LETTERS

Diels-Alder Reaction of 1,3-Diarylbenzo[c]furans with Thiophene *S,S*-Dioxide/Indenone Derivatives: A Facile Preparation of Substituted Dibenzothiophene *S,S*-Dioxides and Fluorenones

Meganathan Nandakumar, Jayachandran Karunakaran, and Arasambattu K. Mohanakrishnan*

Department of Organic Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India

(5) Supporting Information

ABSTRACT: One pot syntheses of substituted dibenzothiophene *S*,*S*-dioxides and fluorenones were successfully achieved by Diels–Alder reaction of benzo[*c*]furans with thiophene *S*,*S*dioxides and indenones, respectively. Photophysical properties of representative seven- and nine-membered dibenzothiophene *S*,*S*-dioxide acenes were also reported.



ibenzothiophene¹ and fluorenone-based² π -conjugated materials have attracted renowned interest due to their promising applications in the area of organic electronics. Barbarella et al. first demonstrated that an introduction of one or more thiophene S,S-dioxide unit into the conjugated oligothiophene backbone provides a considerable reduction of HOMO-LUMO band gap value as well as an enhancement in the electron affinity compared to the parent oligothiophenes.³ The oligothiophene S,S-dioxide also displayed a better solidstate photoluminescence efficiency.⁴ The greater fluorescence efficiency and electron-transport properties of the dibenzothiophene S,S-dioxide-based materials⁵ prompted chemists to undertake a comprehensive study on these compounds.⁶⁻⁸ Perepichka et al. extensively utilized the dibenzothiophene S,Sdioxide unit as material for dual-fluorescence,^{7a} strong solvatochromism,^{7b} and high luminescence efficiency^{7c} by incorporating into the main chain of oligofluorene. Recently, Yang and co-workers successfully synthesized alcohol-soluble amino-functionalized polyfluorene-tethered dibenzothiophene S,S-dioxides and explored their applications in polymer light emitting diodes (PLEDs) and polymer solar cells (PSCs).⁸

Oligo- and polyfluorenes have been explored as OLEDs with high quantum efficiencies.⁹ To overcome the stability issue of fluorenes,¹⁰ 9,9-dialkylfluorenes are being explored.¹¹ Recently, Goel and co-workers reported the donor-acceptor-type fluorene- and fluorenone-based small molecules as stable blue light emitters.¹² The Diels-Alder reaction is one of the ubiquitous reactions in organic synthesis and used for construction of polycyclic aromatics.¹³ Over the years, the benzo[c]furan analogues were being exploited as a dienes in the Diels-Alder reactions to synthesize complex π -conjugated accens.¹⁴

Our aim is to explore the synthetic utility of 1,3-disubstituted benzo[c]furans¹⁵ as a diene in the Diels–Alder reaction to prepare π -conjugated dibenzothiophene *S*,*S*-dioxide and

fluorenone derivatives. Recently, Iniesta and co-workers¹⁶ achieved the preparation of dibenzothiophene *S*,*S*-dioxides through Diels—Alder reaction of benzo[*b*]thiophene *S*,*S*-dioxide and tetraphenylthiophene *S*-oxide. They have also carried out the Diels—Alder reaction of benzo[*b*]thiophene *S*,*S*-dioxide with dienes such as substituted butadiene, furan, cyclopentadiene, and tetracyclone to afford the respective adducts in moderate yields. As a representative case, the Diels—Alder reaction of 1,3- diphenylbenzo[*c*]furan **1a** with benzo-[*b*]thiophene *S*,*S*-dioxide **2**¹⁷ in toluene at reflux for 12 h afforded corresponding adduct **3a** in 84% yield.

Subsequent aromatization of the adduct 3 using p-toluenesulfonic acid (PTSA) led to the formation of the expected benzo[d]naphtho[b]thiophene S,S-dioxide 4a in 83% yield. The Diels-Alder reaction of benzo[c]furan 1a with 2 followed by aromatization without the isolation of intermediate adduct slightly improved the yield of 4a (Scheme 1 and the Supporting Information). The structure of thiophene S,S-oxide 4a was confirmed by a single-crystal X-ray analysis.¹⁸

Scheme 1. Synthesis of Benzo[b]naphtho[d]thiophene S,S-Dioxide 4a





Table 1. Synthesis of Dibenzothiophene S,S-Dioxides



^{*a*}Diels–Alder reaction was allowed to reflux in toluene until the disappearance of furan (\sim 12 h), and for aromatization (PTSA) it was refluxed until disappearance of the adduct (\sim 10 h) was noted. ^{*b*}Isolated yield by column chromatography.

