (ϵ)[c]	emission λ_{em}[b] (λ_{ex})[b]	Φ	$^1E_{1/2}^{RED}$	$^2E_{1/2}^{RED}$	$E_{1/2}^{OX}$
2a	524 (74669)	538 (488)	0.92	−0.59	−0.80	
2b	524 (61578)	537 (488)	0.88	−0.59	−0.79	
1,7-**3a**	526 (49825)	545 (490)	0.82	−0.52	−0.73	
1,7-**3b**	526 (45474)	545 (490)	0.81	−0.54	−0.76	
4a	602 (18481)	727 (600)	0.20	−0.66	−0.86	1.06
4b	601 (18009)	726 (600)	0.19	−0.74	−0.93	1.06
5a	537 (66690)	547 (493)	0.76	−0.61	−0.81	
5b	537 (60348)	546 (493)	0.76	−0.60	−0.80	

[a] All measurements were performed at room temperature, oxidation potentials of **2**, **3**, and **5** are high as typical of PDI systems,[2] beyond the limits allowed by our solvent/electrolyte system. [b] In nm. [c] In M^{-1} cm^{-1}.

intensity (Figure S2) instead of four signals; the latter would be expected for a compound with facile rotation of the imide substituents.

The 500 MHz ^{1}H NMR spectra of **3a** showed the presence of 1,7-**3a** and 1,6-**3a** regioisomers[25] (in a 5:1 ratio, respectively, Figure S3), which could not be separated using column chromatography. The major 1,7-**3a** regioisomer can be purified by repetitive recrystallization from a dichloromethane/hexane mixture (v/v, 1:1), similar to the procedure reported by Würthner et al.[25] The recrystallization process was monitored by 500 MHz ^{1}H NMR spectroscopy (Figure S3). After three successive recrystallizations, the pure regioisomer 1,7-**3a** was obtained as indicated by the ^{1}H (Figure S3b) and ^{13}C NMR spectra (Figure S4b). In the mother liquor, the isomer 1,6-**3a** is a major species (Figures S3 and S4).

Interestingly, exclusive dibromination can be also achieved: reflux of a dichloromethane solution of **1a** with bromine (68 equiv) for 24 h results in exclusive formation of dibrominated compound **3a** (yield 92%, 1,7 to 1,6 isomer ratio 3:1). The regioisomers can be separated using recrystallization as described above.

Bromination of ethylpropyl PDI **1b**[27] (Scheme 1) was performed using conditions similar to those employed for **1a**. The monobromo PDI (**2b**) and dibromo PDI (**3b**) were separated by column chromatography, and pure 1,7-**3b** regioisomer (Figure S5) was obtained after three repetitive recrystallizations from a dichloromethane/hexane mixture (v/v, 1:1). Compounds **2b** and **3b** were fully characterized; see Table 1. Exclusive formation of dibrominated derivative **3b** takes place upon reflux in dichloromethane with bromine for 2 days (89% yield, 1,7 to 1,6 isomer ratio 3:1). Our computational studies (see below) indicate that the rotation of an ethylpropyl group around the N−C bond occurs with a barrier of 17 kcal/mol. The time scale of this rotation (∼300 ms) is comparable to the NMR time scale, in agreement with our experimental observations: at room temperature no rotational isomers were observed, whereas certain broadening of NMR signals is observed for **2a** and **3a**. While ^{1}H NMR is well resolved at room temperature, showing only very slight broadening of several signals, ^{13}C NMR was measured at 50 °C to eliminate signal broadening.

The structure of 1,7-**3b** was further elucidated by X-ray crystallography.[32] Single crystals of 1,7-**3b** suitable for X-ray analysis were grown from dichloromethane/hexane solution. The central six-membered ring is twisted (Figure 1) with dihedral angles of 23.3° and 21° associated with bay area carbon atoms C1−C22−C34−C12 and C6−C23−C33−C7, respectively, these values being similar to the core twist angle of 24° in *N*,*N*′-dicyclohexyl-1,7-dibromo PDI.[25] Overall, the structure of 1,7-**3b** is similar to the reported crystal structure of *N*,*N*′-dicyclohexyl-1,7-dibromo PDI.[25]

