ORGANIC
LETTERS

2009
Vol. 11, No. 17
4026−4028

Concise Synthesis of Halogenated Chrysenes ([4]Phenacenes) that Favor π-Stack Packing in Single Crystals

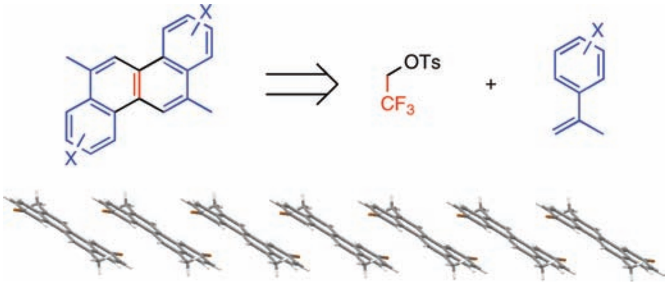
Hiroyuki Isobe,*,[†] Shunpei Hitosugi,[†] Taisuke Matsuno,[†] Takeaki Iwamoto,[†] and Junji Ichikawa[‡]

Department of Chemistry, Tohoku University, Aoba-ku, Sendai 980-8578, Japan, and Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

isobe@m.tains.tohoku.ac.jp

Received July 24, 2009

ABSTRACT



A concise synthesis of halogenated chrysene derivatives from 2,2,2-trifluoroethyl tosylate and halostyrene was established. Friedel−Crafts type cyclization of a 1,1-difluoro-1-alkene bearing halogenated phenyl moieties involved skeletal rearrangement and dehydrogenation to afford the title compound in good to moderate yield. X-ray analysis revealed that the halogen substituents induce π-stack packing of the molecules in the crystals.

Polycyclic aromatic hydrocarbons (PAHs) are attracting renewed interest as base molecules for electronic devices such as field-effect transistors (FETs) or light-emitting diodes (LEDs). Acenes, PAHs with fused benzene rings in a rectilinear arrangement, have long been notable molecules of particular interest, especially those with more than four rings, and the derivatives of acenes with improved properties such as thermal stability or packing structures have contributed significantly to the development of the field of organic devices.[1] Phenacenes, PAHs with fused benzene rings in a zigzag arrangement, have recently emerged as new candidate molecules with ideal properties, such as stability in FETs or blue light emission in LEDs.[2,3] However, synthetic access to the phenacene derivatives is scarce,[4,5] which hampers further exploration of the potential applications of the phenacenes. Here we report on a concise two-step method for the synthesis of chrysene ([4]phenacene) derivatives. Detailed analysis of the crystal structures revealed unique packing features of the π-stack assembly in single crystals.

The method for the synthesis of chrysene derivatives was found unexpectedly during an investigation into the synthesis

---

[†] Tohoku University.

[‡] University of Tsukuba.

(1) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048. Coropceanu, V.; Cornil, J.; Filho, S. D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926–952. Anthony, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 452–483.

(2) Okamoto, H.; Kawasaki, N.; Kaji, Y.; Kubozono, Y.; Fujiwara, A.; Yamaji, M. *J. Am. Chem. Soc.* **2008**, *130*, 10470–10471.

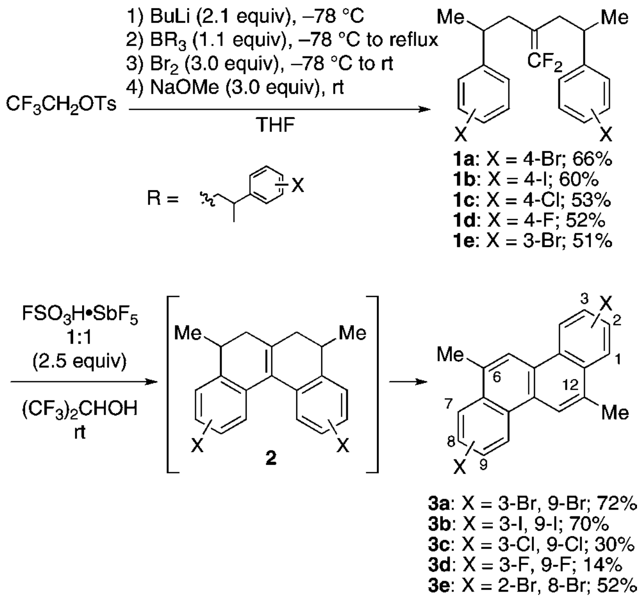
(3) Ionkin, A. S.; Marshall, W. J.; Fish, B. M.; Bryman, L. M.; Wang, Y. *Chem. Commun.* **2008**, 2319–2321.

