J|A|C|S
COMMUNICATIONS

Modular Synthesis of 1*H*-Indenes, Dihydro-*s*-Indacene, and Diindenoindacene—a Carbon-Bridged *p*-Phenylenevinylene Congener

Xiaozhang Zhu, Chikahiko Mitsui, Hayato Tsuji,* and Eiichi Nakamura*

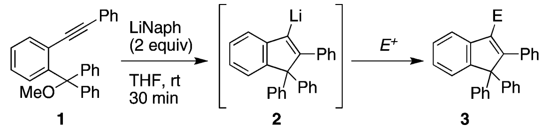
Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received July 8, 2009; E-mail: tsuji@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

Linearly fused aromatic systems[1] such as acenes[2] and fluorenes[3,4] are attracting much interest because of their utility in organic electronic devices. Representing a carbon-bridged phenylenevinylene structure, indacene derivatives are no less interesting.[5,6] For instance, diindenoindacene consisting of seven rings (**7** in Scheme 2) represents a methylene-bridged *p*-(distyryl)benzene,[7] and this planar conjugated system may show better-defined physical properties than the parent compound, *p*-(distyryl)benzene. However, such a compound cannot be easily synthesized by known synthetic methods.[8,9] Because indene represents a partial structure of indacene, we felt that the development of a new indene synthesis[10] may provide an expeditious route to indacenes. We report here a simple and effective synthesis of indenes from commercially available 1-bromo-2-iodobenzene that made available a variety of indenes and indacenes in good to high yields as well as the diindenoindacene **7**. The latter, synthesized in 62% overall yield in five steps from readily available 1,4-dibromo-2,5-diiodobenzene, emits blue light (97% quantum yield) and showed high thermal stability and high electron and hole mobilities on the order of 10^{-3} $cm^2 V^{-1} s^{-1}$, which is a very high value for amorphous materials. Some of the observed physical properties of such compounds can be attributed to the presence of the robust diphenylmethylene bridges and are beneficial for their use as organic semiconductors.

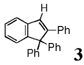
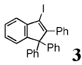
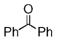
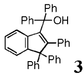
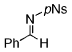
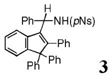
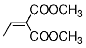
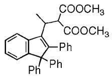
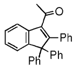
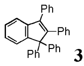
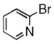
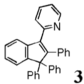
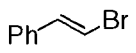
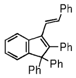
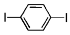
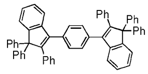
After extensive investigation of the cyclization of 1-alkynyl-2-diphenyl(methoxy)methylbenzene (**1**)[11] and congeners under various conditions, we found that treatment with lithium naphthalenide (LiNaph) at room temperature in THF results in the loss of the methoxy group and smooth formation of the desired indene **3a** in 99% yield upon quenching with water (Table 1, entry 1; >96% deuterium incorporation upon D_2O quenching, as judged by ^1H NMR spectroscopy; see the Supporting Information), indicating the quantitative formation of 3-lithioindene intermediate **2** (Scheme 1).

Scheme 1. Reductive Cyclization To Obtain Substituted 1*H*-Indenes



Utilizing the lithioindene **2** as a synthetic module, we obtained a variety of 3-substituted indenes in good to excellent yields, as shown in Table 1. Iodination of **2** with 1,2-diiodoethane gave 3-iodo-1*H*-indene **3b** in 89% isolated yield (entry 2). The 3-lithioindene **2** added to benzophenone and *N*-4-nitrobenzenesulfonyl (Ns) benzaldimine to give the expected tertiary alcohol **3c** and amine **3d** in 97 and 72% yields, respectively (entries 3 and 4). Copper-mediated reactions of dimethyl 2-ethylidenepropanedioate and acetyl chloride resulted in conjugate addition and acylation[12] to give **3e** and **3f** in 91 and 79% yields, respectively (entries 5 and 6). Negishi cross-coupling reactions were also performed after transmetalation into zinc to obtain 3-phenyl, -pyridyl, and -alkenyl indenes **3g**−**i** in excellent yields (93−99%; entries 7−9). The *p*-phenylene-linked bis(3-indenyl) compound **3j** was also obtained in a similar manner using 1,4-iodobenzene as an electrophile (71%; entry 10).

