This article was downloaded by: [University Of Pittsburgh] On: 11 October 2014, At: 10:22 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Synthesis, X-Ray Analysis, and Evaluation of the Optoelectronic Properties of a New Thia[6]helicene

Souad Moussa ^a , Faouzi Aloui ^a , Pascal Retailleau ^b & Béchir Ben Hassine ^a

^a Laboratoire de Synthèse Organique Asymétrique et Catalyse Homogène, Faculté des Sciences , Monastir , Tunisia

^b ICSN-CNRS, Gif sur Yvette, France Accepted author version posted online: 06 Sep 2011.Published online: 16 Dec 2011.

To cite this article: Souad Moussa, Faouzi Aloui, Pascal Retailleau & Béchir Ben Hassine (2012) Synthesis, X-Ray Analysis, and Evaluation of the Optoelectronic Properties of a New Thia[6]helicene, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:7, 1010-1018, DOI: <u>10.1080/00397911.2010.534572</u>

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2010.534572</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



Synthetic Communications[®], 42: 1010–1018, 2012 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2010.534572

SYNTHESIS, X-RAY ANALYSIS, AND EVALUATION OF THE OPTOELECTRONIC PROPERTIES OF A NEW THIA[6]HELICENE

Souad Moussa,¹ Faouzi Aloui,¹ Pascal Retailleau,² and Béchir Ben Hassine¹

¹Laboratoire de Synthèse Organique Asymétrique et Catalyse Homogène, Faculté des Sciences, Monastir, Tunisia ²ICSN-CNRS, Gif sur Yvette, France

GRAPHICAL ABSTRACT



Abstract The synthesis and structural characterization of a new hexahelicene derivative is reported. This compound features a new type of structure bearing a bromine atom. Suitable crystals of the latter indicate that its conformation closely resembles that of the unsubstituted [6]helicene, whose idealized symmetry is C2. The optoelectronic properties of this helical hexacyclic system were determined and exhibit a very interesting behavior.

Keywords Helicenes; optical band gap; photodehydrocyclization; thiahelicenes; Wittig reaction

Received September 27, 2010.

Address correspondence to Béchir Ben Hassine, Laboratoire de Synthèse Organique Asymétrique et Catalyse Homogène (O1UR1201), Faculté des Sciences, Avenue de l'environnement, 5019 Monastir, Tunisia. E-mail: bechirbenhassine@yahoo.fr

NEW THIA[6]HELICENE

INTRODUCTION

Heterohelicenes are formed by *ortho*-condensed aromatic or heteroaromatic rings. The steric interactions arising in this type of compound do not allow planarity for molecules with sequences of five or more rings and cause the π -conjugated systems to get distorted into helices, which are intrinsically chiral structures.^[1] Furthermore, enantiomerically enriched helicenes have been used as building blocks for helical conjugated polymers,^[2] helical ligands,^[3] structures that act as catalysts^[4] for enantioselective transformations, and asymmetric inducers.^[5] The incorporation of thiophene rings into polycyclic aromatic frameworks has led to considerable success in the design and synthesis of unique organic semiconductors^[6] for organic field effect transistors and high conductivity.^[7] [*n*]-Helicenes constructed through such modification have precisely ordered structures as a result of both the helical conjugation and the stiff structure.^[8] These structures, in particular heterohelicenes, exhibit interesting opto- and photo-electronic properties.^[9]

The present work describes a four-step synthesis of a new helically chiral hexacyclic system, containing one thiophene ring, over a photochemical route. The crystallization of this helically chiral compound by slow evaporation of a methylene chloride/hexane solution afforded single crystals suitable for x-ray diffraction studies.

