Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 357–359

1,3,8,10-Tetrahydro-2,9-diazadibenzo[*cd*,*lm*]perylenes: synthesis of reduced perylene bisimide analogues

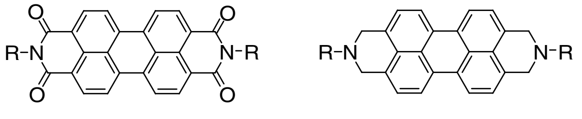
Masaki Takahashi,[a,*] Yousuke Suzuki,[b] Yasunori Ichihashi,[a]
Mitsuji Yamashita[a] and Hideki Kawai[c]

[a] *Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan*
[b] *Graduate School of Science and Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan*
[c] *Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8011, Japan*

Received 19 October 2006; revised 10 November 2006; accepted 16 November 2006

Abstract—A unique family of 1,3,8,10-tetrahydro-2,9-diazadibenzo[*cd*,*lm*]perylenes (THDAP) was prepared through a new synthetic strategy. Completion of the synthesis was achieved in several steps from commercially available perylene-3,4,9,10-tetracarboxylic dianhydride via reactions between 3,4,9,10-tetra(chloromethyl)perylene and primary amines. The successful use of a variety of primary amines in the reactions indicated that the synthetic approach provides a rich opportunity to produce new functionalized perylene derivatives.

Perylene dyes have been recognized as a potent organic material for engineering new applications envisaged in the areas of photonics,[1–6] sensors,[7,8] and electronics[9–12] technologies due to unique photochemical and electrochemical properties. In particular, *N*,*N*′-disubstituted perylene-3,4,9,10-tetracarboxylic bisimides (PBI) represent potentially versatile perylene systems that have been successfully used in a variety of molecular device fabrication.[13–19] In this context, 1,3,8,10-tetrahydro-2,9-diazadibenzo[*cd*,*lm*]perylenes (THDAP) can be regarded as analogous alternatives of the PBI family (Fig. 1). Although specific THDAP-based materials have been prepared through reductive processes from the corresponding PBI derivatives with powerful hydride reducing agents,[20] these approaches have major synthetic limitations due to a low solubility of the substrates in a variety of common organic solvents.[21] In this letter, we disclose the results of our investigations focusing on a new strategy for the preparations of various THDAP analogues.



PBI **THDAP**

Figure 1. Structures of PBI and THDAP.

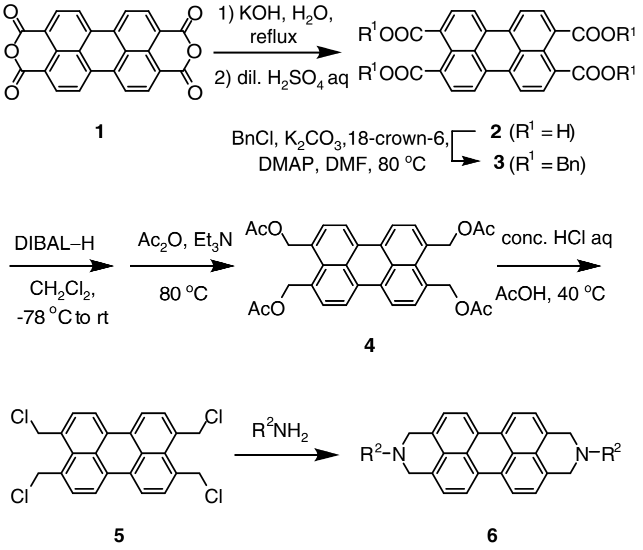
The synthetic route is shown in Scheme 1. Hydration of commercially available perylene-3,4,9,10-tetracarboxylic dianhydride **1** with KOH in refluxing water followed by acidification with dilute H_2SO_4 gave perylene-3,4,9,10-tetracarboxylic acid **2** in 96% yield. Reduction of **2** with either LAH or DIBAL–H failed to react due to the low solvent solubility of the substrate in various solvents. Then, we prepared benzyl ester of **2** to render the resulting molecules adequately soluble in most common organic solvents. Esterification of **2** with benzyl chloride in DMF at 80 °C in the presence of potassium carbonate, 18-crown-6, and DMAP led to tetrabenzyl perylene-3,4,9,10-tetracarboxylate **3** in 86% yield.[22] The benzyl ester moieties of **3** were thoroughly reduced by DIBAL–H in dichloromethane at room temperature, giving rise to 3,4,9,10-tetra(hydroxymethyl)perylene as a single product. Acetylation of this compound with acetic anhydride and triethylamine at 80 °C furnished 3,4,9,10-tetra(acetoxymethyl)perylene **4**, which could be isolated by silica gel column chromatography in

---

Keywords: Synthesis; Perylene; THDAP; PBI.

[*] Corresponding author. Tel./fax: +81 53 478 1621; e-mail: tmtakah@ipc.shizuoka.ac.jp

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.11.100



Scheme 1. Synthetic route to **6**.

85% yield over the two steps. Subsequent transformation of **4** into 3,4,9,10-tetra(chloromethyl)perylene **5** was achieved in 96% yield with concentrated HCl in acetic acid at 40 °C.

