



Carbohelicenes and thiahelicene from phthalaldehydes through Perkin approach

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ABSTRACT

Synthesis and structural features of helical nanographene molecules comprising of seven benzene rings are examined. Thus dibutyl-dicarboxylate functional [7]helicene and its two regioisomers, dinaphtho[1,2-*a*:1',2'-*h*]anthracene and naphtho[2,1-*c*]pentahelicene, have been synthesized in two steps through Perkin approach using naphthalene-2-acetic acid and *ortho*- or *meta*-phthalaldehydes. The feasibility of this approach to construct sulfur doped twisted dithiaarenes is also investigated by using thiophene-3-acetic acid. While dithiaarenes from *meta*-phthalaldehyde remains challenging, synthesis and characterization of planar anthra[1,2-*b*:5,6-*b'*]dithiophene and twisted 1,12-dithiapentahelicene is successful from *ortho*-phthalaldehyde. Conformational analysis with DFT calculation shows unique helicity preference in such doubly helical carbon nanostructures. Absorption and emission behavior of these π -extended molecules shows enhanced conjugation.

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1. Introduction

Synthesis of polycyclic aromatic hydrocarbons and their heteroatomic counterparts as atomically precise carbon nanostructures has drawn immense attention in recent past due to their geometric interest and applications in organic electronics [1]. The electronic nature of these carbon nanostructures highly depends on their overall geometry and it can be tuned further by substitutional doping with heteroatom like sulfur or nitrogen [2,3]. Among various such carbon nanostructures that have been synthesized and studied recently, non-planar helical nanostructures are particularly interesting due to their peculiar topology, enhanced solubility because of less self-aggregation and induced chirality without having any asymmetric carbon [4]. Aromatization or "graphitization" of flexible but highly conjugated precursors in order to generate consecutive *ortho*-fused benzene rings is the key to construct such highly strained polyaromatics. Although there are

several "bottom-up" synthetic methodologies exist to construct such twisted graphene molecules with multiple helicity driven chiral centers, Perkin condensation approach followed by oxidative ring closure, demonstrated by Bock and co-workers [5,6], has come up advantageous due to its facile and scalable synthetic approach, tunable solubility of the resulting graphene fragments and access to a wide ranges of aryl aldehyde and arylacetic acid building blocks to explore variety of nanographenes with different shape and helicity. In this study, three different twisted carbon nanostructures as regioisomers comprising of fully *kata*-condensed seven benzene rings with different helicity have been synthesized through conventional Perkin condensation between naphthalene-2-acetic acid and *ortho*- or *meta*-phthalaldehydes, followed by photo-catalyzed ring closure and their structural and photophysical properties were investigated. While synthesis of functional [7]helicene has already been reported by the glyoxylic variant of this approach [7] and few other methodologies [8], strategies related to synthesis and structural properties of its other doubly helical regioisomers are also significant but little studied [9–12].

Unsubstituted phenacenes with planar geometry or single helicity containing seven benzene rings have recently been synthesized from comparatively larger phenanthrene building blocks [13]. Thus dibutyl-dicarboxylate substituted dinaphtho[1,2-*a*:1',2'-*h*]

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anthracene **1** and naphtho[2,1-*c*]pentahelicene **3** with double helical structures and [7]helicene **2** have been synthesized and studied (Fig. 1). Furthermore, the feasibility of this approach with thiophene-3-acetic acid, which was successfully undertaken for double fold Perkin condensation in the past, although thiophene-2-acetic acid remained unsuccessful, has been attempted [5]. So the synthesis of anthra[1,2-*b*:5,6-*b'*]dithiophene **5** and 1,12-dithiapentahelicene **6**, two structural isomers with planar and helical geometries respectively, have also been successfully achieved and their structural properties have been investigated via computation.

2. Materials and methods

Conventional Perkin condensation reaction between naphthalene-2-acetic acid and *ortho*-phthalaldehyde followed by same-pot esterification was performed to obtain diacrylate precursor **7**, which was further subjected to photo-mediated ring closure to obtain dinaphtho[1,2-*a*:1',2'-*h*]anthracene **1** and [7]helicene **2** as a mixture of two cyclized products at different sides of the benzene ring (Scheme 1). Due to high regioselectivity of 2-naphthyl group in photocyclization, isomers through ring closure at 1-position of naphthyl were obtained [14].