RESULTS AND DISCUSSION

The synthetic route to thia[6]helicene 1 began with the Wittig condensation of the benzothiophene-2-carboxaldehyde 2 with phosphonium salt $\mathbf{3}$,^[10] using sodium methoxide as the base and methanol as the solvent. The mixture was stirred and gently heated for 3 h at 50 °C to give the desired styryl derivatives $4\mathbf{a}$ and \mathbf{b} in 88% yield as a mixture of *cis* and *trans* isomers (*cis/trans* = 4:6). The resulting diarylethenes $4\mathbf{a}$ and \mathbf{b} were subjected to photocyclization in toluene for about 3 h in the presence of iodine, using a 500-W high-pressure mercury immersion lamp, and provided the expected benzo[*c*]phenanthrene system $\mathbf{5}$ in 76% yield after purification by column chromatography (Scheme 1).

The benzo[c]phenanthrene system **5** and 4-bromostyrene (1.5 equiv) underwent a Mizoroki–Heck coupling using 1% of Hermann's catalyst, sodium acetate as the base, and *N*,*N*-dimethylacetamide (DMA) as the solvent, according to Scheme 1. The mixture was heated at 140 °C for about 48 h to afford the desired diarylethelene **6** in 79% yield. The coupled product is assumed to have an (*E*)-stereochemestry at the double bond, based on the mechanism of the Heck reaction and confirmed by ¹H NMR study. The (*Z*)-isomer was neither isolated nor unambiguously identified as a minor product in the reaction mixture. The resulting diarylethene **6** was then subjected to photocyclization in toluene for about 3 h, in the presence of a stoichiometric amount of iodine as an oxidising agent and an excess of propylene oxide,^[11] on a 150mg scale to give the expected 2-bromothia[6]helicene **1** in 65% yield (Scheme 1).

Suitable crystals of compound 1 were obtained as pale yellow plates by the slow evaporation of a methylene chloride/hexane solution. The substance crystallizes in the form of a racemate. It is stable in air and light. The x-ray analysis of the thia[6]-helicene 1 was carried out on a single crystal obtained from the racemic mixture as shown in Fig. 1. The bond lengths are in the range of 0.93–1.46 Å. The torsion angles



Scheme 1. Synthetic strategy for the synthesis of the bromothiahexahelicene 1.

along the inner helical rim (C_2 - C_3 - C_7 - C_{11} , C_3 - C_7 - C_{11} - C_{15} , C_7 - C_{11} - C_{15} - C_{19} , and C_{11} - C_{15} - C_{19} - C_{24}), which vary from 6.9° to 33.4°, are also a convenient measure of the helicity and are in accordance with those observed in other hexahelicenes.

The intensity data were collected at room temperature on a Bruker Smart CCD diffractometer (using a graphite monochromated CuK α radiation, $\lambda = 1.54180$ Å), and crystallographic and experimental details are summarized in Table 1. The structure was solved by direct methods and refined by full matrix least-squares procedures (SHELX-97)^[12] first with isotropic thermal parameters and then with anisotropic



Figure 1. Crystal structure of (\pm) -1: ORTEP drawing, selected dihedral angles (°), and bonding distances (Å) of **1**. (Figure is provided in color online.)

NEW THIA[6]HELICENE

Parameter	Value
Formula	C ₂₄ H ₁₃ BrS
FW	413.31
Crystal system	monoclinique
Space group	P21/n
a (Å)	13.3335(4)
b (Å)	7.2326(2)
c (Å)	18.2038(13)
α (°)	90
β (°)	94.147(7)
γ (°)	90
V (Å ³)	1750.90(14)
Z	4
$D_x (mg \cdot m^{-3})$	1.568
F(0000)	832
Crystal size (mm)	$0.10 \times 0.10 \times 0.10$
$\mu (mm^{-1})$	4.33

 Table 1. Crystal data and structure refinement for compound 1

thermal parameters in the last cycles of refinement for all the nonhydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. All six fused rings show distortion from planar arrangement.