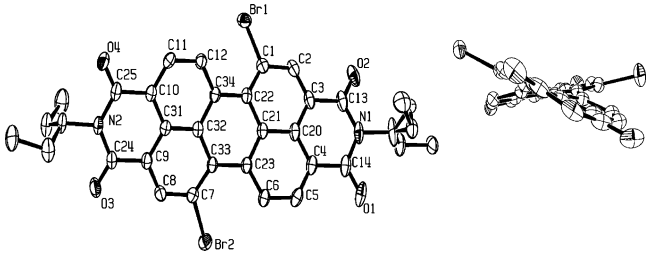
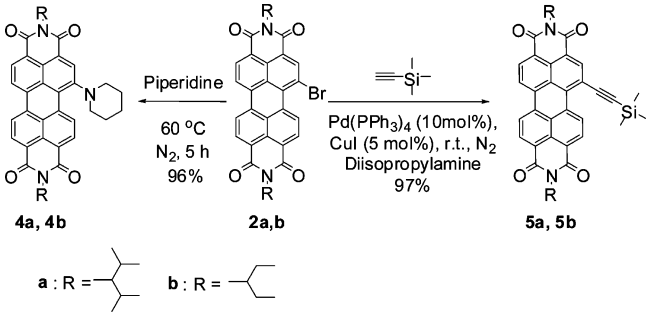


FIGURE 1. ORTEP drawing of structure of 1,7-**3b** (left, 50% probability, hydrogens are omitted for clarity) and view along the N−N axis showing twisted perylene backbone (right, 50% probability, alkyl groups at imide nitrogens and all hydrogens are omitted for clarity). There is a minor disorder in one of the ethylpropyl groups. Selected bond lengths (Å): Br1−C1, 1.905(4); C1−C2, 1.402(5); C2−C3, 1.375(6); C3−C13, 1.486(5); C13−N1, 1.395(6); C13−O2, 1.225(6); C3−C20, 1.406(6); C20−C21, 1.423(5); C21−C22, 1.434(5); C22−C1, 1.403(5); C22−C34, 1.468(5).

SCHEME 2. Monosubstituted PDI Derivatives



Compound **1c**[28] does not undergo bromination at room temperature. It was brominated upon reflux in dichloromethane for 4 days to give *exclusively dibrominated* derivative **3c** (85% yield, mixture of 1,7 and 1,6 regioisomers in 4:1 ratio). The regioisomer separation procedure for **3c** has been previously reported.[25] Harsher conditions had to be employed for bromination of **1c** due to its higher aggregation propensity and lower solubility in comparison with **1a** and **1b**.[3] Under these conditions, the monobrominated derivative most probably reacts further with bromine, resulting in exclusive dibromination.

We observe that the facility of the bromination reactions (as exemplified by the reaction times and temperatures) decreases in the order **1a** > **1b** > **1c**. This trend supports the notion that the reactivity of PDIs depends on their aggregation (which also influences their solubility properties). Notably, while bromination of **1a** is very facile at room temperature, compound **1c** cannot be brominated at ambient temperatures.

While the disubstitution chemistry at 1 and 7 positions of PDIs is well developed,[2] unsymmetrical monosubstitied PDI derivatives are relatively rare.[33−37] As monobrominated PDIs (**2a**,**b**) are readily available through our procedure, they were

(32) Selected crystallographic data for 1,7-**3b**: Crystal system: triclinic, space group: *P*-1, unit cell dimensions: a = 10.5940(2) Å, b = 11.2600-(3) Å, c = 14.3580(3) Å, α = 80.2930(10)°, β = 68.7930(13)°, γ = 89.137-(13)°, V 1571.93(6) Å^3, Z = 2, density (calcd) 1.545 mg/m^3, R indices [I > 2σ(I)]: R1 = 0.0517, wR2 = 0.1422, R indices (all data): R1 = 0.0608, wR2 = 0.1477.

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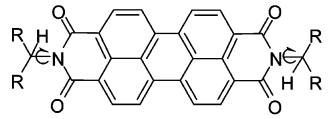

FIGURE 2. Imide substituent rotation in PDIs (**1a**−**c**).