Scheme 2. Diels–Alder Reaction of Indenone 11 with Furan 1a



Inspired by this result, the one-pot syntheses of dibenzothiophene S,S-dioxides 4b-d, 6a-c, 8, and 10 have been successfully achieved in good to excellent yields (Table 1). The Diels-Alder reaction of benzo[c] furans 1b-d with benzo[b]thiophene S,S-dioxide 2 followed by aromatization afforded benzo[d]naphtho[b]thiophene S,S-dioxides 4b-d in good yields (entry 1). Under identical conditions, naphtho [b]thiophene S,S-dioxide 5 reacts with benzo [c] furans 1c-e to furnish dinaphtho[*b*:*d*]thiophene *S*,*S*-dioxides **6a**–**c** in 76–84% yields (entry 2). Interestingly, the bent-naphtho [b] thiophene S,S-dioxide 7 also underwent smooth Diels-Alder reaction followed by aromatization to give dinaphtho[1,2-b:2',3'-d]thiophene S,S-dioxide 8 in 81% yield (entry 3). The electron-rich bis(hexyloxy)dinaphtho[b:d]thiophene S,S-dioxide 9 successfully participated in the one-pot synthesis to give tetrasubstituted five-membered acene 10 in 75% yield (entry 4).

We next investigated the Diels-Alder reaction of benzo[c]-furans with a range of indenones. It should be noted that the indenone 11 and benzo[b]thiophene *S*,*S*-dioxide 2 have similar motifs, differing only at the C-1 position. To our delight, indenone 11¹⁹ upon Diels-Alder reaction with furan 1a in 1,2-dichloroethane (DCE) at reflux for 10 h followed by

Table 2. Synthesis of Substituted Fluorenones





^{*a*}The Diels–Alder reaction was carried out in 1,2-DCE at reflux until disappearance of furan in TLC (10 h), and for aromatization it was refluxed until adduct disappearance (9 h) was noted. ^{*b*}Reaction was carried out in toluene for 14 h, and aromatization was allowed for 12 h. ^{*c*}Isolated yield by column chromatography.



Figure 1. Single-crystal X-ray structures of 6a and 16e.

aromatization furnished diphenylbenzo[b]fluorenone 12a in 88% yield (Scheme 2).

Next, the indenone 11, naphtho[b]indenone 13, as well as the diaryl-substituted naphtho[b]indenone 15a,b also participated in the Diels–Alder reaction followed by aromatization to afford the corresponding benzo/naphthofluorenones 12b-d, 14a-d, and 16a-e in excellent yields (Table 2). It is worth mentioning that the indenones 11 and 13 require lower temperature than that of diaryl substituted indenone 15a,b. The structures of thiophene *S*,*S*-dioxide 6a and fluorenone 16e were confirmed by single-crystal X-ray analyses (Figure 1).¹⁸

After demonstrating the preparation of a variety of benzo/ naphtho dibenzothiophene *S*,*S*-dioxides and fluorenones by the Diels–Alder reaction of 1,3-diarylbenzo[*c*]furans, we next initiated the reduction^{1e} of dibenzothiophene *S*,*S*-dioxides. As a representative case, diphenyldibenzothiophene *S*,*S*-dioxide **4a** upon reduction with lithium aluminum hydride (LAH) in diethyl ether at 0 °C to rt for 2 h afforded diphenyldibenzothiophene derivative **17a** in 74% yield (Scheme 3). Similarly, Scheme 3. Preparation of Dibenzothiophene Derivatives 17a,b



Scheme 4. Synthesis of Seven-Membered Thiophene S,S-Dioxide Acenes 20a-e



dibenzothiophene *S*,*S*-dioxide **4b** also converted into the corresponding dibenzothiophene **17b** in good yield.

To explore the scope further, synthesis of higher acenes containing thiophene *S*,*S*-dioxide units has been initiated. The bis(hexyloxy)benzodithiophene and *N*-dodecyldithieno carbazole derivatives have been synthesized and incorporated in polymers due to their potential optical properties.²⁰ Hence, the required bis(hexyloxy)benzodithiophene *S*,*S*-dioxide **19a/19b** was prepared by the routinely used HCO₂H/H₂O₂ procedure.¹⁷ Gratifyingly, the one-pot synthesis of hexaaryl-substituted thiophene *S*,*S*-dioxide fused seven member acenes **20a**–**e** have been successfully achieved in good yields (Scheme 4).