OPTICAL PROPERTIES

The optical properties of the synthesized 2-bromo-11-thiahexahelicene were investigated using ultraviolet (UV)–visible absorption in dilute CHCl₃ solution as shown in Fig. 2. The UV–visible spectrum of the compound exhibit a strong absorption in the region of 300–410 nm due to the π – π * and n– π * electronic transitions.^[13] However, the band corresponds to the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy gap, which depends on the nature and efficiency of the conjugated π system. The optical band gap (Eg^{Opt}) was estimated using the following equation^[14]:

$$Eg^{Opt} = h\nu$$

The optical band gap of the helical compound established from the onset of its absorption was 2.9 eV. The band gap can be determined by fitting the absorption data to the direct transition equation by extrapolation of the linear portions of the curves to the absorption equal to zero (Fig. 2).^[15]

In this article, we have reported the synthesis and characterization of a new racemic unsymmetrical thiahexahelicene starting from readily available and inexpensive materials. We completed the synthesis of the target helicene in four steps and with an overall yield of 34%. This heterohelicene derivative shows an optical band gap of about 2.90 eV. It may also serve as a model system to investigate the structure–property



Figure 2. The absorption spectrum of the bromohelicene derivative in a dilute $CHCl_3$ solution. (Figure is provided in color online.)

relationships with respect to the electronic, electrochemical, photoconductive, and nonlinear optical properties of π -conjugated polymers.

EXPERIMENTAL

All reactions were performed under an argon atmosphere and monitored by thin-layer chromatographic (TLC) Merck 60 F-254 silica-gel plates (layer thickness 0.25 mm). Column chromatography was performed on silica gel (70–230 mesh) using ethyl acetate and cyclohexane mixture as eluents. Melting temperatures were determined on an Electrothermal 9002 apparatus and were reported uncorrected. NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 MHz (¹H) and 75 MHz (¹³C). All chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane. Toluene was distilled from sodium prior to use, and *N*,*N*-dimethylacetamide was distilled over CaH₂. Photocyclizations were carried out in a 1.5-L water-cooled quartz photoreactor equipped with a high-pressure mercury immersion lamp (Heraeus TQ 500). Electron-impact (EI) mass spectra were determined at an ionizing voltage of 70 eV.

Diarylethenes (4a–b)

Sodium methoxide (1 M in methanol) was added over 0.5 h under Ar to a solution of triphenylphosphonium salt (2 g, 3.90 mmol) and benzothiophene-2-carbaldehyde **2** (0.57 g, 3.55 mmol) in dry methanol (25 mL). The mixture was heated at 50 °C for 3 h. The reaction mixture was cooled to room temperature and

NEW THIA[6]HELICENE

concentrated under vaccum to half its volume. Water was added, and the solution was extracted many times with a large volume of CH_2Cl_2 . After drying and solvent evacuation, the residue was chromatographed on silica gel using cyclohexane/ethyl acetate (99:01) to give 0.393 g of the (Z)-isomer **4a** (35%) and 0.589 g of the (E)-isomer **4b** (53%).

(Z)-Isomer (4a). Mp = 56–58 °C; ¹H NMR (300 MHz, CDCl₃): δ = 6.62 (d, J = 12 Hz, 1H), 7.35 (d, J = 12 Hz, 1H), 7.22 (s, 1H), 7.24–7.33 (m, 4H), 7.50 (d, J = 8.4 Hz, 2H), 7.67 (dd, J = 7.2 Hz, J = 1.8 Hz, 2H) ppm; ¹³C NMR (75 MHz CDCl₃): δ = 121.94, 122.12, 123.43, 124.40, 124.56, 124.81, 125.49, 125.52, 129.85, 130.80, 131.69, 135.67, 139.02, 139.53, 140.10 ppm.

(*E*)-lsomer 4b. Mp = 139–141 °C;¹H NMR (300 MHz, CDCl₃): δ = 7.248–7.512 (m, 4H), 7.52–7.58 (m, 3H); 7.63–7.71 (m, 4H) ppm; ¹³C NMR (75 MHz CDCl₃): δ = 128.82, 128.98, 132.20, 132.33, 132.36, 132.42, 132.55, 133.01 ppm.

General Procedure for the Photocyclodehydroganation Reaction

A solution of the respective diarylethene (1 equiv), iodine (1.1 equiv), and propylene oxide (100 equiv) in toluene (1.5 L) was irradiated for 3 h, under Ar, in a photoreactor fitted with a water-cooled immersion well and a high-pressure Hg lamp (500 W, Heraeus). Evaporation of the solvent and column chromatography (SiO_2) yielded the pure compound. Experimental details and specific data for individual compounds are given.

