Tetrahedron 69 (2013) 8155–8160

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Orientation of bromination in bay-region of perylene diimides

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ARTICLE INFO

Article history:
Received 22 May 2013
Received in revised form 5 July 2013
Accepted 11 July 2013
Available online 16 July 2013

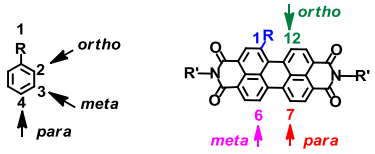
Keywords:
Orientation
Bromination
Perylene diimides

ABSTRACT

We found that the entering position of the bromination in the bay-region (e.g., 1,6,7,12-positions) was precisely determined by the orientation director(s), either individually or cooperatively. In particular, a combination of two directors shows precisely positioning for the third entering bromo with an effect of '1+1>2'.

1. Introduction

It is well-known that nature of the first group attached at the benzene nucleus can significantly influence the substituted position and reactivity of the second entering group.[1] Perylene diimides (PDIs) have been paid much attention in the past decades because of their outstanding optoelectronic and self-assembling properties and the potential applications in the fields of organic electronics.[2–6] Because of the nodes of the HOMO and LUMO at the imide nitrogen atoms, substitutions at the bay-region, e.g., 1,6,7,12-positions are the most elaborate synthetic strategy to fine-tune the optoelectronic properties.[2] Since the first introduction by Seybold et al. at BASF in 1987,[7] functionalizations at the bay-region have been well developed. However, the possible orientation of the substitutions at the 1,6,7,12-positions (Scheme 1) has been submerged by the fast advances of perylene diimide chemistry. Understanding the orientation of the first group on the second entering group and further the cooperative effects of the first and second groups on the third entering group are both not only basically important for the advances of perylene diimide chemistry, but it is also a key approach to precisely position functions at the 1,6,7,12-positions and further fine-tune the optoelectronic properties for the utilizations in the organic electronics.



Scheme 1. Definitions of the *ortho*-, *meta*-, and *para*-position at the bay-region of a modeling 1-substituted PDI compound, with respect to the conventional nomenclature in the benzene nucleus.

2. Results and discussion

To demonstrate the orientation of bromination in the bay-region, we chose 2-methoxyethoxyl (EG) as the electron-donating group, while bromo (Br) and cyano (CN) as the weak and strong electron-withdrawing groups (Scheme 2), respectively. Selection of EG is because the EG-functionalized PDIs are more easily purified than the alkoxyl-substituted ones.[8] The reaction of bromination was conducted at reflux temperature in dichloromethane (DCM) and using bromine as the bromination reagent.[9]

Substitution of monobrominated PDI **2** with EG[8] and CN[10] yielded **3** (Scheme 2) and mono-CN PDI **4** (Fig. S1) in yields of 95% and 99%, respectively. Bromination of **3** preferably gave **5a** in a yield of over 95%, whereas no 6- or 12-brominated isomer (**5b** or **5c**) was detected. We noted that **5a** can be further brominated at its 12-position (vide post), but practically, it can be obtained in a very high yield by controlling the stoichiometric ratio and carefully monitoring the reaction using TLC. This is due to the relative decrease of the electron density at the *ortho*-carbon (−0.210 |e| vs −0.207 |e|) after the *para*-carbon was brominated (**3** vs **5a**, Table S1 vs S2). Structure of **5a** was fully determined by using the ^{1}H NMR, NOESY, and HMBC spectra (Figs. S1–S4). Unique formation of **5a** means that the electron-donating EG group is a preferable 1→7

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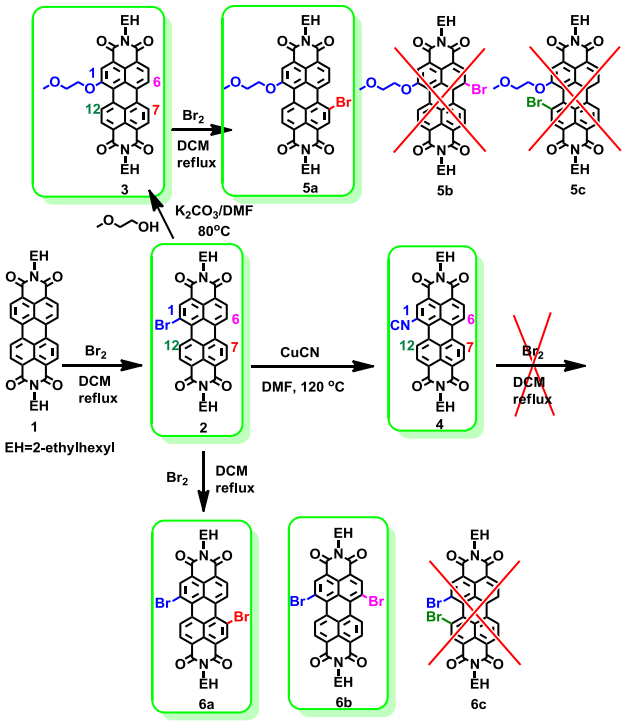
0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.07.035

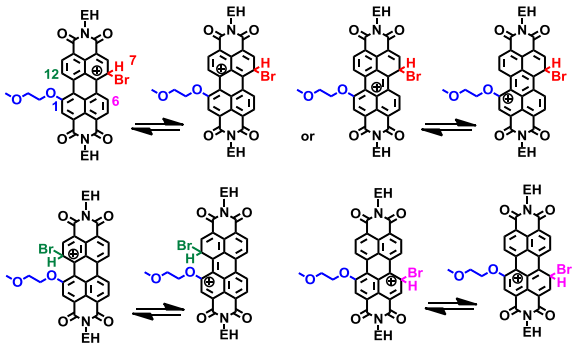


Scheme 2. Orientation of bromination at the *ortho*-, *meta*-, and *para*-position of three typical 1-substituted PDI derivatives.

director. Hereafter, we used *ortho*- (12-), *meta*- (6-), and *para*- (7-) to describe the orientation with respect to that director at the 1-position, as similarly used for the benzene nucleus (Scheme 1). Accordingly, EG is a *para*-director.