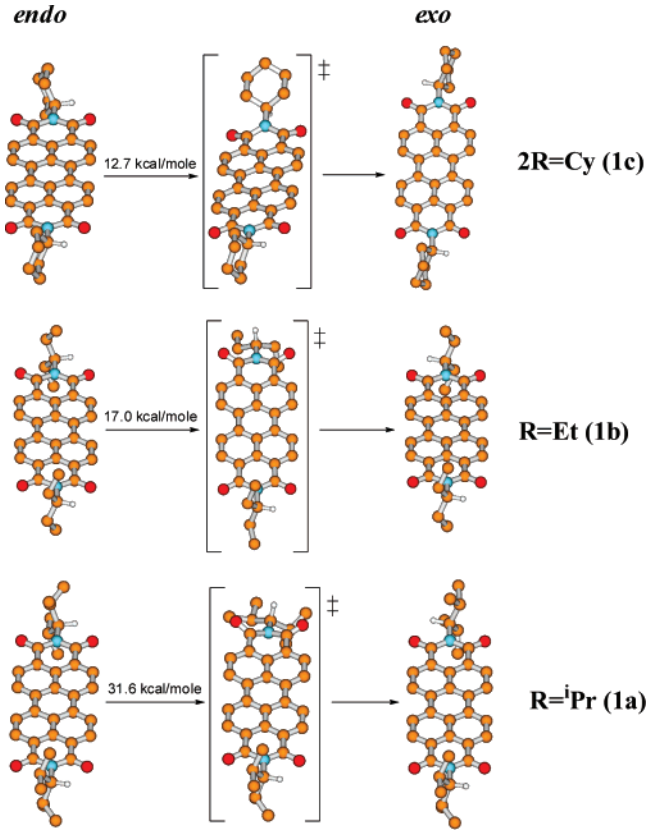

FIGURE 3. Computed structures for rotational isomers and the transition states for imide group rotation. Hydrogens (except for NC*H*R_2) are omitted for clarity.

used for further functionalization at the bay position to give novel unsymmetrical derivatives; see Scheme 2 and Table 1. The nucleophilic substitution of mono bromoperylene diimide (**2a**,**b**) with piperidine[38,39] (Scheme 2) afforded the corresponding monopiperidinyl diimides **4a**,**b**. Sonogashira cross-coupling afforded ethynyl derivatives **5a**,**b** (Scheme 2).

Photophysical and redox properties of monobrominated PDI derivatives **2a**,**b** are similar to those of dibrominated **3a**,**b**. The properties of the latter are very similar to the reported photophysical and redox characteristics of 1,7-dibromo-PDIs.[2] The absorption and emission maxima of mono- and dibrominated PDIs are almost identical to those of nonsubstituted PDIs,[2] despite the PDI core twist in the brominated compounds and electron-withdrawing nature of Br groups. This effect is well

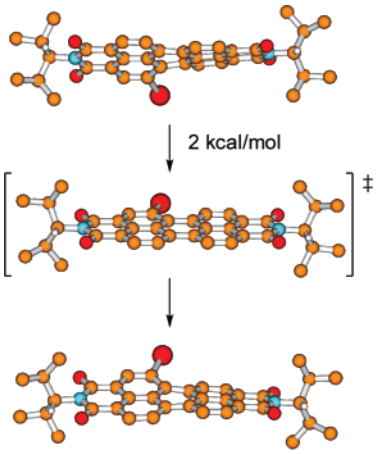

FIGURE 4. Core twist in monobromo-PDI, **2a**.

documented;[2] it is most probably due to an interplay of several factors that result in similar HOMO−LUMO gaps for the brominated and nonsubstituted PDIs. Monopiperidinyl PDI derivatives **4a**,**b** show absorption and emission that are less red-shifted than those observed for disubstituted piperidinyl derivatives (absorption maximum at 680 nm, emission at 770 nm)[38] as expected for lower electron-donating ability of one piperidine group vs two such groups. The emission quantum yields (0.2) are identical for **4a**,**b** and the 1,7-dipiperidinyl PDI derivative.[38] Compounds **5a**,**b** show slightly red-shifted absorption and fluorescence, which is apparently due to extended conjugation involving acetylene groups.

Computational Studies. Imide substituent rotation and PDI ring twist (in the case of brominated derivatives) represent essential properties of the systems described above and can lead to isomer formation. These PDI characteristics are also of fundamental interest, since they describe the inherent dynamics of PDI molecules. To gain insight into these phenomena, we performed DFT studies on imide rotation and ring twist in PDI systems.

DFT calculations at the B3LYP/cc-pVDZ//B3LYP/D95V level of theory were performed for the PDI derivatives used in our studies (Figure 2). For each compound we have located two isomers: exo, where the NC*H*R_2 hydrogen atoms point in opposite directions, and endo, where they point in the same direction (Figure 3).