Compound 5

350 mg (1.11 mmol) of compounds **4a** and **b** were irradiated for about 3 h, according to procedure A. After evaporation of the solvent, the final product was purified by chromatography using cyclohexane as the eluent ($R_f = 0.72$). The desired product was obtained as a white solid in 76% yield. Mp = 139–141 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.53$ (t, J = 4.5 Hz, 1H), 7.17–7.66 (m, 2H), 7.81 (d, J = 5.1 Hz, 1H), 7.86 (d, J = 5.1 Hz, 1H), 7.90 (d, J = 5.1 Hz, 1H), 7.98 (d, J = 4.8 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H), 9.10 (s, 1H) ppm; ¹³C NMR (75 MHz CDCl₃): $\delta = 121.46$, 121.55, 123.23, 124.39, 125.03, 125.53, 125.70, 127.35, 127.99, 128.15, 130.28, 130.79, 131.44, 136.09, 139.55, 139.68 ppm.

Diarylethene (6)

A solution of compound 5 (1.0 g, 3.19 mmol), 4-bromostyrene (0.82 g, 4.46 mmol), and dry sodium acetate (0.28 g, 3.50 mmol) in *N*,*N*-dimethylacetamide (5 mL) was placed in a Schlenk tube under an argon atmosphere. The mixture was heated to 100 °C before addition of a solution of the Herrmann catalyst (29.9 mg, 1%) in *N*,*N*-dimethylacetamide (2 mL). The mixture was heated then to 140 °C, and heating was maintained for about 48 h. The workup procedure involves hydrolysis, extraction with CH₂Cl₂, and drying over MgSO₄. After column chromatography using cyclohexane–ethyl acetate (98:2) as the eluent (R_f =0.39), the final product **6** was obtained in 79% yield as a pale yellow solid. Mp=158–160 °C; ¹H NMR

(300 MHz, CDCl₃): δ = 7.27 (d, *J* = 16.5 Hz, 1H, H_{vinyl}), 7.44 (d, *J* = 16.5 Hz, 1H, H_{vinyl}), 7.50–7.56 (m, 5H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 9 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 8.03 (d, *J* = 8 Hz, 1H), 8.90 (d, *J* = 8.5 Hz, 1H), 8.98 (s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ = 121.18, 121.57, 122.09, 122.71, 123.29, 124.68, 124.88, 125.35, 127.52, 128.12, 128.36, 129.01, 129.86, 129.92, 130.95, 131.59, 131.88, 135.69, 136.25, 136.63, 139.18, 139.85 ppm.

Thiahexahelicene (1)

The photocyclization of 150 mg (0.36 mmol) of compound **6**, according to procedure A, yielded 65% of 2-bromothiahexahelicene as a yellow solid, after 3 h of irradiation followed by column chromatography on silica gel using cyclohexane/ethyl acetate (99:01) as the eluent ($R_{\rm f}$ =0.50), mp=198–200 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.9 (dd, J=4.8 Hz, J=0.9 Hz, 2 H), 7.36 (t, J=8.1 Hz, 1 H), 7.54 (dd, J=8.7 Hz, J=1.8 Hz, 1 H), 7.85–8.12 (m, 8 H), 8.15 (s, 1 H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ = 120.50, 122.18, 122.73, 122.97, 124.86, 126.02, 126.17, 126.54, 127.06, 127.37, 127.96, 128.62, 129.18, 129.56, 130.27. 131.42, 131.63, 131.72, 132.03, 132.98, 136.06, 138.90, 140.38 ppm; MS (EI, 70 eV): m/z = 413 ([M⁺], 100%).