The separation of two isomers was done through column chromatography (see ESI). Interestingly the yield of formation of highly strained [7]helicene **2** was little higher than its sterically less demanding regioisomer **1**, which was unexpected as the previous studies have reported formation of either only sterically more stable dinaphthoanthracene or both, along with [7]helicene in comparatively much lower yield, from photocyclization of stilbene type precursors [10,15]. Contrarily, reaction between naphthalene-2-acetic acid and *meta*-phthalaldehyde followed by the similar photo-mediated ring closure provided only one isomer, naphtho[2,1-*c*]pentahelicene **3**, in good yield. The regioselectivity of this double cyclization can be explained from the electron density in the DFT optimized structure of **8** in its most stable transoid geometry with aryl groups are in *cis* relation [16]. HOMO-LUMO distribution at **8** shows enhanced reactivity at 2-position of benzene ring in compare to its bis-stilbene counterpart (see ESI, Fig. S4), which gave sterically less demanding dinaphtho[1,2-*a*:2',1'-*j*]anthracene either as sole photocyclized product [14], or along with naphtho[2,1-*c*]pentahelicene as more resonance stabilized product [12].

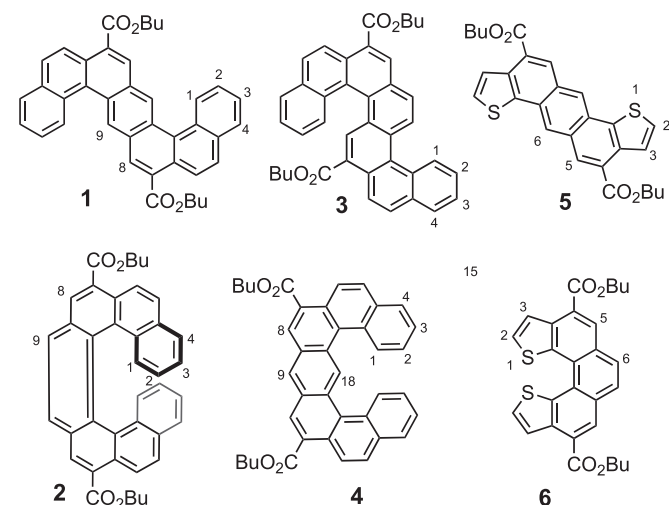


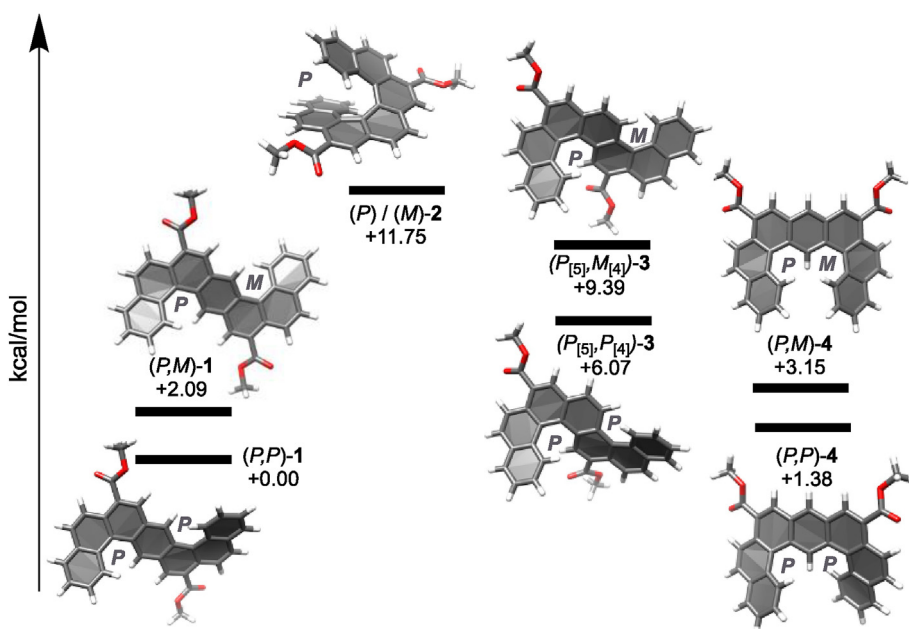
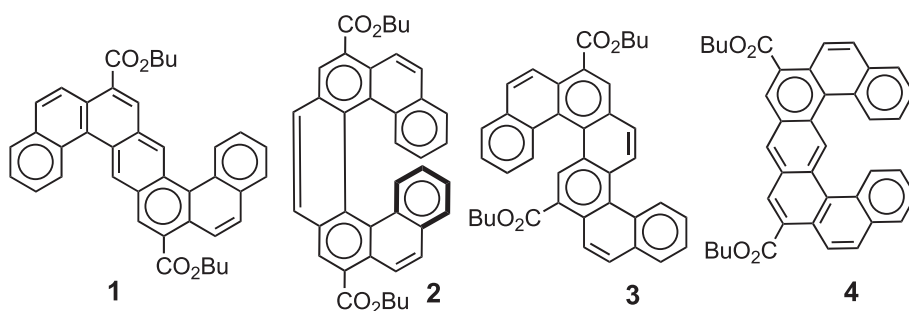
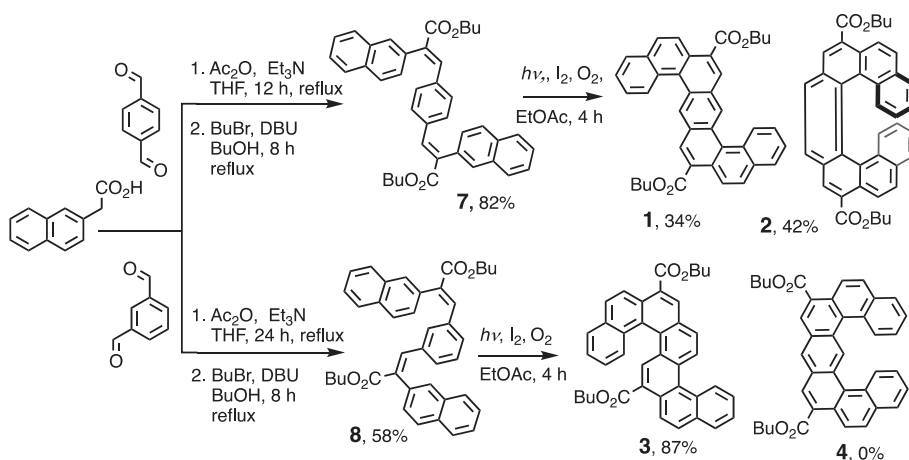
Fig. 1. Highly twisted carbohelicenes (**1–4**), sulfur embedded planar dithiaanthracene (**5**) and thiahelicene (**6**).