For each isomer couple we have located the transition state for the rotation around the N−C(sp^3) bond (Figure 3). The rotation free energy kinetic barriers around the N−CHR_2 bonds correspond well to the steric bulk of the imide substituents: 12.7 kcal/mol for 2R = Cy, 17.0 kcal/mol for R = Et, and 31.6 kcal/mol for R = ^{i}Pr. These findings show that the rotation around the N−C bond for 2R = Cy and R = Et can occur at room temperature, while the rotation around the N−C bond for R = ^{i}Pr is restricted because of the larger steric bulk of the dimethylpentyl group, in agreement with our experimental observations. The rotation around the N−C bond for R = Et (rotation time of ca. 300 ms as estimated from Eyring equation) is somewhat comparable to the NMR time scale, which is in agreement with slight broadening of the ^{1}H and ^{13}C NMR signals of **2b**−**5b**. In the case of brominated PDI derivatives the rotational barriers are similar to the nonbrominated molecules. Thus, for monobrominated PDI with R = ^{i}Pr, the N−C

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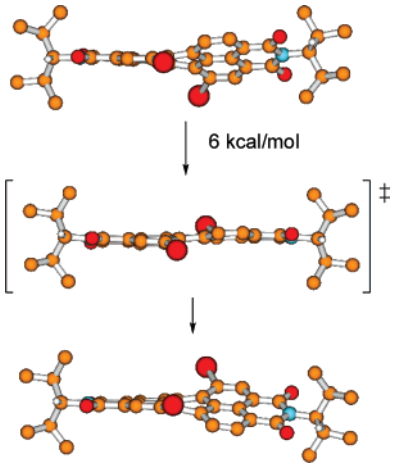

FIGURE 5. Core twist in dibromo-PDI, 1,7-**3a**.

rotation barrier was found to be 32.8 kcal/mol, and for the 1,7-dibrominated PDI with R = ^{i}Pr the barrier for rotation is 32.5 kcal/mol.

In order to address the motion associated with the PDI core twist, we have calculated the structure of the PDI−Br (where R = ^{i}Pr) compound (**2a**, Figure 4). In this case we have found the PDI skeleton to be twisted, as expected for the congested bay region.[2] The free energy barrier for the PDI aromatic core twisting (Figure 4) was found to be rather low, 2 kcal/mol; therefore, core twist is expected to be facile. Accordingly, no additional isomers are expected to be observed as a result of PDI bromination. Similar results were obtained for the PDI derivative with two Br atoms (compound **3a**). The core twist barrier for this case was found to require a slightly higher energy of 6 kcal/mol (Figure 5). It should be noted that the aromatic core structure of the calculated dibromo-PDI (**3a**) corresponds well to the X-ray structure (**3b**), with the similar core twist (dihedral angles associated with the bay area in calculated **3a** are 21.1° and 21.6°; these angles are 23.3° and 21° in the X-ray structure of **3b**).

Conclusions

Brominated perylene diimides, typically used as starting materials in PDI chemistry, are usually synthesized by bromination of perylene dianhydride upon heating in sulfuric acid, followed by imidization. Our study has shown that reaction of PDI with bromine under mild condition results in facile bromination to afford mono- and dibrominated perylene diimides. The variation of reaction conditions also allows bromination of PDIs to exclusively afford dibrominated derivatives in good yields (both 1,7 and 1,6 regioisomers are formed; the major 1,7 isomer can be purified by recrystallization). To the best of our knowledge, the known procedures for PDI bromination do not result in exclusive dibromination, but in mixtures of brominated PDI derivatives.[2]

Readily available monobrominated PDIs (**2a** and **2b**) were utilized to synthesize novel unsymmetrical derivatives, exemplifying the potential chemical diversity that can be achieved. Since the brominated PDI derivatives can be functionalized through a wide variety of available methods, our study provides a convenient synthetic route to mono- and disubstituted PDI derivatives.

Employing DFT calculations, we have addressed the rotation of imide substituents around the N−C bond and PDI aromatic core twist. Bulky substituents such as dimethylpentyl show restricted rotation (barrier of 32 kcal/mol) resulting in observation of two rotational isomers. Smaller groups, such as cyclohexyl (rotation barrier 12.7 kcal/mol) and ethylpropyl (17 kcal/mol) show rotation at room temperature, which is more facile in the case of the less bulky cyclohexyl group. The aromatic core twist is facile for both mono- and dibromo-PDI derivatives, the kinetic barrier for the twist being 2 and 6 kcal/mol, respectively. Thus, while imide substituent rotation can result in isomers, the PDI core twist is fast at ambient conditions and should not result in isomer formation, in agreement with our experimental observations.

Experimental Section

Bromination of *N,N′*-Bis(2,4-dimethylpent-3-yl)perylene-3,4:9,10-tetracarboxylic Diimide (1a). A mixture of **1a**[26] (1 g, 1.7 mmol) and bromine (18.66 g, 0.116 mol) in 60 mL of dichloromethane was stirred at 22−24 °C in a closed round-bottom flask for 2 days. The excess of bromine was removed by air bubbling, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with chloroform as an eluent. The first band was collected to afford dibromo perylene diimide (mixture of 1,7-**3a** and 1,6-**3a** in 5:1 ratio) as an orange solid (330 mg, 26%). The second band afforded 1-bromo *N,N′*-bis(2,4-dimethylpent-3-yl)perylene diimide **2a** (650 mg, 57%) as an orange solid. The third band gave the unreacted perylene diimide **1a** (150 mg, 15%). The regioisomers, 1,7-**3a** and 1,6-**3a**, could not be separated by column chromatography.