(4) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Brondyke, E. J.; Mallory, C. W.; Yang, C.; Ellenstein, A. *J. Am. Chem. Soc.* **1997**, *119*, 2119–2124. Hwang, K.-J.; O'Neil, J. P; Katzenellenbogen, J. A. *J. Org. Chem.* **1992**, *57*, 1262–1271.

(5) Cahana, E. R.; Schmidt, G. M. J.; Shah, K. H. *J. Org. Chem.* **1959**, *24*, 557–559.

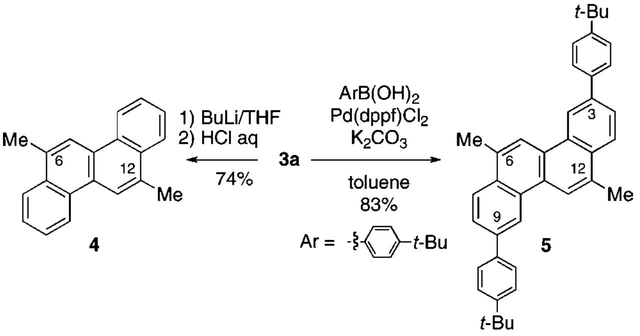
10.1021/ol901693y CCC: $40.75

of halogenated [4]helicene derivatives using a method developed by one of the authors.[6] Thus, we prepared the starting material, difluoroalkene **1a** bearing a 4-bromophenyl group, by a slightly modified method in 66% yield from commercially available CF_3CH_2OTs (Scheme 1),[7] and **1a** was subjected to the acid-promoted reaction conditions previously optimized for nonhalogenated [4]helicene derivatives. Together with the expected tetrahydro[4]helicene derivative **2**, an aromatic compound was obtained as a white precipitate. Structural analysis of this aromatic compound by NMR spectroscopy and X-ray diffraction of the single crystal (*vide infra*) unequivocally showed that the compound was the unexpected product 3,9-dibromo-6,12-dimethylchrysene **3a**. We then optimized the reaction conditions simply by extending the reaction time to six hours, and obtained **3a** in 72% yield (Scheme 1). A similar reaction involving the skeletal rearrangement and dehydrogenation took place with other difluoroalkenes **1** with different halogen substituents or regiochemistry, and we obtained a series of halogenated chrysene derivatives **3b**−**3f** in 14−70% yields (Scheme 1). The reaction of **1** bearing nonhalogenated phenyl moieties or 2-bromophenyl moieties did not afford the corresponding chrysene derivatives.


Scheme 1. Synthesis of Halogenated Chrysene Derivatives

When we analyzed the reaction of **1a**, tetrahydro[4]helicene **2** was detected as the immediate intermediate after the addition of magic acid within a few minutes,[8] which is followed by the formation of chrysene derivative **3a** as the result of the skeletal rearrangement and dehydrogenation. Since a similar rearrangement of nonhalogenated tetrahydro[4]helicene **2** is promoted by polyphosphoric acid,[5] we suppose that the present reaction is also initiated by the protonation of **2** with magic acid. However, the nonhalogenated tetrahydro[4]helicene itself did not afford **3** under the present reaction conditions, and hence we assume that the rearrangement and subsequent dehydrogenation may also involve the reaction/interaction of aromatic moieties with magic acid.[9,10] Details of the reaction may be of theoretical interest and will be investigated in a further mechanistic study.