3. Results and discussion

The structures of these nanocarbons were assigned by ¹H NMR. Due to the presence of a C₂-axis in both regioisomers **1** and **2**, eight aromatic proton signals were observed for total sixteen aromatic protons in ¹H NMR including two singlets, four doublets and two triplets for each regioisomer. The unsymmetrical structure of **3** was also confirmed by ¹H NMR spectra with sixteen aromatic protons, unlike dinaphthoanthracene **4**, which should have nine aromatic proton signals with a highly deshielded singlet peak above 10 ppm for the sterically compressed H₁₈ [12]. Due to the presence of an anthracene segment, less aromatic sextets can accommodate in **1** (and also in **4**), enhancing "acene-type" π -delocalization and resulting in deshielded aromatic proton signals, in comparison to **2** and **3** with sextets in every alternative rings (Fig. 2). Thus, while H₉ singlet of **1** (Fig. 1) characteristically appeared at 9.63 ppm resulting from the γ -proton of embedded anthracene moiety at sterically demanding and twisted position, the singlet for H₉ of **2** appeared with significant upfield shift at 8.12 ppm due to its more "vinylic" nature resulted from rigidly localized sextets in the adjacent rings [for NMR spectra, See ESI]. Further [7]helicene **2** can coexist with its enantiomeric *P* and *M* helicity separately without racemization at room temperature due to a high energy barrier for racemization (41 kcal/mol at 300 K) and thus can be defined as "rigid" structure [17]. However, dinaphthoanthracene **1** with two oppositely facing [4]helicene moieties can also exist with energetically equivalent (*P,P*) or (*M,M*) and energetically dissimilar (*P,M*) [or (*M,P*)] double helicity (Fig. 3), although these conformers are in fast equilibrium at room temperature as previous studies have theoretically predicted that the racemization energy barrier of [4]helicene is only about 4 kcal/mol and thus can be defined as "flexible" structure [17].

For naphtho[2,1-*c*]pentahelicene **3**, between its inversely facing [5]helicene and [4]helicene segments, the helicity of the former should be preserved at room temperature due to relatively higher racemization energy barrier (23 kcal/mol at 293 K) and hence, will determine the chirality of the molecule [17]. Whereas, due to fast racemization at [4]helicene moiety, the overall molecular geometry of **3** will be rapidly interchanging between its two energetically dissimilar diastereomers (*P* [5],*P* [4]) and (*P* [5],*M* [4]) (or between (*M* [5],*M* [4]) and (*M* [5],*P* [4])). So while the NMR signals for **2** were generated from a rigid [7]helicene structure with magnetically equivalent *P* and *M* helical enantiomers, signals for **1** and **3** came from flexible structures with fast exchange among different helical conformers. To understand the energetics of these helical nanocarbons, the structures of possible diastereomers of **1–4** have been optimized with DFT calculation at B3LYP/6-31G(d,p) level (Fig. 3). Interestingly, for all doubly helical nanocarbons, **1**, **3** and **4**, conformers with both *P* helicity (*P,P*) are more stable than their respective alternatively helical (*P,M*) counterparts. Dinaphthoanthracene **1** with (*P,P*) helicity is the most stable conformer among all and it is calculated to be 2.09 kcal/mol and 11.75 kcal/mol more stable than respectively its (*P,M*)-counterpart and [7]helicene **2** that was obtained from the same reaction.