Next, we began to construct more complex and challenging higher acenes containing carbazole-fused thiophene S,Sdioxides. The Diels—Alder reaction of diphenylbenzo[c]furan 1a with thiophene S,S-dioxide 22 followed by adduct bridge cleavage furnished dithienocarbazole-fused nine-membered acene 23a in 75% yield. Finally, the anisyl/thienyl-tethered dithienocarbazole-fused nine-membered acenes 23b/23c have also been achieved using a one-pot Diels—Alder synthetic strategy (Scheme 5).

Scheme 5. Synthesis of Nine-Membered Thiophene S,S-Dioxide Acenes 23a-c





Figure 2. Absorption and emission spectra of thiophene *S*,*S*-dioxides 20a, 20b, 23b, and 23c.

Table 3. Photophysical Studies of Thiophene S,S-Dioxides

entry	product	$absorption^{a} \ \lambda_{\max(abs)} \ (nm)$	$\substack{ \text{emission}^{a,b} \\ \lambda_{\max(\text{em})} \text{ (nm)} }$	Stokes shift ^c (cm ⁻¹)	quantum yield Φ^a
1	20a	275	478	15443	0.210
2	20b	265	488	17244	0.019
3	20c	274	479	15619	0.180
4	20d	266	486	17017	0.018
5	23b	382	467	4764	0.054
6	23c	392	466	4051	0.045

^{*a*}Recorded in CH₃CN at 25 °C. ^{*b*}Excited at the longest wavelength of the absorption maxima. ^{*c*}Stokes shift = $\lambda_{max(abs)} - \lambda_{max(em)}$ (cm⁻¹).



Figure 3. Luminescence color upon illumination at 365 nm.

Table	4. Fluor	rescence	Lifetin	nes of 2	0a, 20b,	23b, and	23c*
compd	$\tau_1 \ (ps)$	τ_2 (ns)	$\tau_3~(\mathrm{ns})$	A1 (%)	A2 (%)	A3 (%)	χ^2
20a			1.20			100	1.148
20b	43.30	0.25	0.90	16.13	61.13	22.74	0.943
23b		1.50	3.39		10.84	89.16	1.081
23c		0.627	1.86		25.97	74.03	1.226
ske							

^{*}Measured using the TCSPC technique and excited at 370 nm and monitored at their respective emission maximum.

The optical properties of the novel thiophene *S*,*S*-dioxides **20a**, **20b**, **23b**, and **23c** were investigated by UV-vis and fluorescence spectroscopy (Figure 2, Table 3). The absorption spectra of thiophene *S*,*S*-dioxides **23b** and **23c** shifted to lower energies compared to the compounds **20a** and **20b**. Figure 3 shows the emission color of **20a**, **20b**, **23b**, and **23c** in acetonitrile upon illumination at 365 nm. The thiophene *S*,*S*-dioxides **23b** and **23c** (Table **3**). The fluorescence quantum yield was measured using quinine sulfate as a standard (0.1 N H₂SO₄) $\Phi_f = 0.54$ at an excitation wavelength of 366 nm. It is worth mentioning that among thiophene *S*,*S*-dioxide-based acenes, compounds **20a** and **20c** displayed much enhanced fluorescence quantum yields (Table 3).

Next, the time-correlated single photon counting (TCSPC) measurement of thiophene *S*,*S*-dioxides **20a**, **20b**, **23b**, and **23c** were carried out in acetonitrile at room temperature (Table 4 and the Supporting Information). It should be noted that the fluorescence lifetime decay of compounds **20a** and **20b**

displayed single-exponential and triexponential behavior, while both **23b** and **23c** exhibited biexponential behavior (Table 4). The triexponential fluorescence lifetime decay of **20b** may be attributed to the different conformational isomers visualized through the restricted rotation of thiophene units. However, the VT ¹H NMR spectra of **20b** did not provide any evidence for such conformational isomers (see the Supporting Information). Further photophysical studies on **20b** and other structurally related compounds may provide a possible reason for triexponential/biexponential behavior of these compounds.