X-Ray Crystal Structure Determination of Thiahexahelicene 1

Single crystals of 1 were obtained by slow evaporation of a methylene chloride/ hexane solution at ambient temperature. X-ray data were recorded on a a Bruker Smart CCD diffractometer. Chemical formula $C_{24}H_{13}BrS$, M=413.31, crystal dimensions $0.10 \times 0.10 \times 0.10$ mm, monoclinic, space group P21/n. At 20 °C: a=13.3335(4) Å, b=7.2326(2) Å, c=18.2038(13) Å, volume 1750.90(14) Å³, Z=4, $\rho_{calcd}=1.568$ g/cm³, x-ray source Cu Ka, $\lambda=01.54180$ Å, measured reflections 6591, independent reflections 3100, reflections used 3100, refinement type Fmls, parameters refined 236, R1=0.088, wR2=0.306. CCDC 781749 contains the supplementary crystallographic data for thiahexahelicene. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033 or e-mail: deposit@ ccdc.cam.ac.uk).

ACKNOWLEDGMENT

The authors are grateful to the DGRS (Direction Générale de la Recherche Scientifique) of the Tunisian Ministry of Higher Education and Scientific Research for financial support.

REFERENCES

- Martin, R. H.; Marchant, M.-J.; Baes, M. Rapid synthesis of hexa- and heptahelicenes. *Helv. Chim. Acta* 1971, 54, 358–360.
- 2. (a) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. Synthesis and properties of optically active helical metallocene

oligomers. J. Am. Chem. Soc. 1993, 115, 3182–3198; (b) Dai, Y.; Katz, T. J. Synthesis of helical conjugated ladder polymers. J. Org. Chem. 1997, 62, 1274–1285; (c) Fox, J. M.; Lin, D.; Itagaki, Y.; Fujita, T. Synthesis of conjugated helical acetylene-bridged polymers and cyclophanes. J. Org. Chem. 1998, 63, 2031–2038.