In order to tune the electronic nature of these helical carbon nanostructures with heteroatom doping, naphthalene-2-acetic acid was replaced with thiophene-3-acetic acid. Annulation of electron-rich thiophene rings in polyaromatic hydrocarbons, although challenging, is extremely interesting for tailoring the band gap via different sulfur configurations and to achieve interesting topology through embedded five-membered rings [18–20]. Thiophene-3-acetic was previously undertaken for double-fold Perkin condensation with 1,5-diformylnaphthalene followed by a tricky DDQ/MeSO₃H mediated oxidative cyclization at high dilution to avoid unwanted dimerization [5]. However, it was found that thiophene-



3-acetic acid can undergo double-fold Perkin condensation smoothly with *ortho*-phthalaldehyde to obtain **9**, but remained challenging with *meta*-phthalaldehyde even after several attempts and only single Perkin condensation product **11** was obtained

(Scheme 2). Photocyclization of **9** resulted in formation of two dithiaarene molecules, anthra[1,2-*b*:5,6-*b'*]dithiophene **5** and 1,12-dithiapentahelicene **6**, in high yields. The double cyclization of **9** was occurred at both side of the benzene ring through only

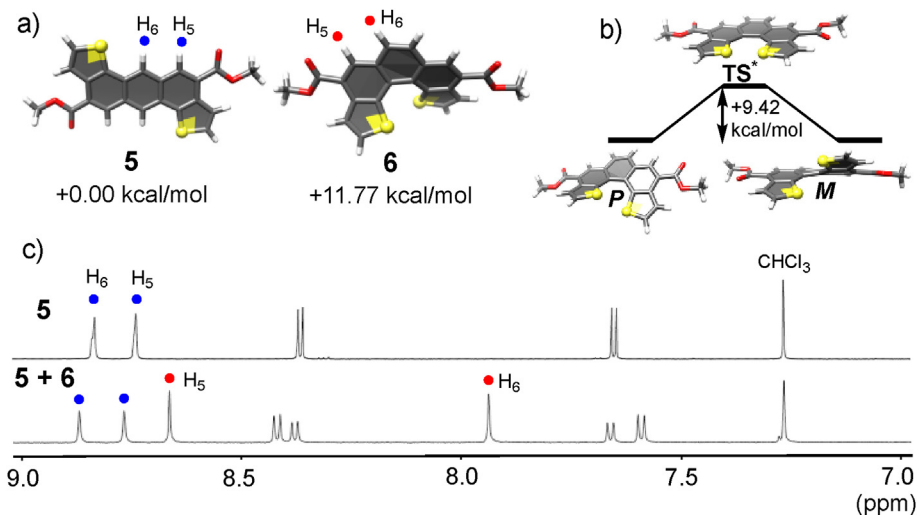


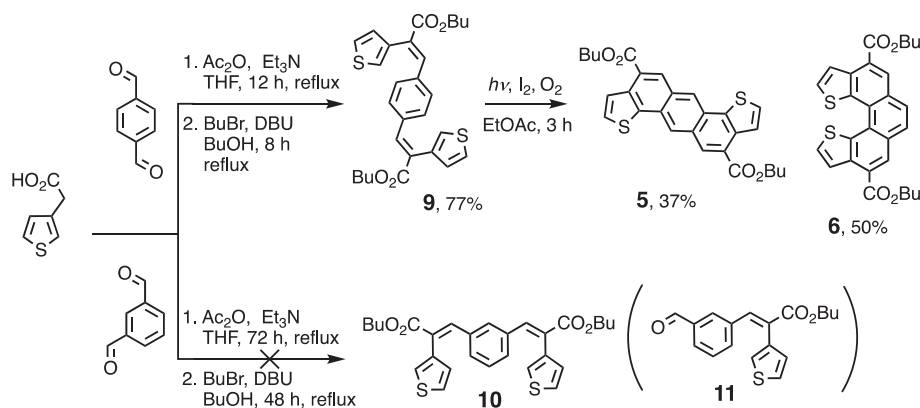
Fig. 4. a) Optimized structures with relative energies of **5** and **6** by DFT calculations (B3LYP/6-31G(d,p)). Blue and red dots indicate the singlet protons in ^1H NMR spectrum for **5** and **6** respectively. b) Transition state (TS^*) for racemization of **6** calculated by QST3 at B3LYP/6-31G(d,p) level. c) Aromatic region of the ^1H NMR spectra of the mixture of **5** and **6** after column chromatography (bottom) and isolated **5** as precipitate from the crystallization (top).

