5H,13*H*-5,13a-[1′,2′]Benzenocyclopenta[*rst*]pentaphen-13-one: A New Triptycene Derivative with a Strained Structure

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The title compound, a new anthracene-containing triptycene derivative, was synthesized. The crystal structure shows its strained configuration and intermolecular π–π stacking arrangement. Photochemical [4 + 4] dimerization occurs easily in solution and in the solid state, even under visible-light irradiation.

The rigid three-dimensional framework of triptycene and its derivatives has been found to confer unique properties with the possibility of attractive applications not only in structural organic chemistry but also in supramolecular chemistry and materials science.[1] Certain triptycene derivatives have been shown to be candidates for synthetic molecular machines.[2] Also, π-systems with an anthracene structure have been the subject of much interest due to their photophysical and photochemical properties, and unique reactivities. In particular, inter- or intramolecular [4 + 4] photodimerization of anthracene derivatives is a very useful property for switching functions.[3] Several triptycene derivatives containing anthracene have been synthesized with an emphasis on their fluorescent properties and the construction of an extended three-dimensional rigid framework.[4] In the course of our studies concerning novel π-systems with an anthracene structure,[5] we prepared a new triptycene derivative with an anthracene moiety, 5*H*,13*H*-5,13a-[1′,2′]benzenocyclopenta[*rst*]pentaphen-13-one (**1**). We here report the synthesis, structure, photochemical properties, and reactions of **1**.

Synthesis of **1** was carried out by dehydration of the precursor ketone **2**, prepared from di(9-anthryl)methanone by photochemical [4 + 2] cycloaddition (Scheme 1).[5,6] Compound **1** is an orange crystalline substance, and ^{1}H and ^{13}C NMR spectra reflect its highly symmetrical structure.[7] The UV–vis spectrum of **1** shows the typical pattern of a 9-carbonylanthracene chromophore (Figure 1). The longest absorption maximum is at 453 nm, which is about 70 nm longer than that of 9-acetylanthracene.[8] The coplanar arrangement of the carbonyl group with the anthracene ring accounts for the bathochromic shift.[4c] A solution of **1** shows a strong fluorescence with a high quantum yield ($\Phi = 0.62$), while the precursor **2** shows weak fluorescence ($\Phi = 0.002$). This photophysical property is ascribed to the presence of the anthracene fluorophore in **1** and its rigid structure.

Recrystallization of **1** from a dichloromethane–hexane mixture afforded a single crystal suitable for X-ray crystallography.[7,9] Figure 2 shows the crystal structure of **1**. The inter-arene angles of the triptycene group are all close to 120° (118.4, 120.2, and 121.4°). Because only one sp^2 carbon (C29) is connected between the bridgehead carbon (C9) and the central-ring carbon of the anthracene moiety (C23), the bicyclo[2.2.2]octane skeleton of the triptycene group is slightly deformed. The C9–C15 length is 1.485(4) Å, whereas that of C10–C16 is 1.539(4) Å. Moreover, the long bond length of C9–C29 (1.572(4) Å) and spread angle of C9–C29–C23 (128.1(3)°) indicate the strained structure of **1**. In the crystal, stacking of the anthracene planes is observed; two molecules face each other in head-to-tail manner (Figure 2c). The shortest distance between two anthracene planes is 3.42 Å.

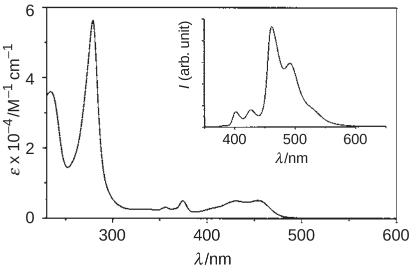


Figure 1. UV–vis spectrum of **1** in CH$_2$Cl$_2$. Inset: Emission spectrum of **1** in CH$_2$Cl$_2$.