Further bromination of **2** yielded a mixture of **6a** (1,7-isomer) and **6b** (1,6-isomer) in a total yield of >95%. Because of the very close polarity at TLC, it is very difficult to isolate **6a** and **6b**.[9,11] The ratio of **6a**/**6b** was then estimated from ^{1}H NMR spectrum as 70–80% and 20–30%, respectively (Fig. S5). It is well-known that no 1,12-isomer (**6c**) was formed from this reaction.[9,11] Furthermore, as shown vide post, substitutions of the mixture of **6a** and **6b** with the EG and CN groups did not give any clues for the existence of **6c** in the mixture of **6a** and **6b**, further strongly supporting that no **6c** was formed. This indicates that bromo is a *para*-/*meta*-director. In a striking contrast, CN is a strong electron-withdrawing group, and it causes deactivation of the PDI nucleus. No further bromination takes place from **4**.

Similar to the bromination in the benzene nucleus, the orientation of bromination in the bay-region of PDI nucleus can be described by the resonant structures (Scheme 3). The positive charge



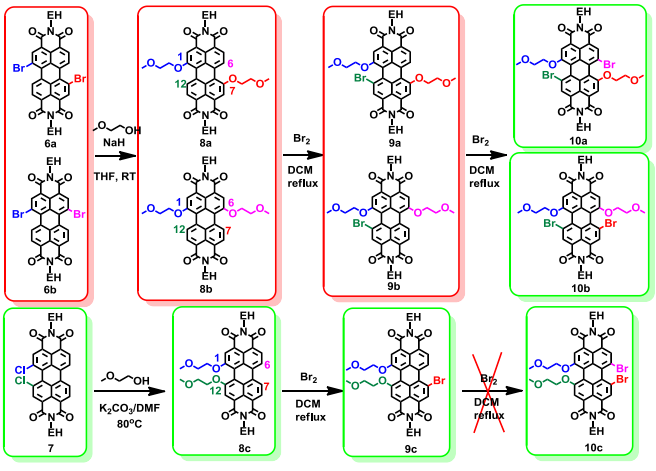
Scheme 3. Resonant structures along the PDI nucleus after the *para*-, *ortho*- and *meta*-carbon were attacked by one bromo, respectively.

at the *para*- and *ortho*-position created after attack of one bromo can move to the 1-carbon along the conjugated backbone, where it may be stabilized by the electron-donating EG-oxygen. However, the positive charge created at the *meta*-position cannot.

Quantum chemical calculations (Table S1) revealed that the electron density at the 1-, 6-, 7-, and 12-carbon of PDI **1**, in which the bay-positions are all free of substitutions, was the same, all being −0.204 |e|. Hereafter, this value was used as a reference: higher or lower than this value represents that position may be activated or deactivated by the director(s). When 1-carbon is brominated, affording **2**, the electron density at the *para*- and *meta*-carbon is slightly raised to −0.205 |e|, whereas that at the *ortho*-carbon is slightly down to −0.200 |e|, which is consistent with the *para*-/*meta*-orientation results. Similarly, with respect to the reference value of −0.204 |e|, the electron density at the *para*-, *meta*- and *ortho*-carbon is either increased or decreased slightly after 1-position is substituted with the EG (**3**) or CN (**4**) group, and the changing tendency is all consistent with the experimental observations from the corresponding directors, for example, the *para*-orientation for the EG group. Noted that the electron density at the *ortho*-carbon of **3** is also higher enough for the bromination. Although no *ortho*-brominated products were obtained from **3**, as shown from the following-presented experimental results, the EG group really shows the *ortho*-orientation, and so it is a preferable *para*-director and also an *ortho*-director.

After realizing the orientation of the EG, Br, and CN groups individually, we turned to study the cooperation from both of them. Firstly, we demonstrated the cooperative effect from two same groups.

Scheme 4 displays the cooperative orientation from two EG groups. From the mixture of 1,7- and 1,6-diBr isomers, 1,7- and 1,6-diEG PDIs (**8a** and **8b**) were got in a total yield of over 92%. Their molar ratio was estimated as 80%/20% from the ^{1}H NMR spectrum (Fig. S6), consistent well with the molar ratio of the reactants of **6a** and **6b**. The 1,12-diEG derivative (**8c**) was obtained from the 1,12-dichlorinated PDI (**7**).[12]



Scheme 4. Cooperative orientation of bromination from the diEG-substituted PDI derivatives.

Full bromination of the **8a**/**8b** mixture yielded 1,7-diEG-6,12-diBr (**10a**) and 1,6-diEG-7,12-diBr (**10b**) PDIs. These two isomers were fully isolated by chromatography, both in yields of 79% (**10a**) and 18% (**10b**) (Fig. S7), respectively, which are both very close to that molar ratio of **6a** and **6b** (80% vs 20%).

We then carefully monitored the bromination of the **8a**/**8b** mixture with TLC and stopped the reaction when most **8b** was likely converted. From this reaction pure **10a** and **10b** were isolated.