Table 1. Modular Synthesis of 1*H*-Indene Derivatives

Entry	E+	Additive or catalyst	Product	Yield / %[a]
1	H^+		 **3a**	99
2			 **3b**	89
3			 **3c**	97
4[b]			 **3d**	72
5		CuCN•2LiCl	 **3e**	91
6		CuCN•2LiCl	 **3f**	79
7	Ph–I	$ZnCl_2/Pd(PPh_3)_4$	 **3g**	99
8		$ZnCl_2/Pd(PPh_3)_4$	 **3h**	93
9		$ZnCl_2/Pd(PPh_3)_4$	 **3i**	95
10		$ZnCl_2/Pd(PPh_3)_4$	 **3j**	71

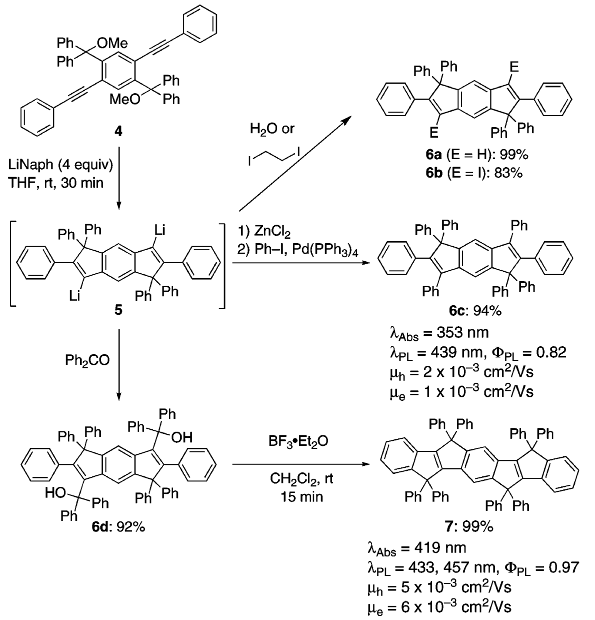
[a] Isolated yield based on **1**. [b] Ns = *N*-4-nitrobenzenesulfonyl group.[13]

The scope of this modular approach[14] can be readily expanded to the synthesis of dihydro-*s*-indacenes (hereafter called indacenes) as well (Scheme 2). Thus, diacetylene **4** was treated with 4 equiv of LiNaph at room temperature in THF for 30 min and then quenched with either water or diiodoethane, affording a 3,7-diprotonated or 3,7-diiodinated indacene derivative in excellent yield (99 or 83% yield, respectively). We thus conclude that a dilithio intermediate **5** formed quantitatively and hence served as a synthetic module for indacene synthesis. For instance, diphenylation of **5**

10.1021/ja905626b CCC: $40.75

proceeded under the conditions of Negishi coupling to afford the octaphenylindacene **6c** in 94% yield. Similarly, addition of benzophenone to **5** afforded the diol **6d** (92%). Intramolecular Friedel−Crafts reaction using $BF_3 \cdot OEt_2$ gave diindenoindacene **7**, which has a carbon-bridged phenylenevinylene skeleton, in 99% yield as a yellow solid.

Scheme 2. Modular Synthesis of Dihydro-*s*-indacenes **6** and Diindenoindacene **7**



The maximum absorption wavelengths of two indacenes, octaphenylindacene **6c** and diindenoindacene **7**, are 353 and 419 nm, respectively, in CH_2Cl_2 (spectra shown in the Supporting Information). The longer absorption wavelength of **7** relative to **6c** is consistent with the more enhanced conjugation in **7**, which possesses two additional diphenylmethylene bridges (see the Supporting Information). Upon photoexcitation, both compounds **6c** and **7** showed blue emission, with maximum wavelengths of 439 and 433 nm, respectively. The emission quantum yields of the two compounds are very high: 0.82 for **6c** and 0.97 for **7**, as determined by the absolute method.

We next examined the solid-state properties (carrier mobilities and thermal stability) of **6c** and **7**. The carrier mobilities were measured by the time-of-flight method for vacuum-deposited amorphous films of the compounds, which showed a dispersive transient current for both hole and electron upon irradiation with a laser pulse. Octaphenylindacene **6c** showed a hole mobility of 2×10^{-3} cm^2 V^{-1} s^{-1} (at an electric field $E = 2.5 \times 10^5$ V/cm) and an electron mobility of 1×10^{-3} cm^2 V^{-1} s^{-1} (at $E = 3.3 \times 10^5$ V/cm) at room temperature. Diindenoindacene **7** showed higher hole and electron mobilities: 5×10^{-3} and 6×10^{-3} cm^2 V^{-1} s^{-1}, respectively, at $E = 2.5 \times 10^5$ V/cm. The mobilities of these compounds are 1−3 orders of magnitude higher than those of poly(phenylenevinylene) compounds[15] and on the same order of magnitude as those of oligofluorenes.[16]

Because of their structural rigidity, compounds **6c** and **7** are thermally very stable. The temperature at which these compounds lose 5% of their mass is as high as 378 °C (evaporation after melt at 339−341 °C) and 472 °C (decomposition). In contrast, the nonbridged counterpart, *trans*,*trans*-1,4-distyrylbenzene, melts at a lower temperature (mp 268 °C).[17] We consider that the planarity of the compounds contributes to the high mobilities and the high stability.

