

Short Note

## 10,10'-Dimethoxy-9,9'-biazuleno[2,1-*c*]phenanthrene

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**Abstract:** The title compound was prepared by the regioselective homocoupling of 10-methoxyazuleno[2,1-*c*]phenanthrene in the presence of ammonium persulfate. The structure of the synthesized compound was assigned on the basis of its <sup>1</sup>H-NMR, FT-IR, and mass spectral data. Its crystal structure and electrochemical properties are also reported.

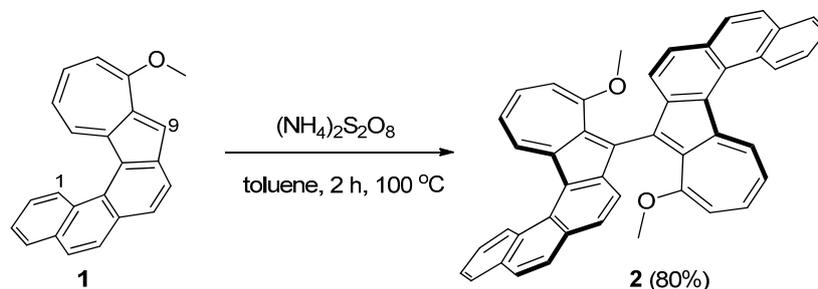
**Keywords:** azulene-fused helicene; homocoupling reaction; ammonium persulfate

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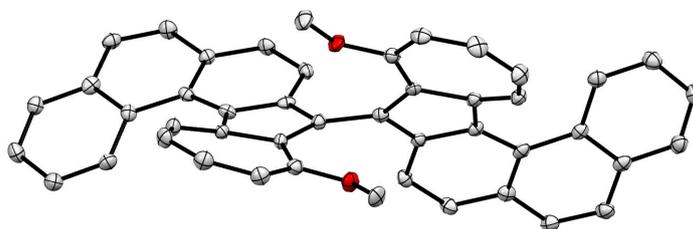
Azulene and its derivatives, which are brilliant blue nonbenzenoid aromatic hydrocarbons, have garnered significant attention because of their remarkable electronic and optical properties. Significantly, the parent molecule exhibits a large dipole moment due to charged aromatic partial structures. Hence, azulene possesses donor-acceptor characteristics that may be exploited in advanced functional electronic, optoelectronic, and electrochromic devices. Among azulene derivatives, expansion of the  $\pi$ -conjugated system of 1,1'-biazulene derivatives has attracted significant interest owing to their unique spectral and redox properties [1–3]. In that context, we recently reported that azulene-fused helicenes could be formed through 1-functionalized [5]helicenes by Pt(II)-catalyzed cycloisomerization [4,5].

As a part of our research program, we herein report the synthesis of 10,10'-dimethoxy-9,9'-biazuleno[2,1-*c*]phenanthrene (**2**) using 10-methoxyazuleno[2,1-*c*]phenanthrene (**1**) and ammonium persulfate (APS) as a radical initiator (Scheme 1) [6]. The observed

regioselectivity was attributed to the electron-rich 9-position of **1**. The structure of **2** was assigned on the basis of its  $^1\text{H-NMR}$ , FT-IR, and mass spectral data. Green crystals of **2** were obtained by recrystallization from dichloromethane/diethyl ether (1:1) (Figure 1) [7]. Intermolecular interactions were found in the crystals of enantiomers of **2**, ((*P, P, S*) and (*M, M, R*)) (Figure S1).



**Scheme 1.** Synthesis of 10,10'-dimethoxy-9,9'-biazulenophenanthrene (**2**).



**Figure 1.** ORTEP drawing of the X-ray crystal structure of **2**. Dichloromethane and H-atoms have been omitted for clarity.

Compound **2** was investigated by cyclic voltammetry in *o*-dichlorobenzene (Figure S2). The cyclic voltammogram of **2** revealed reversible two-stage one-electron oxidation processes ( $E_1^{\text{OX}} = 0.46$ ,  $E_2^{\text{OX}} = 0.75$  V (vs  $\text{Fc}/\text{Fc}^+$ )) despite the twisted geometry of the neutral species. Such redox behavior may be attributed to the planar conformation, and may lead to spin and/or charge delocalization over the entire  $\pi$ -system [8,9]. The title compound is thus a good candidate for constructing reversible multistage redox systems.

## Experimental Section

### General Information

NMR spectra were recorded in  $\text{CDCl}_3$  at ambient temperature on *Bruker Avance III* (500 MHz) spectrometer. The chemical shifts ( $\delta$ ) were recorded in ppm with residual  $\text{CHCl}_3$  signal referenced to 7.26 ppm. Coupling constants ( $J$ ) are reported in Hz and refer to the apparent peak multiplicities. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br s = broad singlet, br d = broad doublet, br t = broad triplet. FT-IR spectra were recorded on a *Perkin-Elmer Spectrum One (FT-IR)* spectrometer (Yokohama, Japan). FT-IR absorptions were recorded in  $\text{cm}^{-1}$ . Melting point was recorded on a *Yanako MP-13* (Tokyo, Japan). High resolution mass spectra were recorded on a *Bruker micrOTOF (ESI-TOF)* spectrometer (Yokohama, Japan).

*Synthesis of 10,10'-Dimethoxy-9,9'-biazuleno[2,1-c]phenanthrene (2)*

10-Methoxyazuleno[2,1-c]phenanthrene (**1**) was synthesized according to our previously reported method [3]. Under an argon atmosphere, a mixture of compound **1** (50 mg, 0.16 mmol) and APS (183 mg, 0.80 mmol) in degassed toluene (25 mL) was heated at 100 °C for 1 h. Additional APS (183 mg, 0.80 mmol) was added and the mixture was stirred for 2 h at 100 °C. After cooling to room temperature, the reaction mixture was washed with brine, and extracted with CHCl<sub>3</sub>. The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel 60N (spherical neutral, 40–50 μm, Kanto Chemical Co., Inc., Hexane/AcOEt = 50:1) to give **2** (40 mg, 80% yield) as a green solid.

Melting point: no change until 300 °C.

FT-IR (neat):  $\nu_{\max}$  (cm<sup>-1</sup>): 2922, 1571, 1499, 1446, 1261, 1218, 954, 834, 789, 758, 729, 697, 682.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ 9.54 (d,  $J = 7.7$  Hz, 2H), 9.35 (d,  $J = 8.2$  Hz, 2H), 7.99 (dd,  $J = 8.0, 0.9$  Hz, 2H), 7.86 (br d,  $J = 8.0$  Hz, 2H), 7.80 (d,  $J = 8.5$  Hz, 2H), 7.74 (br s, 2H), 7.60 (dt,  $J = 7.0, 1.0$  Hz, 2H), 7.52 (t,  $J = 7.4$  Hz, 2H), 7.34 (br t,  $J = 9.8$  Hz, 4H), 6.75 (t,  $J = 9.7$  Hz, 2H), 6.55 (br s, 2H), 3.12–3.25 (m, 6H).

HRMS (ESI-TOF): [M]<sup>+</sup> calcd for C<sub>46</sub>H<sub>30</sub>O<sub>2</sub> 614.2240; found 614.2210.

### Acknowledgments

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### Author Contributions

The listed authors contributed to this work in the following ways: K. Yamamoto and R. Nakamae performed the synthesis and identification; H. Suemune and K. Usui prepared the manuscript. All authors read and approved the final manuscript.

### Conflicts of Interest

The authors declare no conflict of interest.

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