Regioisomerically pure 1,7-dibromoperylene diimide (1,7-**3a**) was obtained by repetitive crystallization. The mixure (330 mg) of 1,7-**3a** and 1,6-**3a** (5:1) was crystallized from 50 mL of CH_2Cl_2:hexane (v/v, 1:1) mixture at room temperature for 5 days. The crystallization was repeated at the same conditions for two more times to yield 180 mg (55%) of pure 1,7-**3a** as an orange solid.

1-Bromo-*N,N′*-bis(2,4-dimethylpent-3-yl)perylene-3,4:9,10-tetracarboxylic Diimide (2a). ^{1}H NMR: δ 9.8 (m, 2H), 8.96 (s, 1H), 8.93 (s, 1H), 8.6−8.75 (m, 10H), 4.75 (m, 4H), 2.72 (m, 8H), 1.13 (d, 12H, J = 6.5 Hz), 1.12 (d, 12H, J = 7.0 Hz), 0.95 (d, 12H, J = 7.0 Hz), 0.94 (d, 12H, J = 6.5 Hz). ^{13}C {^{1}H} NMR: δ 165.3, 164.94, 164.89, 164.13, 164.09, 163.81, 163.77, 162.9, 139.6, 138.9, 134.0, 133.94, 133.91, 133.88, 133.63, 133.60, 133.58, 133.57, 133.5, 131.6, 131.1, 130.9, 130.4, 128.92, 128.91, 128.72, 128.71, 128.11, 128.09, 127.0, 124.03, 124.02, 123.9, 123.84, 123.78, 123.75, 123.6, 123.5, 123.41, 123.39, 123.3, 123.2, 123.01, 123.00, 122.98, 122.96, 122.9, 122.7, 122.6, 120.97, 120.95, 120.9, 65.41, 65.35, 65.20, 65.19, 29.11, 29.10, 29.06, 29.0, 21.8, 21.7, 20.6, 20.51, 20.50. MS 664.50 [M^{+}] (calcd 664.19). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 524 (74 669), 488 (48 630), 458 (18 465). Fluorescence ($CHCl_3$): λ_{max} = 538 nm, fluorescence quantum yield Φ_f = 0.92. Anal. Calcd for $C_{38}H_{37}BrN_2O_4$: C, 68.57; H, 5.60; N, 4.21. Found: C, 68.43; H, 5.61; N, 4.33.

1,7-Dibromo-*N,N′*-bis(2,4-dimethylpent-3-yl)perylene-3,4:9,-10-tetracarboxylic Diimide (1,7-3a). ^{1}H NMR: δ 9.52 (d, 1H, J = 8.0 Hz), 9.50 (d, 1H, J = 8.0 Hz), 8.95 (s, 1H), 8.92 (s, 1H), 8.73 (d, 1H, J = 8.0 Hz), 8.68 (d, 1H, J = 8.0 Hz), 4.75 (two triplets merged t, 2H, J = 8.5 Hz), 2.72 (m, 4H), 1.12 (d, 12H, J = 7.0 Hz), 0.94 (d, 12H, J = 7.0 Hz). ^{13}C {^{1}H} NMR: δ 164.7, 164.2, 163.5, 163.0, 138.5, 137.9, 132.90, 132.88, 132.84, 132.77, 132.7, 130.6, 129.9, 129.3, 128.5, 127.1, 123.6, 123.24, 123.22, 123.02, 123.00, 122.64, 122.62, 120.8, 65.44, 65.36, 29.05, 29.02, 21.7, 20.5. MS 742.38 [M^{+}] (calcd 742.10). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 526 (49 825), 490 (33 702), 463 (13 458). Fluorescence ($CHCl_3$): λ_{max} = 545 nm, fluorescence quantum yield Φ_f = 0.82. Anal.Calcd for $C_{38}H_{36}Br_2N_2O_4$: C, 61.30; H, 4.87; N, 3.76. Found: C, 61.35; H, 4.89; N, 3.80.