With the key intermediate **5** in hand, we prepared a number of variously substituted THDAP derivatives **6** in 85–90% isolated yields (Table 1) by substitution/cyclization reactions of **5** with primary amines (R^2NH_2 in Scheme 1).[23] In most cases, efficient product formations were achieved at an ambient temperature, except that reaction with neat *tert*-butylamine required heating at reflux for a complete conversion of the substrate (entry 4). As a matter of fact, the reactions with neat primary amines (more than 100 equiv per **5**) produced exclusively **6**, whereas making use of 6 equiv of the amines resulted only in low yields of the products.[24] In this regard, control experiments on the stoichiometric ratios led to a definitive conclusion that the reaction with 20 equiv of the amines in THF gave the best isolated yields as observed for **6e** and **6f** (entries 5 and 6). Additionally, it should be noted that utilization of diamines for this reaction allowed a direct construction of primary-amine-containing THDAP systems (entries 7–9). These remarkable examples imply that this reaction gives potential applications for creating new THDAP building blocks containing additional functional groups.

Table 1. Substitution/cyclization reactions of **5** with primary amines (R^2NH_2)

Entry	Product	R^2	Temperature	Isolated yield (%)
1	**6a**	*n*-Pr	rt	85
2	**6b**	*i*-Pr	rt	87
3	**6c**	*n*-Bu	rt	86
4	**6d**	*tert*-Bu	Reflux	90
5	**6e**	Bn	rt	86
6	**6f**	*n*-$C_{12}H_{25}$	rt	88
7	**6g**	$(CH_2)_2NH_2$	rt	86
8	**6h**	$(CH_2)_4NH_2$	rt	88
9	**6i**	$(CH_2)_6NH_2$	rt	90

In conclusion, we have reported the efficient synthesis of a new class of the reduced PBI analogues. The synthetic approach presented here has been demonstrated to be a mild and efficient method for preparing variously functionalized THDAP analogues in good to excellent yields. Detailed investigations of the chromophoric properties and application of this methodology for the development of new potent perylene materials will be addressed in future work.

Acknowledgments

This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (Grant 13740393) and Research Foundation for the Electrotechnology of Chubu (REFEC).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.11.100.

References and notes

1. Tomizaki, K.; Loewe, R. S.; Kirmaier, C.; Schwartz, J. K.; Retsek, J. L.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 6519–6534.
2. Qu, J.; Liu, D.; De Feyter, S.; Zhang, J.; De Schryver, F. C.; Müllen, K. *J. Org. Chem.* **2003**, *68*, 9802–9808.
3. De Boni, L.; Constantino, C. J. L.; Misoguti, L.; Aroca, R. F.; Zilio, S. C.; Mendonça, C. R. *Chem. Phys. Lett.* **2003**, *371*, 744–749.
4. Elemans, J. A. A. W.; van Hameren, R.; Nolte, R. J. M.; Rowan, A. E. *Adv. Mater.* **2006**, *18*, 1251–1266.
5. Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 7390–7398.
6. Takahashi, M.; Morimoto, H.; Miyake, K.; Yamashita, M.; Kawai, H.; Sei, Y.; Yamaguchi, K. *Chem. Commun.* **2006**, 3084–3086.
7. Bowden, N. B.; Willets, K. A.; Moerner, W. E.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 8122–8125.
8. Sauer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1790–1793.
9. Lu, W.; Gao, J. P.; Wang, Z. Y.; Qi, Y.; Sacripante, G. G.; Duff, J. D.; Sundararajan, P. R. *Macromolecules* **1999**, *32*, 8880–8885.
10. Gregg, B. A.; Cormier, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 7959–7960.
11. Malenfant, P. R. L.; Dimitrakopoulos, C. D.; Gelorme, J. D.; Kosbar, L. L.; Graham, T. O. *Appl. Phys. Lett.* **2002**, *80*, 2517–2519.
12. van Herrikhuyzen, J.; Syamakumari, A.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 10021–10027.
13. Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229–1233.
14. Langhals, H.; Krotz, O.; Polborn, K.; Mayer, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 2427–2428.
15. Yukruk, F.; Dogan, A. L.; Canpinar, H.; Guc, D.; Akkaya, E. U. *Org. Lett.* **2005**, *7*, 2885–2887.
16. Ishi-i, T.; Murakami, K.; Imai, Y.; Mataka, S. *Org. Lett.* **2005**, *7*, 3175–3178.

17. Addicott, C.; Oesterling, I.; Yamamoto, T.; Müllen, K.; Stang, P. J. *J. Org. Chem.* **2005**, *70*, 797–801.
18. Würthner, F.; Stepanenko, V.; Sautter, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1939–1942.
19. Würthner, F.; Chen, Z.; Dehm, V.; Stepanenko, V. *Chem. Commun.* **2006**, 1188–1190.
20. Hsu, S.-Y.; Chiang, L.-Y. *Synth. Commun.* **1989**, *19*, 1885–1889.
21. For syntheses of perylene-ring-modified analogues, see: (a) Würthner, F.; Sautter, A.; Thalacker, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 1243–1245; (b) Würthner, F.; Sautter, A.; Schilling, J. *J. Org. Chem.* **2002**, *67*, 3037–3044.
22. For a previous procedure for the synthesis of **3**, see: Takahashi, M.; Morimoto, H.; Suzuki, Y.; Yamashita, M.; Kawai, H. *Polym. Prepr.* **2004**, *45*, 959–960.
23. Experimental details and characterization data for all the synthetic intermediates and THDAP derivatives are provided as the Supplementary data to this letter.
24. Utilization of trapping agents such as triethylamine and pyridine for this reaction resulted in complex mixtures.