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Short Note

# 7,7-Difluoropentaphen-6(7H)-one

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**Abstract:** New fluorinated pentaphene derivative has been obtained as a potential precursor for fluorinated polycyclic aromatic hydrocarbons. In this work 7,7-difluoropentaphen-6(7H)-one was prepared from 1,1-difluoroanthracen-2(1H)-one via Diels-Alder reaction with *o*-quinodimethane generated *in situ* from *o*-bis(dibromomethyl)benzene. The structure of newly synthesized compound was confirmed by <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR, IR and UV/Vis spectroscopy as well as high-resolution mass spectrometry.

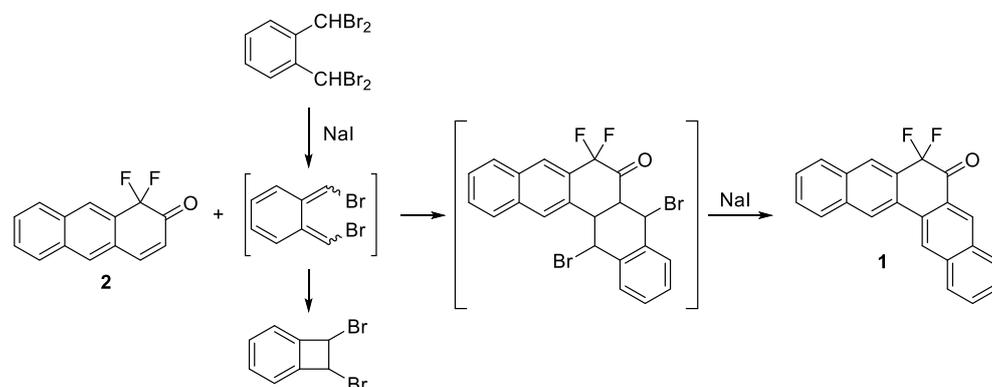
**Keywords:** Diels-Alder reaction; polycyclic compounds; fluorinated compounds

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of great interest as semiconducting materials for use in organic electronic and optoelectronic devices including field effect transistors, light-emitting diodes and solar cells[1,2]. Design of fluorinated PAHs has also been an ongoing task for many research groups: the introduction of fluorine atom allows one to tune electronic properties, increase stability of materials and significantly influence their solid state organization[3,4]. The Diels-Alder reaction has been widely used for PAH synthesis[5,6] and the development of new fluorinated building blocks for cycloaddition is currently of interest. Herein, we report the synthesis of 7,7-difluoropentaphen-6(7H)-one as a potential precursor for fluorinated small molecule PAHs via the Diels-Alder reaction of difluoroanthracenone as dienophile.

## 2. Results and Discussion

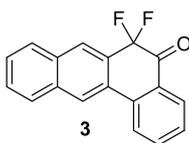
7,7-Difluoropentaphen-6(7H)-one **1** was synthesized according to our previously developed method based on Cava procedure (Scheme 1)[7].



**Scheme 1.** Synthesis of 7,7-difluoropentaphen-6(7H)-one **1**.

The dibromo-*o*-quinodimethane generated *in situ* from *o*-bis(dibromomethyl)benzene in presence of NaI acts as a diene and upon trapping by **2** and subsequent aromatization of primary cycloadduct gives the target pentaphene derivative **1**. The workup includes washing the reaction mixture from iodine and DMF with aqueous solution of sodium thiosulphate and water respectively, depositing the residue on short silica column and rinsing it with hexane to eliminate the byproducts generated from diene (mainly dibromobenzocyclobutane identified by GCMS and reported in literature[8]). Finally, the product is washed off with chloroform and recrystallized to isolate **1** as yellow solid in 20% yield.

The structure of 7,7-difluoropentaphen-6(7*H*)-one **1** was confirmed by means of <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR, IR and UV/Vis spectroscopy as well as high-resolution mass spectrometry. As expected, the <sup>1</sup>H NMR spectrum contains 4 singlets of protons in positions 5, 8, 13 and 14. <sup>13</sup>C NMR signals also display highly characteristic C-F coupling constants of 243 Hz (CF<sub>2</sub>), 26 Hz (CO) and 4.6-22 Hz for other carbon atoms adjacent to CF<sub>2</sub> group. The spectral data is consistent with that of previously reported 6,6-difluorotetraphen-5(6*H*)-one **3**, tetraphenone analogue of **1**[7]. The addition of conjugated ring results in slight redshift of UV/Vis absorption maxima (295 and 406 nm for **1** vs 284 and 398 nm for **3**) and a shift in IR spectrum (1704 cm<sup>-1</sup> for C=O bond in **1** vs 1719 cm<sup>-1</sup> for **3**).



**Figure 1.** 6,6-Difluorotetraphen-5(6*H*)-one **3**.

We believe the obtained fluorinated pentaphenone may serve as a precursor for fully aromatic pentaphene derivatives via reductive aromatization similarly to its tetraphenone analogue giving angular fluorinated PAH representative.