The halogen substituents provide an access to further derivatization of chrysene, and we preliminarily examined two basic transformations (Scheme 2). Thus, lithium−halogen exchange reaction and protonation afforded 6,12-dimethylchrysene **4** in 74% yield, and Suzuki−Miyaura coupling reaction with arylboronate gave 3,9-di(*tert*-butylphenyl)-6,12-chrysene **5** in 83% yield.


Scheme 2. Derivatization of Halogenated Chrysenes

We obtained single crystals of all the halogenated chrysene derivatives **3** as well as the nonhalogenated congener **4** and found that the halogen substituents induce π-stack packing of the molecules in the crystals. Defining the x and y vectors along the short and long axes of the molecule, we measured the packing parameters of nearest-neighbor cofacial molecules in the crystal structures in order to determine the

---

(6) Ichikawa, J.; Yokota, M.; Kudo, T.; Umezaki, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4870–4873.

(7) The synthesis with halogenated series using the reported method afforded the desired product **1a** in 4% yield. The order of the addition of bromine and methoxide as well as the reaction temperature for the first migration step after the addition of vinyllithium has been modified. See Supporting Information for the details.

(8) When we terminated the reaction within a shorter period, tetrahydro[4]helicene **2** was obtained as a major product in 57% yield, and the subsequent dehydrogenation with $Ph_3C{\bullet}BF_4$ afforded dibromo[4]helicene derivatives.

(9) Olah, G. A.; Schilling, P.; Gross, I. M. *J. Am. Chem. Soc.* **1974**, *96*, 876–883.

(10) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086–4090.

(11) Curtis, M. D.; Cao, J.; Kampf, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 4318–4328.

(12) Burns, D. M.; Iball, J. *Proc. R. Soc. London, Ser. A.* **1960**, *257*, 491–514.

(13) Moon, H.; Zeis, R.; Borkent, E. -J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322–15323.

(14) Robertson, J. M. In *Crystal Engineering*; Desiraju, G. R., Ed.; Elsevier: New York, 1989; Chapter 6.

(15) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

(16) Jaeger, H. M.; Swenson, D. W. H.; Dykstra, C. E. *J. Phys. Chem. A* **2006**, *110*, 6399–6407.

(17) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 651–669.

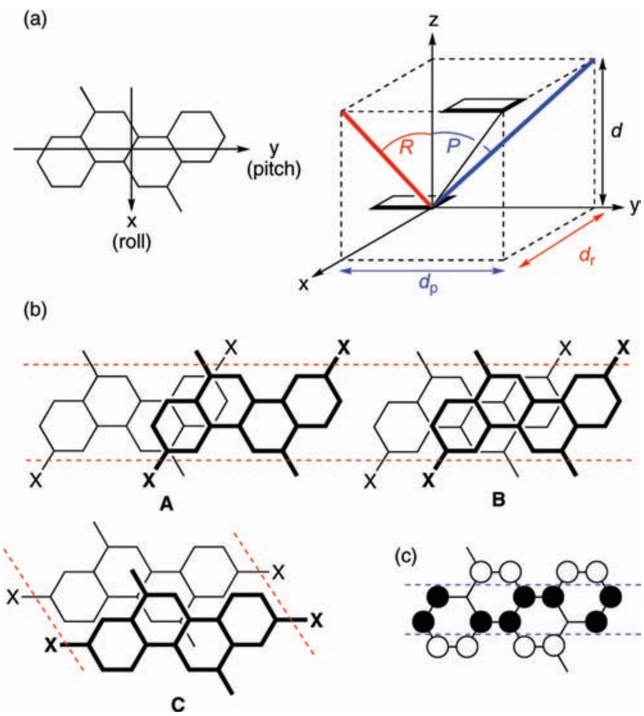


Figure 1. Structural features of chrysene derivatives in single crystals. (a) Definition of the packing parameters (angles and distances) listed in Table 1. (b) Three π-stack motifs observed with halogenated chrysenes in single crystals. **A** for X = F, Cl, Br; **B** for X = I; **C** for X = Br. Bond orders are not shown for clarity. See Supporting Information for the details of crystal structures. Red dotted lines show the nodal plane of HOMO wave functions generated by the halogen substituents. (c) A HOMO wave function of chrysene π-systems with blue dotted lines showing the nodal plane.