thiophene 2-positions, and not through thiophene 4-positions, which was not observed previously in photocyclization of two thiophene containing bis-stilbene type derivatives [20]. Although 3-arylvinyli-thiophenes are known to be cyclized at thiophene 2-position [21], such regioselectivity for the diacrylate **9** is more expected as the DFT optimized structure showed selective distribution of HOMO-LUMO over thiophene 2-positions indicating enhanced reactivity at this position (see ESI, Fig. S5). Although separation of these two isomers remained difficult through simple column chromatography, fortunately both ^1H and ^{13}C NMR signals for **5** and **6** are quite distinctive in the mixture, and can be assigned properly for structural identification without separation.

A small amount of **5** was isolated from the product mixture by slow crystallization from cold dichloromethane, due to its slightly less solubility resulting from planar structure, and the structural analysis was done by ^1H and ^{13}C NMR. First, formation of planar **5** with a C_2 -axis through cyclization of **9** at only thiophene 2-positions was confirmed from two aromatic singlets and two aromatic doublets in ^1H NMR, as cyclization at thiophene 4-positions should give all four singlets. The singlets were obtained for H_5 and H_6 protons with its characteristic highly deshielded H_6 singlet (Fig. 4c (top)) [19]. The remaining proton signals after excluding the peaks for **5** from the NMR of the mixture, another pairs of doublets and singlets indicating cyclization at thiophene 2-positions, could be assigned for **6** (Fig. 4c (bottom)). The phenanthrene segment of **6** typically showed a less deshielded singlet for H_6 due to its similar "vinylic" nature compare to its more "benzylic" H_5 singlet. Dithiapentahelicene **6** is the very first generation of dithiahelicene with both sulfur atoms located inwards facing each other at the helical centre. Structures of both **5** and **6** were optimized by DFT calculation showing **5** with a planar geometry and 11.77 kcal/mol more stabilized than its strained helical isomer **6** with strong electronic repulsion between bulky sulfur atoms. The total torsional angle in **6** was calculated about 61° . QST3 calculation was conducted to investigate the racemization energy of **6** between *P* and *M* helicity and it was calculated to be 9.42 kcal/mol indicating fast racemization at room temperature.

The electronic band gaps were obtained from the DFT optimized structures, which showed highest energy band gap for **3** (Fig. 5). The energy band gap for twisted dithiaarene **6** is also significantly higher than its planar counterpart.

The optical absorption and emission spectra of isolated **1**, **2**, **3** and **5** were measured in dilute chloroform solution. While **1** showed "phenacene-type" band-like and absorptions with λ_{max} at 343 nm, validating its planar geometry, helically twisted **2** and **3** with more rigid structure showed continuous absorption with λ_{max} at 314 nm and 330 nm respectively (Fig. 6). Interestingly, **1** and **2** showed identical absorption edges at 465 nm corresponding to an optical band gap of 2.67 eV indicating similar extent of seven-ring conjugation in these two systems. Optical band gap for **3** was calculated 2.82 eV (absorption edge at 440 nm), which is higher than its [7]helicene analogous indicating reduced conjugation. This phenomenon could be explained as fully *kata*-condensed naphtho fused [5]helicene **3** is less conjugated than its [7]helicene counterpart **2**, whereas partially edge peri-condensed naphtho fused [5]helicene is more conjugated than its [7]helicene analog due to increased π -surface [22]. Thiaarene **5** has optical bandgap of 2.75 eV (absorption edge at 450 nm) with λ_{max} at 328 nm, which is nicely matching with the theoretical spectra obtained from time-dependent DFT calculation, predicting "band-like" absorption for planar geometry. Thus, it confirmed our structural assignment for **5** from ^1H - and ^{13}C NMR spectroscopy. A similar time-dependent DFT calculation for **6** predicted spectra with continuous absorption and oscillator strength much lower than **5** (See ESI, Fig. S6). Although the optical band gaps are expected to be lower for these molecules than their unsubstituted counterparts due to the presence of two butylcarboxylate groups resulting in enhanced conjugation, this effect should be negligible among these molecules as distance between two substituents are almost equal in **1**–**6**. The fluorescence spectra of **1**, **2**, **3** and **5** were measured upon excitation at their corresponding absorption maxima in chloroform (Fig. 6). The regioisomers **1** and **2** fluoresce very similarly with emission maxima at 482 nm and 484 nm respectively and a significant 38 nm red shift for the emission of **2** from unsubstituted [7]helicene was observed [13]. The emission spectrum of **3** was considerably shifted hypsochromically showing similar absorption and emission properties as naphthalene fused [5]helicenes [22]. Compound **2** and **3** with persistent helical structures showed characteristic overlap of absorption and emission band. Both absorption and emission spectra of **5** were notably red-shifted from its unsubstituted counterpart with a 24 nm redshift of absorption maxima and a drastic 57 nm red shift of emission maxima [19]. Each of the



Scheme 2. Synthesis of planar dithiaarene **5** and thiahelicene **6** via Perkin approach.