Bromination of *N,N′*-Bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide (1b). A mixture of **1b**[27] (2 g, 3.77 mmol) and bromine (31.1 g, 0.194 mol) in 100 mL of dichloromethane was stirred at 22−24 °C in a closed round-bottom flask for 4 days. The excess of bromine was removed by air bubbling, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with chloroform as an eluent. The first band was collected to afford dibromoperylene diimide (red solid, 650 mg, 25%) as a mixture of regioisomers (1,7-**3b**: 1,6-**3b** = 5:1). The second band yielded 1-bromo-*N,N′*-bis-(ethylpropyl)perylene diimide **2b** (1.15 g, 50%) as a red solid. The third band gave the unreacted perylene diimide (500 mg, 25%). The regioisomeric dibromoperylene diimides 1,7-**3b** and 1,6-**3b** could not be separated by column chromatography.

Regioisomerically pure 1,7-dibromoperylene diimide (1,7-**3b**) was obtained by repetitive crystallization. The mixure (200 mg) of 1,7-**3b** and 1,6-**3b** (5:1) was crystallized from 50 mL of CH_2Cl_2: hexane (v/v, 1:1) mixture at room temperature for 5 days. The crystallization was repeated at the same conditions for two more times to yield 80 mg (40%) of pure 1,7-**3b** as a red solid.

1-Bromo-*N,N′*-bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide (2b). ^{1}H NMR: δ 9.78 (d, 1H, J = 8.5 Hz), 8.92 (s, 1H), 8.69 (m, 3H), 8.62 (d, 1H, J = 8.5 Hz), 8.61 (d, 1H, J = 8.0 Hz), 5.07 (m, 2H), 2.27 (m, 4H), 1.95 (m, 4H), 0.94 (t, 6H, J = 7.5 Hz), 0.93 (t, 6H, J = 7.5 Hz). ^{13}C {^{1}H} NMR (323K): δ 164.1, 163.8, 163.7, 162.9, 139.0, 133.9, 133.6, 133.5, 130.9, 130.4, 129.0, 128.8, 128.2, 128.0, 127.1, 124.0, 123.9, 123.5, 123.2, 122.8, 120.8, 58.1, 57.9, 25.04, 24.99, 11.08, 11.06. MS 608.36 [M$^+$] (calcd 608.13). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 524 (61 578), 488 (40 027), 458 (15 254). Fluorescence ($CHCl_3$): λ_{max} = 537 nm, fluorescence quantum yield Φ_f = 0.84. Anal. Calcd for $C_{34}H_{29}BrN_2O_4$: C, 67.00; H, 4.80; N, 4.60. Found: C, 66.81; H, 4.90; N, 4.53.

1,7-Dibromo-*N,N′*-bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide (1,7-3b). ^{1}H NMR: δ 9.50 (d, 2H, J = 8.0 Hz), 8.9 (s, 2H), 8.7 (d, 2H, J = 8.0 Hz), 5.06 (m, 2H), 2.25 (m, 4H), 1.94 (m, 4H), 0.92 (t, 12H, J = 7.5 Hz). ^{13}C {^{1}H} NMR (323K): δ 163.7, 163.1, 138.3, 138.0, 133.0, 132.8, 130.2, 129.9, 129.5, 128.6, 128.5, 127.4, 123.7, 123.3, 120.8, 58.2, 25.2, 11.3, 11.2. MS 686.28 [M$^+$] (calcd 686.04). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 526 (45 474), 490 (30 652), 458 (12 208). Fluorescence ($CHCl_3$): λ_{max} = 545 nm, fluorescence quantum yield Φ_f = 0.81. Anal. Calcd for $C_{34}H_{28}Br_2N_2O_4$: C, 59.32; H, 4.10; N, 4.07. Found: C, 59.23; H, 4.16; N, 4.03.

Exclusive Formation of Dibrominated Perylene Diimide Derivatives. A mixture of perylene diimide **1a** (50 mg, 0.085 mmol) and bromine (0.935 g, 5.8 mmol) in 3 mL of dichloromethane was heated to 50 °C in a closed vial (equipped with a Teflon liner) for 1 day. The excess of bromine was removed by air bubbling, and the solvent was removed under vacuum. Silica gel column chromatography using chloroform as an eluent afforded **3a** (1,7-**3a**:1,6-**3a** = 3:1) as an orange solid (58 mg, 92%).

An analogous procedure applied to **1b** (50 mg, 0.094 mmol) and **1c** (50 mg, 0.09 mmol) with heating for 2 days and 4 days, respectively, afforded **3a** (1,7-**3b**:1,6-**3b** = 3:1) as a red solid (57 mg, 89%) and **3c** (1,7-**3c**:1,6-**3c** = 4:1) as a red solid (55 mg, 85%).