In summary, we have successfully exploited the Diels–Alder reaction of benzo[c]furans with annulated thiophene S,S-dioxides and indenones that provides a new method for the preparation of π -conjugated thiophene S,S-dioxides and fluorenones. Synthesis and photophysical properties of sevenas well as nine-membered acenes and also the fluorescence lifetime decay of selected thiophene S,S-dioxides have been carried out. Further studies toward the synthesis and optical application of thiophene S,S-dioxide-based hetero acenes are in progress.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure, copies of NMR spectra, and X-ray crystallographic data of 4a, 6a, and 16e (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*mohanakrishnan@unom.ac.in; mohan_67@hotmail.com.

Notes

The authors declare no competing financial interest.

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DEDICATION

This paper is dedicated to Prof. Ganesh Pandey on the occasion of his 60th birthday.

REFERENCES

(1) (a) Dong, S.-C.; Zhang, L.; Liang, J.; Cui, L.-S.; Li, Q.; Jiang, Z.-Q.; Liao, L.-S. J. Phys. Chem. C 2014, 118, 2375. (b) Jin, E.; Du, C.; Wang, M.; Li, W.; Li, C.; Wei, H.; Bo, Z. Macromolecules 2012, 45, 7843. (c) Jeong, S. H.; Lee, J. Y. J. Mater. Chem. 2011, 21, 14604. (d) Huang, T.-H.; Whang, W.-T.; Shen, J. Y.; Lin, J. T.; Zheng, H. J. Mater. Chem. 2005, 15, 3233. (e) Sirringhaus, H.; Friend, R. H.; Wang, C.; Leuninger, J.; Müllen, K. J. Mater. Chem. 1999, 9, 2095.

(2) (a) Lincker, F.; Heinrich, B.; Bettignies, R. D.; Rannou, P.; Pécaut, J.; Grévin, B.; Pron, A.; Donnio, B.; Demadrille, R. J. Mater. Chem. 2011, 21, 5238. (b) Rathnayake, H. P.; Cirpan, A.; Karasz, F. E.; Odoi, M. Y.; Hammer, N. I.; Barnes, M. D.; Lahti, P. M. Chem. Mater. 2007, 19, 3265. (c) Zhu, Y.; Kulkarni, A. P.; Jenekhe, S. A. Chem. Mater. 2005, 17, 5225. (d) Chen, C.-T.; Lin, J.-S.; Moturu, M. V. R. K.; Lin, Y.-W.; Yi, W.; Tao, Y.-T.; Chien, C.-H. Chem. Commun. 2005, 3980. (3) Barbarella, G.; Favaretto, L.; Zambianchi, M.; Pudova, O.; Arbizzani, C.; Bongini, A.; Mastragostino, M. *Adv. Mater.* **1998**, *10*, 551.

(4) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Bongini, A.; Arbizzani, C.; Mastragostino, M.; Anni, M.; Gigli, G.; Cingolani, R. *J. Am. Chem. Soc.* **2000**, *122*, 11971.

(5) (a) Liu, J.; Hu, S.; Zhao, W.; Zou, Q.; Luo, W.; Yang, W.; Peng, J.; Cao, Y. *Macromol. Rapid Commun.* **2010**, 31, 496. (b) Liu, J.; Zou, J.; Yang, W.; Wu, H.; Li, C.; Zhang, B.; Peng, J.; Cao, Y. *Chem. Mater.* **2008**, 20, 4499. (c) Huang, T.-H.; Whang, W.-T.; Shen, J. Y.; Wen, Y.-S.; Lin, J. T.; Ke, T.-H.; Chen, L.-Y.; Wu, C.-C. *Adv. Funct. Mater.* **2006**, 16, 1449.

(6) Moss, K. C.; Bourdakos, K. N.; Bhalla, V.; Kamtekar, K. T.; Bryce, M. R.; Fox, M. A.; Vaughan, H. L.; Dias, F. B.; Monkman, A. P. J. Org. Chem. **2010**, 75, 6771.

(7) (a) King, S. M.; Perepichka, I. I.; Perepichka, I. F.; Dias, F. B.; Bryce, M. R.; Monkman, A. Adv. Funct. Mater. 2009, 19, 586. (b) Dias, F. B.; Pollock, S.; Hedley, G.; Pålsson, L.-O.; Monkman, A.; Perepichka, I. I.; Perepichka, I. F.; Tavasli, M.; Bryce, M. R. J. Phys. Chem. B 2006, 110, 19329. (c) Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Pålsson, L.-O. Chem. Commun. 2005, 3397.

(8) Xiao, H.; Miao, J.; Cao, J.; Yang, W.; Wu, H.; Cao, Y. Org. Electron. 2014, 15, 758.