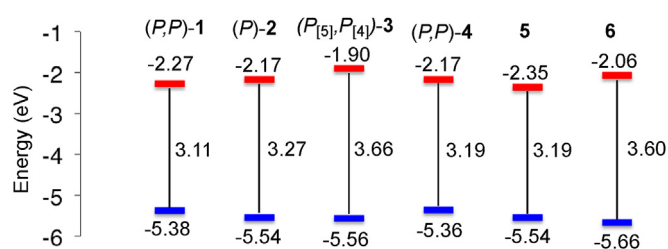


Fig. 5. HOMO (blue) and LUMO (red) energies and energy band gaps for the most stable configurations of **1–6** obtained from DFT calculations (B3LYP/6-31G(d,p)).

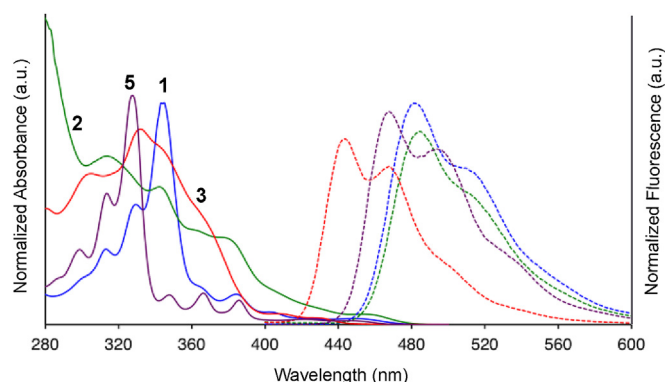


Fig. 6. Absorption (continuous line) and emission (dashed) spectra for carbohelicene **1–3** and dithiaarene **5**.

molecules possesses characteristic emission spectrum with a shoulder or hump at 24–26 nm afterwards of their corresponding emission maxima.

4. Conclusions

To conclude, three dibutyl-dicarboxylate functional nanographene regioisomers comprising of seven benzene rings have been synthesized with structural assignment through ^1H - and ^{13}C NMR spectroscopy. The conformational analysis of the doubly helical structures through DFT studies revealed a unique structural preference for such molecules attaining same helicity for both helical segments. The regioselectivity of double cyclization for less ordered diacrylate Perkin condensation product **8** was also justified thru DFT calculation indicating enhanced reactivity at sterically hindered arene 2-position for such 1,3-disubstituted aryl-

diacrylates. The feasibility of Perkin approach to obtain planar dithiaarene and twisted thiahelicene via double cyclization of bis-(3-thiophenyl) substituted aryl-diacrylates has also demonstrated and investigation of the racemization energy for the later was performed through computation, revealing fast racemization at room temperature of 1,12-dithiapentahelicene. Interestingly, in all three cases, only high-energy diastereomers with comparatively more sterically demanding structures have been formed either as the sole product (**3**) or as major product (**2** and **6**) via photocyclization at sterically hindered benzylic proton of the starting material (**8**) or mono cyclized intermediate (for **7** and **9**). Photophysical properties of these molecules showed extended conjugation with slightly "donor"-type nature due to edge functionalization with two ester groups. Although the isolation of helical 1,12-dithiapentahelicene **6** remained challenging but the viability of this approach with *ortho*-phthalaldehyde via multiple photocyclization appeared promising. Thus thiophene embedded narrow-width planar and helical graphene nanoribbons by using bifunctional thiophene acetic acids, e.g. thiophene-3,4-diacetic acid, with this approach could be possible.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2019.05.118>.