- Fox, J. M.; Katz, T. J. Conversion of a [6]helicene into an [8]helicene and a helica. J. Org. Chem. 1999, 64, 302–305.
- (a) Tsuneomi, K.; Kenta, K.; Emanuela, L.; Alberto, B.; Stefano, M.; Kenso, S. Enantio-selective synthesis induced by tetrathia-[7]-helicenes in conjunction with asymmetric autocatalysis. *Tetrahedron: Asymmetry* 2006, *17*, 2050–2053; (b) Reetz, M. T.; Sostmann, S. 2,15-Dihydroxy-hexahelicene (HELIXOL): Synthesis and use as an enantioselective fluorescent sensor. *J. Organomet. Chem.* 2000, *603*, 105–109; (c) Dreher, S. D.; Katz, T. J.; Lam, K. C.; Rheingold, A. L. Application of the russig laatsch reaction to synthesize a bis[5]helicene chiral pocket for asymmetric catalysis. *J. Org. Chem.* 2000, *65*, 815–822; (d) Okubo, H.; Yamaguchi, M.; Kabuto, C. Macrocyclic amides consisting of helical chiral1,12-dimethylbenzo[c]phenanthrene-5,8-dicarboxylate. *J. Org. Chem.* 1998, *63*, 9500–9509; (e) Reetz, M. T.; Beuttenmuller, E. W.; Goddart, R. First enantioselective catalysis using a helical diphosphane. *Tetrahedron Lett.* 1997, *38*, 3211–3214.
- (a) Ben Hassine, B.; Gorsane, M.; Geerts-Evrard, F.; Pecher, J.; Martin, R. H.; Castelet, D. Synthèses et synthèses ennthioselectives d'epoxydes derivant du (*E*)-stilbene et de l'αmethylstilbene par la methode de payne. *Bull. Soc. Chim. Belg.* **1986**, *95*, 547–556; (b) Ben Hassine, B.; Gorsane, M.; Pecher, J.; Martin, R. H. Diastereoselective NaBH₄ reductions of (dl) α-ketoesters. *Bull. Soc. Chim. Belg.* **1985**, *94*, 597–603.
- (a) Tovar, J. D.; Rose, A.; Swager, T. M. Functionalizable polycyclic aromatics through oxidative cyclization of pendant thiophenes. *J. Am. Chem. Soc.* 2002, *124*, 7762–7769; (b) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. Synthesis, morphology, and field-effect mobility of anthradithiophenes. *J. Am. Chem. Soc.* 1998, *120*, 664–672.
- (a) Boorum, M. M.; Vasilev, Y. V.; Drewello, T.; Scott, L. T. Groundwork for a rational synthesis of C₆₀: Cyclodehydrogenation of a C₆₀H₃₀ polyarene. *Science* 2001, 294, 828–831; (b) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. A rational chemical synthesis of C₆₀. *Science* 2002, 295, 1500–1503; (c) Rabideau, P. W.; Abdourazak, A. H.; Marcinow, Z.; Sygula, R.; Sygula, A. Buckybowls, 2:Toward the total synthesis of buckminsterfullerene (C₆₀): Benz[5,6]-as-indaceno-[3,2,1,8,7-mnopqr]indeno[4,3,2,1-cdef]chrysene. *J. Am. Chem. Soc.* 1995, *117*, 6410–6411; (d) Sygula, A.; Rabideau, P. W. A practical, large scale synthesis of the corannulene system. *J. Am. Chem. Soc.* 2000, *122*, 6323–6324.
- (a) Wynberg, H. Some observations on the chemical, photochemical, and spectral properties of thiophenes. Acc. Chem. Res. 1971, 4, 65–67; (b) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. Synthesis and properties of an aggregating heterocyclic helicene. J. Am. Chem. Soc. 2001, 123, 11899–11907; (c) Kitahara, Y.; Tanaka, K. Synthesis, crystal structure and properties of thiaheterohelicenes containing phenolic hydroxy functions. Chem. Commun. 2002, 932–933; (d) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. Chiral molecular glass: Synthesis and characterization of enantiomerically pure thiophene-based [7]-helicene. Chem. Eur. J. 2004, 10, 6531–6539; (e) Maiorana, S.; Papagni, A.; Licandro, E.; Annunziata, R.; Paravidino, P.; Perdicchia, D.; Giannini, C.; Bencini, M.; Clays, K.; Persoons, A. A convenient procedure for the synthesis of tetrathia-[7]-helicene. Tetrahedron 2003, 59, 6481–6488.
- Caronna, T.; Sinisi, R.; Catellani, M.; Luzzati, S.; Abbate, S.; Longhi, G. Chiroptical properties of some monoazapentahelicenes. *Synth. Met.* 2001, *119*, 79–80.
- (a) Tanaka, K.; Osuga, H.; Suzuki H. Diastereocontrolled synthesis of optically pure functionalized heterohelicenes. *Tetrahedron: Asymmetry* **1993**, *4*, 1843–1856; (b) Murguly, E.; McDonald, R.; Branda, N. R. Chiral discrimination in hydrogen-bonded [7]helicenes. *Org. Lett.* **2000**, *2*, 3169–3172; (c) Stammel, C.; Fröhlich, R.; Wolff, C.; Wenck, H.;

Mattay, J. Efficient phenanthrene, helicene, and azahelicene syntheses. *Eur. J. Org. Chem.* **1999**, 1709–1718.

- Aloui, F.; El Abed, R.; Ben Hassine, B.; Marinetti, A. A new approach to 3,14-dihydroxyhexahelicene: Resolution and attribution of the absolute configuration. C. R. Chimie 2009, 12, 284–290.
- 12. Sheldrick, M. Program for Crystal Structure Refinement, University of Göttingen; Germany, 1997. SHELXL-97:
- Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. Improved methodology for photocyclization reactions. J. Org. Chem. 1991, 56, 3769–3775.
- Ku, C.-H.; Kuo, C.-H.; Leung, M.-K.; Hsieh, K.-H. Carbazole–oxadiazole containing polyurethanes as phosphorescent host for organic light emitting diodes. *Eur. Polym. J.* 2009, 45, 1545–1553.
- Phokaa, S.; Laokul, P.; Swatsitang, E.; Promarak, V.; Seraphinc, S.; Maensiri, S. Synthesis, structural and optical properties of CeO₂ nanoparticles synthesized by a simple polyvinyl pyrrolidone (PVP) solution route. *Mater. Chem. Phys. A* 2009, *115*, 423–428.