angular and lateral deviations from the perfect cofacial π-stack (Figure 1a, Table 1).[11] The structure of the nonhalogenated chrysene derivative **4** was a herringbone packing, similar to that of the parent chrysene,[12] and showed that two cofacial molecules were far separated by a distance of 7.4 Å (Table 1). On the other hand, all the halogenated chrysene derivatives **3** showed π-stack structures with distances in the range of a typical $\pi-\pi$ contact distance (~3.4 Å). The results show that the halogen substituents induce the cofacial contact of chrysene molecules, which is similar to what is observed with haloarenes such as halogenated tetracenes in FET devices.[13−15]

Among the π-stack structures we observed three different motifs that differed in the angular and lateral deviation from the perfect cofacial stack (Figure 1b). Thus, halogen substituents on the roll-side (3,9-position) of the molecule induce the "pitched" π-stack (motif **A** for F, Cl, Br and motif **B** for I), and the bromine substituent on the pitch-side (2,8-position) induces the "rolled" π-stack of **3e** (motif **C**; Figure 2, Table 1). The halogenated chrysene molecules in this study have quadrupolar charge fields on the π-systems due to the halogen substituents at the symmetric positions, and such characteristics may have allowed the structural variations in the π-stack motifs.[16,17] It is also interesting to note that both the pitched or rolled slides resulted in the shift of the molecules along the nodal plane of HOMO wave functions and maintain the intermolecular in-phase overlap of the orbitals (Figures 1b and c).[18−20]

Table 1. Packing Parameters of Nearest-Neighbor Cofacial Molecules in Single Crystals of Chrysene Derivatives

	packing structure	d (Å)	R (deg)	P (deg)	d_p (Å)	d_r (Å)
3a	π-stack	3.42	2.3	58.3	5.54	0.14
3b	π-stack	3.40	2.1	39.1	2.76	0.13
3c	π-stack	3.36	1.0	59.1	5.61	0.06
3d	π-stack	3.39	0.3	59.2	5.69	0.02
3e	π-stack	3.41	37.7	32.6	2.18	2.64
4	herringbone	7.39	13.2	17.4	1.73	2.31

In summary, we have developed a concise method for the synthesis of halogenated chrysene derivatives. The synthesis, which can be easily upscaled and tolerate the structural variations especially at 6,12-positions, may facilitate further investigation of the molecules in organic electronics. Cofacial π-stacking of phenacene molecules in single crystals has rarely been observed, and the first π-stack motifs of halogenated series may be useful for designs of device molecules.[1,2,11,13] The fine-tuning of electronic and packing structures of π-systems with halogenated phenacenes and derivatives may be of great interest in future studies.

Acknowledgment. We thank Dr. W. Nakanishi (Tohoku University) for helpful discussion, JEOL for generous time of DART MS measurment, Central Glass Co. for the gift of HFIP and Nacalai Tesque for a sample column. This work was partly supported by KAKENHI (20108015/21685005) and by Nagase Foundation. S.H. thanks Global COE program (Molecular Complex Chemistry) for predoctoral fellowship.

Supporting Information Available: Experimental procedures, spectral data and crystallographic data (CIF) of **3a−e**, **4** and dibromo[4]helicene derivative. This material is available free of charge via the Internet at http://pubs.acs.org.

OL901693Y

---

(18) Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804–5809.

(19) Kazmaier, P. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1994**, *116*, 9684–9691.

(20) Wiberg, K. B. *J. Org. Chem.* **1997**, *62*, 5720–5727.