References

- [1] (a) Y. Segawa, H. Ito, K. Itami, Structurally uniform and atomically precise carbon nanostructures, *Nat. Rev. Mater.* 1 (2016) 15002–15015; (b) L. Chen, Y. Hernandez, X. Feng, K. Müllen, From nanographene and graphene nanoribbons to graphene sheets: Chemical synthesis, *Angew. Chem. Int. Ed.* 51 (2012) 7640–7654; (c) A. Narita, X.-Y. Wang, X. Feng, K. Müllen, New advances in nanographene chemistry, *Chem. Soc. Rev.* 44 (2015) 6616–6643; (d) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Organic*

- semiconductors for solution-processable field-effect transistors (OFETs), *Angew. Chem. Int. Ed.* 47 (2008) 4070–4098;
- (e) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, Semiconducting π -conjugated systems in field-effect transistors: A material odyssey of organic electronics, *Chem. Rev.* 112 (2012) 2208–2267.
- [2] (a) Y.-F. Zhang, Y. Zhang, G. Li, J. Lu, Y. Que, H. Chen, R. Berger, X. Feng, K. Müllen, X. Lin, Y.-Y. Zhang, S. Du, S.T. Pantelides, H.-J. Gao, Sulfur-doped graphene nanoribbons with a sequence of distinct band gaps, *Nano Res.* 10 (2017) 3377–3384;
- (b) D. Miao, M. Daigle, A. Lucotti, J. Boismenu-Lavoie, M. Tommasini, J.-F. Morin, Toward thiophene-annulated graphene nanoribbons, *Angew. Chem. Int. Ed.* 57 (2018) 3588–3592.
- [3] (a) C. Bronner, S. Stremmlau, M. Gille, F. Brauße, A. Haase, S. Hecht, P. Tegeder, Aligning the band gap of graphene nanoribbons by monomer doping, *Angew. Chem. Int. Ed.* 52 (2013) 4422–4425;
- (b) P. Sarkar, I.-R. Jeon, F. Durola, H. Bock, Tetraazaarenes by the ceramidonine approach, *New J. Chem.* 36 (2012) 570–574.
- [4] (a) H. Saito, A. Uchida, S. Watanabe, 5663, *J. Org. Chem.* 82 (2017);
- Y. Hu, X.-Y. Wang, P.-X. Peng, X.-C. Wang, X.-Y. Cao, X. Feng, K. Müllen, and A. Narita, Benzo-fused double [7]Carbohelicene: Synthesis, structures, and physicochemical properties, *Angew. Chem. Int. Ed.* 56, 2017, 3374–3378;
- (b) M. Ferreira, G. Naulet, H. Gallardo, P. Dechambenoit, H. Bock, F. Durola, A naphtho-fused double [7]Helicene from a maleate-bridged chrysene trimer, *Angew. Chem. Int. Ed.* 56 (2017) 3379–3382;
- (c) M. Gingras, One hundred years of helicene chemistry. Part 3: Applications and properties of carbohelicenes, *Chem. Soc. Rev.* 42 (2013) 1051.
- [5] P. Sarkar, P. Dechambenoit, F. Durola, H. Bock, Synthesis of carboxy-functionalized polycyclic arenes by oxidative cyclizations of 2,3-diarylacrylates, *Asian J. Org. Chem.* 1 (2012) 366–376.
- [6] P. Sarkar, F. Durola, H. Bock, Dipyrreno- and diperyleno-anthracenes from glyoxylic Perkin reactions, *Chem. Commun.* 49 (2013) 7552–7554.
- [7] H. Bock, D. Subervie, P. Mathey, A. Pradhan, P. Sarkar, P. Dechambenoit, E. Hillard, F. Durola, Helicenes from diarylmaleimides, *Org. Lett.* 16 (2014) 1546–1549.
- [8] (a) S.K. Collins, A. Grandbois, M.P. Vachon, J. Côté, *Angew. Chem.* Preparation of helicenes through olefin metathesis, *Chem. Int. Ed.* 45 (2006) 2923–2926;
- (b) R.E. Abed, B.B. Hassine, J.-P. Genêt, M. Gorsane, A. Marinetti, An alternative procedure for the synthesis of [5]- and [7]Carbohelicenes, *Eur. J. Org. Chem.* 7 (2004) 1517–1522;
- (c) F. Teply, I.G. Stará, I. Stary, A. Kollárovič, D. Šaman, L. Rulíšek, P. Fiedler, Synthesis of [5]-, [6]-, and [7]Helicene via Ni(0)- or Co(I)-Catalyzed isomerization of aromatic cis,cis-dienetriynes, *J. Am. Chem. Soc.* 124 (2002) 9175–9180.
- [9] H.R. Talele, A.R. Chaudhary, P.R. Patel, A.V. Bedekar, Expedient synthesis of helicenes using an improved protocol of photocyclodehydrogenation of stilbenes, *ARKIVOC* 201 (2011) 15–37.