(9) (a) Marsitzky, D.; Müllen, K. In Advances in Synthetic Metals, Twenty Years of Progress in Science and Technology; Bernier, P., Lefrant, S., Bidan, G., Eds.; Elsevier: New York, 1999; p 1. (b) Mullen, K.; Wegner, G. Electronic Materials: The Oligomer Approach; Wiley-VCH: Weinheim, 1998. (c) Akcelrud, L. Prog. Polym. Sci. 2003, 28, 875.

(10) (a) Liu, L.; Qiu, S.; Wang, B.; Zhang, W.; Lu, P.; Xie, Z.; Hanif, M.; Ma, Y.; Shen, J. J. Phys. Chem. B 2005, 109, 23366. (b) List, E. J. W.; Guentner, R.; Freitas, P. S. D.; Scherf, U. Adv. Mater. 2002, 14, 374. (c) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. Macromolecules 1999, 32, 361.

(11) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. J. Am. Chem. Soc. 2007, 129, 11910.

(12) Goel, A.; Chaurasia, S.; Dixit, M.; Kumar, V.; Prakash, S.; Jena, B.; Verma, J. K.; Jain, M.; Anand, R. S.; Manoharan, S. S. *Org. Lett.* **2009**, *11*, 1289.

(13) Carruthers, W. Cycloaddition Reactions in Organic Synthesis; Pergamon Press: New York, 1990.

(14) (a) Wang, T.; Han, J.; Zhang, Z.; Xu, B.; Huang, J.; Su, J. Tetrahedron 2012, 68, 10372. (b) Nishina, Y.; Kida, T.; Ureshino, T. Org. Lett. 2011, 13, 3960. (c) Kuninobu, Y.; Seiki, T.; Kanamaru, S.; Nishina, Y.; Takai, K. Org. Lett. 2010, 12, 5287. (d) Qu, H.; Chi, C. Org. Lett. 2010, 12, 3360. (e) Klassen, S. A.; Boehme, R.; Derrick, S. D.; Moock, K.; Baker, E. A.; Fogg, D. E.; Boeré, R. T.; Dibble, P. W. Can. J. Chem. 2009, 87, 738. (f) Paraskar, A. S.; Reddy, A. R.; Patra, A.; Wijsboom, Y. H.; Gidron, O.; Shimon, L. J. W.; Leitus, G.; Bendikov, M. Chem.—Eur. J. 2008, 14, 10639. (g) Rainbolt, J. E.; Miller, G. P. . J. Org. Chem. 2007, 72, 3020. (h) Mondal, R.; Shah, B. K.; Neckers, D. C. J. Org. Chem. 2006, 71, 4085. (i) Miller, G. P.; Briggs, J. Org. Lett. 2003, 5, 4203. (j) Dodge, J. A.; Bain, J. D.; Chamberlin, A. R. J. Org. Chem. 1990, 55, 4190. (k) Smith, J. G.; Fogg, D. E.; Munday, I. J.; Sandborn, R. E.; Dibble, P. W. J. Org. Chem. 1988, 53, 2942.

(15) (a) Sivasakthikumaran, R.; Nandakumar, M.; Mohanakrishnan, A. K. J. Org. Chem. 2012, 77, 9053. (b) Nandakumar, M.; Sivasakthikumaran, R.; Mohanakrishnan, A. K. Eur. J. Org. Chem. 2012, 3647.

(16) Iniesta, J.; Matsumoto, T.; Thiemann, T. J. Chem. Res. 2008, 2, 109.

(17) Rademacher, P. M.; Woods, C. M.; Huang, Q.; Szklarz, G. D.; Nelson, S. D. *Chem. Res. Toxicol.* **2012**, *25*, 895.

(18) CCDC numbers for **4a**, **6a**, and **16e** are 997380, 997383, and 997450, respectively (see the Supporting Information).

(19) Hauser, F. M.; Zhou, M.; Sun, Y. Synth. Commun. 2001, 31, 77. (20) (a) Wang, X.; Jiang, P.; Chen, Y.; Luo, H.; Zhang, Z.; Wang, H.; Li, X.; Yu, G.; Li, Y. Macromolecules 2013, 46, 4805. (b) Deng, Y.; Chen, Y.; Liu, J.; Liu, L.; Tian, H.; Xie, Z.; Geng, Y.; Wang, F. ACS Appl. Mater. Interfaces 2013, 5, 5741.