1-Piperidinyl-*N,N′*-bis(2,4-dimethylpent-3-yl)perylene-3,4:9,-10-tetracarboxylic Diimide (4a). Compound **2a** (100 mg, 0.15 mmol) was dissolved in 10 mL of piperidine. The solution was heated to 60 °C under dry nitrogen for 5 h with stirring. Excess of piperidine was removed under vacuum, and the residue was subjected to column chromatography on silica gel using chloroform as an eluent to afford **4a** (96 mg, 96%) as a green solid. ^{1}H NMR: δ 9.87 (m, 1H), 8.63 (m, 6H), 4.77 (m, 2H), 3.52 (d, 2H, J = 11.5 Hz), 2.97 (t, 2H, J = 11.0 Hz), 2.72 (m, 4H), 1.90 (m, 6H), 1.12 (two doublets merged, 12H, J = 6.5 Hz), 0.95 (two doublets merged, 12H, J = 6.5 Hz). ^{13}C {^{1}H} NMR: δ 165.5, 165.4, 165, 3, 165.2, 164.4, 164.3, 164.2, 164.1, 152.69, 152.86, 152.83, 136.02, 136.00, 135.95, 135.9, 134.87, 134.85, 134.81, 134.79, 134.1, 134.03, 134.01, 133.98, 132.0, 131.5, 131.2, 130.8, 129.4, 129.2, 129.04, 129.02, 128.5, 127.1, 126.10, 126.08, 125.38, 125.36, 125.3, 124.7, 124.0, 123.9, 123.69, 123.67, 123.4, 123.32, 123.26, 123.2, 122.93, 122.91, 122.77, 122.76, 122.69, 122.67, 122.65, 122.6, 122.31, 122.29, 121.72, 121.69, 121.54, 121.51, 121.08, 121.05, 65.2, 65.04, 64.95, 64.9, 53.0, 29.7, 29.14, 29.09, 25.8, 23.7, 21.9, 21.84, 21.77, 20.68, 20.66, 20.61, 20.60. MS 669.71 [M$^+$] (calcd 669.36). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 602 (18 481), 447 (14 425). Fluorescence ($CHCl_3$): λ_{max} = 727 nm, fluorescence quantum yield Φ_f = 0.2. Anal. Calcd for $C_{43}H_{47}N_3O_4$: C, 77.10; H, 7.07; N, 6.27. Found: C, 77.11; H, 7.11; N, 6.08.

1-Piperidinyl-*N,N′*-bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide (4b). Compound **2b** (100 mg, 0.164 mmol) was reacted with piperidine following the procedure analogous to the synthesis of **4a** to afford **4b** (97 mg, 96%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.86 (d, 1H, J = 8.4 Hz), 8.60 (m, 6H), 5.10 (m, 2H), 3.50 (m, 2H), 2.97 (m, 2H), 2.30 (m, 4H), 1.82−2.0 (m, 10H), 0.95 (two triplets merged, 12H, J = 7.5 Hz). ^{13}C NMR (100 MHz, 323K): δ 164.4, 164.3, 164.2, 164.1, 152.7, 135.8, 134.8, 134.1, 131.4, 131.1, 131.0, 130.72, 130.66, 129.5, 129.1, 128.7, 128.4, 127.2, 125.8, 125.5, 124.91, 124.87, 123.9, 123.6, 123.4, 123.3, 123.2, 123.0, 121.7, 121.5, 121.3, 121.2, 57.8, 57.6, 53.0, 29.5, 25.9, 25.1, 23.7, 11.2, 11.1. MS 613.63 (calcd 613.29). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 601 (18 009), 447 (14 076). Fluorescence ($CHCl_3$): λ_{max} = 726 nm, fluorescence quantum yield Φ_f = 0.19. Anal. Calcd for $C_{39}H_{39}N_3O_4$: C, 76.32; H, 6.40; N, 6.85. Found: C, 76.43; H, 6.52; N, 6.59.