In conclusion, we have developed efficient modular syntheses of 1*H*-indenes, dihydro-*s*-indacenes, and a diindenoindacene containing a carbon-bridged phenylenevinylene framework. Because of the beneficial presence of the robust diphenylmethylene bridges, these compounds showed clear signs of enhanced π-conjugation: red-shift in absorption, high quantum yield of light emission, high carrier mobilities, and high thermal stability. The balanced ambipolar mobility profile of **7** is noteworthy and suggests the potential of the indacene class of materials for use in organic semiconductor devices.

Acknowledgment. We thank Dr. Yoshiharu Sato for helpful discussions and MEXT for financial support (KAKENHI for E.N., no. 18105004, H.T., no. 20685005, and the Global COE Program for Chemistry Innovation). Z.X. thanks the JSPS for a Postdoctoral Fellowship for Foreign Researchers (no. P 09046). C.M. thanks JSPS for the Research Fellowship for Young Scientists (No. 21•9262).

Supporting Information Available: Experimental details and photophysical and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592. (b) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2.
(2) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.
(3) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910.
(4) (a) Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489. (b) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987. (c) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O. *J. Am. Chem. Soc.* **2002**, *124*, 11576.
(5) Adams, C.; Morales-Verdejo, C.; Morales, V.; MacLeod-Carey, D.; Manríquez, M.; Chávez, I.; Muñoz-Castro, A.; Delpech, F.; Castel, A.; Gornitzka, H.; Rivière-Baudet, M.; Rivière, P.; Molins, E. *Eur. J. Inorg. Chem.* **2009**, 784.
(6) Fukazawa, A.; Li, Y.; Yamaguchi, S.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2007**, *129*, 14164.
(7) (a) Hancock, J. E. H.; Pavia, D. L. *J. Org. Chem.* **1961**, *26*, 4350. (b) Hellwinkel, D.; Hasselbach, H.-J.; Lämmerzahl, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 705.
(8) Bell, W. L.; Curtis, C. J.; Eigenbrot, C. W.; Pierpont, C. G.; Robbins, J. L.; Smart, J. C. *Organometallics* **1987**, *6*, 266.
(9) Dahrouch, M. R.; Jara, P.; Mendez, L.; Portilla, Y.; Abril, D.; Alfonso, G.; Chavez, I.; Manriquez, J. M.; Rivière-Baudet, M.; Rivière, P.; Castel, A.; Rouzaud, J.; Gornitzka, H. *Organometallics* **2001**, *20*, 5591.
(10) (a) Miyamoto, M.; Harada, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2008**, *10*, 2975. (b) Ali Khan, Z.; Wirth, T. *Org. Lett.* **2009**, *11*, 229. (c) Yang, S.; Li, Z.; Jian, X.; He, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 3999.
(11) When the methoxy group in **1** was replaced by a chlorine atom and the chloride compound was treated with BuLi (halogen−lithium exchange), the cyclization did not take place; instead, the reaction gave the corresponding dechlorinated, protonated product. When the diphenylmethyl group in **1** was replaced by a diisopropyl group and treated with LiNaph, the cyclization reaction did not take place either. The observations suggest that the reported cyclization takes place via a radical anion species.
(12) Yoshikai, N.; Iida, R.; Nakamura, E. *Adv. Synth. Catal.* **2008**, *350*, 1063.
(13) Kan, T.; Fukuyama, T. *Chem. Commun.* **2004**, 353.
(14) For examples, see: (a) Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 11902. (b) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 4240.
(15) (a) Lee, S. H.; Yasuda, T.; Tsutsui, T. *J. Appl. Phys.* **2004**, *95*, 3825. (b) Inigo, A. R.; Chiu, H.-C.; Fann, W.; Huang, Y.-S.; Jeng, U.-S.; Lin, T.-L.; Hsu, C.-H.; Peng, K.-Y.; Chen, S.-A. *Phys. Rev. B* **2004**, *69*, 075201. (c) Choulis, S. A.; Nelson, J.; Kim, Y.; Poplavskyy, D.; Kreouzis, T.; Durrant, J. R.; Bradley, D. D. C. *Appl. Phys. Lett.* **2003**, *83*, 3812.
(16) Wu, C.-C.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chen, Y.-M.; Chien, Y.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 3710.
(17) Renak, M. L.; Bartholomew, G. P.; Wang, S.; Ricatto, P. J.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 7787.

JA905626B