### 3. Materials and Methods

<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on Bruker AV-300, AV-400, DRX-500 and AV-600 spectrometers at room temperature, chemical shifts ( $\delta$ ) are given in ppm relative to TMS and CFCl<sub>3</sub> respectively. GC/MS spectra were recorded on Agilent 6890 instrument operating at 70 eV with MSD Agilent 5973. High resolution mass spectra (HRMS) were measured using Thermo Fisher Scientific Double Focusing System (DFS) Magnetic Sector high resolution mass-spectrometer operating at 70 eV electron ionization and 200°C ion source temperature. The DFS mass-spectrometer was calibrated with respect to the standard lines of perfluorokerosene (PFK) prior to measurements. IR spectra were recorded on Bruker Vector 22 spectrometer and UV-Vis spectra were recorded on Varian Cary 5000 spectrophotometer (lg( $\epsilon$ ) is indicated in brackets). Melting points were recorded on Mettler-Toledo FP81. Column chromatography was carried out on silica gel (40-63  $\mu$ m) and TLC analysis was performed on silica gel TLC plates. All reactants were of commercial purity and used without further purification except 1,1-difluoroanthracen-2(1*H*)-one **2** synthesized according to previously reported method[9] and DMF dried over 3Å molecular sieves.

**Synthesis of 7,7-difluoropentaphen-6(7*H*)-one **1**:** To a solution of 1,1-difluoroanthracen-2(1*H*)-one **2** (230 mg, 1.0 mmol) in 7 ml of anhydrous DMF were added *o*-bis(dibromomethyl)benzene (2.65 g, 6 mmol) and finely ground NaI (8.9 g, 60 mmol) in 3 equal portions with 30 min interval under vigorous stirring at 80°C. After the last portion, reaction mixture was stirred for another 30 min at 80°C. Solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (17.4 g, 70 mmol of pentahydrate in 25 ml of water) was added and the resulting mixture was extracted with chloroform (4×50 ml). The combined organic phase was separated, washed with brine and dried over MgSO<sub>4</sub>. Solvent was removed under reduced pressure. The residue

was percolated on silica with hexane to wash off dihalobenzocyclobutenes. Product was washed off with chloroform, evaporated in vacuum and recrystallized from hexane-chloroform 1:1 mixture giving the product as yellow solid. Yield 65 mg (20%). Decomposes without melting.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ),  $\delta$ : 7.60 – 7.66 (m, 2H), 7.69 (t,  $J=7.7$  Hz, 1H), 7.75 (t,  $J=7.7$  Hz, 1H), 8.07 – 8.14 (m, 3H), 8.19 (d,  $J=8.0$  Hz, 1H), 8.52 (s, 1H), 8.72 (s, 1H), 8.94 (s, 1H), 8.96 (s, 1H).  $^{13}\text{C}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ),  $\delta$ : 109.67 (t,  $J=243.2$  Hz), 124.19 (s), 125.09 (s), 125.53 (s), 126.40 (t,  $J=22.2$  Hz), 127.28 (t,  $J=5.5$  Hz), 127.83 (s), 127.94 (s), 128.35 (t,  $J=4.6$  Hz), 128.44 (s), 128.53 (s), 128.69 (s), 128.89 (s), 130.08 (s), 130.36 (s), 130.62 (s), 130.90 (s), 132.02 (s), 132.22 (s), 134.69 (s), 136.70 (s), 185.45 (t,  $J=25.9$  Hz).  $^{19}\text{F}$  NMR (282 MHz,  $\text{DMSO}-d_6$ ),  $\delta$ : -99.8 (s). HRMS: Calcd. for  $(\text{C}_{22}\text{H}_{12}\text{OF}_2)^+$ : 330.0851. Found: 330.0845. IR (KBr,  $\text{cm}^{-1}$ ): 3054, 2924, 1704  $\nu(\text{CO})$ , 1620, 1289, 1115, 747. UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  = 280 nm (3.72), 295 nm (3.62), 406 nm (1.96).

**Supplementary Materials:** The following are available online: copies of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR, IR, UV/Vis and HR mass spectra for compound 1.

**Author Contributions:** Conceptualization, O.T.D. and P.A.Z.; methodology, O.T.D.; software, O.T.D.; validation, O.T.D.; formal analysis, O.T.D.; investigation, O.T.D.; resources, P.A.Z.; data curation, O.T.D.; writing – original draft preparation, O.T.D.; writing – review and editing, P.A.Z.; visualization, O.T.D.; supervision, P.A.Z.; project administration, O.T.D.; funding acquisition, O.T.D. and P.A.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Russian Foundation for Basic Research, projects 19-33-60101 and 20-03-00700.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** Authors thank the Multi-Access Chemical Research Centre SB RAS at N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS for spectral analysis

**Conflicts of Interest:** The authors declare no conflict of interest.

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