- [10] (a) A. Sudhakar, T.J. Katz, Directive effect of bromine on stilbene photocyclizations. an improved synthesis of [7]helicene, *Tetrahedron Lett.* 27 (1986) 2231–2234;
- (b) R.H. Martin, M.-J. Marchant, M. Baes, Rapid syntheses of hexa and heptahelicene, *Helv. Chim. Acta* 54 (1971) 358–360.
- [11] C. Romero, D. Peña, D. Pérez, E. Guitián, Palladium-catalyzed [2 + 2 + 2] cycloadditions of 3,4-didehydrophenanthrene and 1,2-didehydrotriphenylene, *J. Org. Chem.* 73 (2008) 7996–8000.
- [12] J. Brison, C. Bakker, N. Defay, F. Geerts-Evrard, M.-J. Marchant, R.H. Martin, *Bull. Soc. Chim. Belg.* 92 (1983) 901–912.
- [13] S. Fujino, M. Yamaji, H. Okamoto, T. Mutai, I. Yoshikawa, H. Houjou, F. Tani, Systematic investigations on fused π -system compounds of seven benzene rings prepared by photocyclization of diphenanthrylenes, *Photochem. Photobiol. Sci.* 16 (2017) 925–934.
- [14] F.B. Mallory, C.W. Mallory, S.E. Loeb, Photochemistry of stilbenes. 7. Formation of a dinaphthanthracene by a stilbene-like photocyclization, *Tetrahedron Lett.* 26 (1985) 3773–3776.
- [15] R.H. Martin, M. Flamang-Barbieux, J.P. Cosyn, M. Gelbeke, 1-Synthesis of octa- and nonahelicenes. 2-New syntheses of hexa- and heptahelicenes. 3-Optical rotation and O.R.D. of heptahelicene, *Tetrahedron Lett.* 9 (1968) 3507–3510.
- [16] T. Rosen, in: B. Trost (Ed.), *Comprehensive Organic Synthesis*, vol. 2, Pergamon Press, Oxford, 1991, p. 395.
- [17] (a) R.H. Janke, G. Haufe, E.-U. Würthein, J.H. Borkent, Racemization barriers of Helicenes: a computational study, *J. Am. Chem. Soc.* 118 (1996) 6031–6035;
- (b) J. Barroso, J. Cabellos, S. Pan, F. Murillo, X. Zarate, M.A. Fernandez-Herrera, G. Merino, Revisiting the racemization mechanism of helicenes, *Chem. Commun.* 54 (2018) 188–191.
- [18] (a) D. Miao, M. Daigle, A. Lucotti, J. Boismenu-Lavoie, M. Tommasini, J.-F. Morin, Toward thiophene-annulated graphene nanoribbons, *Angew. Chem. Int. Ed.* 57 (2018) 3588–3592;
- (b) Y.-F. Zhang, Y. Zhang, G. Li, J. Lu, Y. Que, H. Chen, R. Berger, X. Feng, K. Müllen, X. Lin, Y.-Y. Zhang, S. Du, S.T. Pantelides, H.-J. Gao, Sulfur-doped graphene nanoribbons with a sequence of distinct band gaps, *Nano Res.* 10 (2017) 3377–3384.
- [19] (a) A. Pietrangelo, M.J. MacLachlan, M.O. Wolf, B.O. Patrick, Synthesis and structures of novel luminescent bent acenedithiophenes, *Org. Lett.* 9 (2007) 3571–3573;
- (b) E. Sankar, P. Raju, J. Karunakaran, A.K. Mohanakrishnan, Synthetic utility of arylmethylsulfones: Annulative π -extension of aromatics and heteroaromatics involving Pd(0)-catalyzed heck coupling reactions, *J. Org. Chem.* 82 (2017) 13583–15593.
- [20] S. Moussa, F. Aloui, B.B. Hassine, Synthesis and Optoelectronic Properties of Some New Thiahelicenes, *Synth. Commun.* 41 (2011) 1006–1016.
- [21] (a) M. Iwao, M.L. Lee, R.N. Castle, Synthesis of phenanthro[*b*]thiophenes, *J. Heterocyclic Chem.* 12 (1980) 1259–1264;
- (b) R.M. Kellogg, M.B. Groen, H. Wynberg, Photochemically induced cyclization of some furyl- and thienylethenes, *J. Org. Chem.* 32 (1967) 3093–3100;
- (c) G. DeLuca, G. Martelli, S. Spagnolo, M. Tiecco, Photochemical cyclisation of some iodophenyl- and iodothieryl-(thienyl)-ethylenes, *J. Chem. Soc. (C)* (1970) 2504–2508.
- [22] A.-C. Bédard, A. Vlassova, A.C. Hernandez-Perez, A. Bessette, G.S. Hanan, M.A. Heuft, S.K. Collins, Synthesis, crystal structure and photophysical properties of pyrene–helicene hybrids, *Chem. Eur J.* 19 (2013) 16295–16302.