1-Trimethylsilylacetylene-*N,N′*-bis(2,4-dimethylpent-3-yl)-perylene-3,4:9,10-tetracarboxylic Diimide (5a). In a glove box filled with dry nitrogen compound **2a** (100 mg, 0.15 mmol), Pd-(PPh_3)$_4$ (17 mg, 0.015 mmol), trimethylsilyl acetylene (22 mg, 0.22 mmol), and 2 mL of diisopropylamine were mixed in a vial equipped with a magnetic stirrer, and then CuI (1.5 mg, 0.008 mmol) was added to the mixture. The mixture was allowed to stirr at room temperature overnight. The solvent was removed under vacuum, and the resulting mixture was subjected to silica gel chromatography using chloroform as an eluent to yield 98 mg (96%) of **5a** as a red solid. ^{1}H NMR: δ 10.42 (two doublets, 2H, J = 8.5 Hz), 8.82 (s, 1H), 8.80 (s, 1H), 8.40 (m, 10H), 4.78 (m, 4H), 2.77 (m, 8H), 1.14 (two doublets merged, 24H, J = 6.5 Hz), 0.96 (two doublets merged, 24H, J = 6.5 Hz), 0.42 (s, 9H). ^{13}C {^{1}H} NMR: δ 165.3, 165.1, 164.6, 164.2, 164.00, 163.97, 163.5, 139.4, 138.7, 134.7, 134.6, 134.54, 134.52, 134.33, 134.32, 134.30, 134.28, 134.0, 133.94, 133.90, 133.87, 131.8, 131.53, 131.46, 131.1, 130.80, 130.76, 129.08, 129.07, 128.63, 128.61, 127.23, 127.19, 127.15, 126.7, 124.04, 124.02, 123.83, 123.80, 123.50, 123.45, 123.43, 123.41, 123.21, 123.18, 123.1, 123.03, 123.01, 122.99, 122.88, 122.85, 122.6, 122.5, 121.98, 121.96, 120.0, 119.93, 119.90, 107.21, 107.15, 107.1, 105.9, 65.27, 65.25, 65.19, 65.18, 29.12, 29.10, 29.05, 29.0, 21.80, 21.76, 21.7, 20.58, 20.56, 20.51, 20.49, −0.40. MS 682.47 [M$^+$] (calcd 682.32). UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 537 (66 690), 499 (39 606), 467 (14 050). Fluorescence ($CHCl_3$): λ_{max} = 547 nm, fluorescence quantum yield Φ_f = 0.76. Anal. Calcd for $C_{43}H_{46}N_2O_4Si$: C, 75.63; H, 6.79; N, 4.10. Found: C, 75.99; H, 6.98; N, 3.82.

1-Trimethylsilylacetylene-*N,N′*-bis(ethylpropyl)perylene-3,4:9,10-tetracarboxylic Diimide (5b). Compound **5b** was obtained as a red solid in 97% yield using procedure analogous to the one used for the synthesis of **5a**. ^{1}H NMR: δ 10.15 (d, 1H, J = 8.0 Hz), 8. 32 − 8.63 (m, 6H), 5.06 (m, 2H), 2.27 (m, 4H), 1.98 (m, 4H), 0.98 (m, 12H), 0.45 (s, 9H). ^{13}C NMR (323K): δ 164.3, 164.1, 163.6, 138.9, 134.8, 134.7, 134.4, 134.1, 131.3, 131.0, 130.9, 129.4, 128.9, 127.5, 127.39, 127.35, 127.0, 124.2, 124.0, 123.6, 123.4, 123.0, 122.7, 120.2, 107.3, 106.3, 58.2, 58.1, 25.3, 25.2, 11.30, 11.26, −0.34. MS 626.70 [M$^+$] (calcd 626.26) (UV/vis ($CHCl_3$): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 537 (60 348), 499 (35 877), 467 (12 743), 433 (5 562). Fluorescence ($CHCl_3$): λ_{max} = 546 nm, fluorescence quantum yield Φ_f = 0.76. Anal. Calcd for $C_{39}H_{38}N_2O_4Si$: C, 74.73; H, 6.11; N, 4.47. Found: C, 74.45; H, 6.27; N, 4.10.

Computational Methods. All calculations were carried out using Density Functional Theory as implemented in Gaussian 03 program.[40] Geometry optimizations for minima were carried out using the standard Schlegel algorithm[41,42] in redundant internal coordinates until in the neighborhood of the solution and then continued using analytical second derivatives.[43] Optimizations for transition states were carried out with an initial guess for the transition state being generated from manual manipulation of the geometry using MOLDEN.[44] Geometries were optimized using the default pruned (75,302) grid, or when necessary for conversion with the "ultrafine" grid, i.e., a pruned (99 590) grid.

The B3LYP[45,46] exchange correlation functional (three-parameter hybrid density functional method) was employed together with two basis sets. The first, D95V, is the Huzinaga−Dunning double-ζ basis[47] set and the second, cc-pVDZ, is the Dunning correlation-consistent polarized valence double-ζ basis set.[48] Geometry optimizations were carried out using the former basis set while the energetics of the reaction were calculated at these geometries with the latter basis set, to increase the accuracy of the results. Zero-point and RRHO (rigid rotor-harmonic oscillator) thermal corrections were obtained from the unscaled computed frequencies.

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Supporting Information Available: X-ray crystallographic data of 1,7-**3b** (CIF), *xyz* coordinates of computed structures, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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