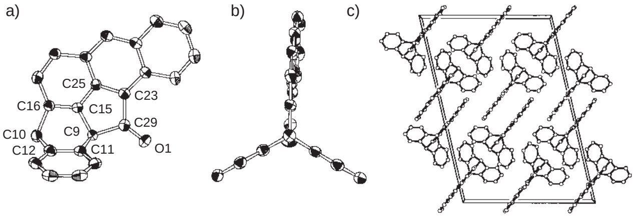
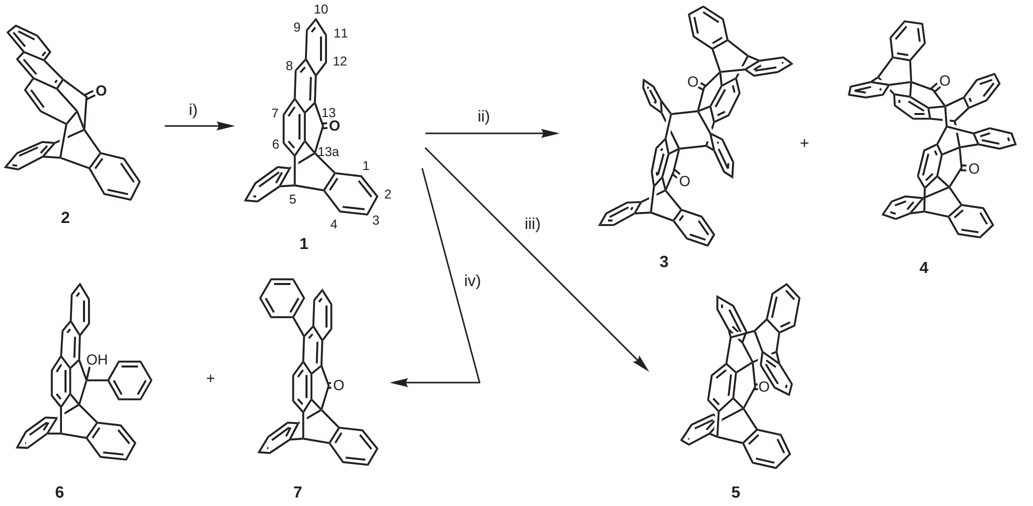


Figure 2. Molecular structure of **1**. a) Side view; b) view along the C9–C10 axis; c) crystal packing viewed along the *b*-axis.

Compound **1** is thermally stable (mp 324 °C), but it possesses unique photoreactivity. A photochemical [4 + 4] cycloaddition reaction proceeded gradually when a chloroform solution of **1** was allowed to stand in sunlight; after several days, colorless crystals were obtained and identified as the head-to-tail dimer **3** (containing one chloroform molecule in the unit cell) by X-ray crystallography.[7,9]

The cycloaddition reaction under photoirradiation was monitored by NMR spectroscopy. A CDCl$_3$ solution of **1** was photoirradiated using a 500-W Xenon lamp. The signal intensity of the bridgehead proton (δ 5.73) immediately decreased and two sets of singlet signals (δ 5.24/4.76 and 5.36/4.66) appeared with a 1:1 molar ratio. One is assigned to head-to-tail dimer **3** based on data of the pure sample; therefore, the other must be head-to-head dimer **4** (Scheme 1).[10] The reaction was completed within 30 min, and notably, proceeded even under visible light. When irradiated with light through a 450 nm cut-off filter, **1** was completely consumed to give **3** and **4**, although the reaction time was prolonged to 3 h.

This property of photodimerization via visible-light irradiation enabled us to prepare a cross-photoadduct with anthracene.[11] Visible-light irradiation ($\lambda > 450$ nm) of a mixture of



Scheme 1. i) DDQ, benzene, reflux, 92%; ii) $h\nu$ (500-W Xenon lamp)/$CDCl_3$, 30 min, >99% (**3**:**4** = 1:1); iii) $h\nu$ (>450 nm), anthracene (30 equiv.), benzene, 6 h, >99%; iv) 10 equiv. PhLi/THF, −78 °C, 30 min, then 0 °C, 1 h, 53% for **6**, 26% for **7**.

1 and anthracene (molar ratio 1:30) caused excitation only of **1**, and the excited state of **1** was quenched by the surrounding anthracene to form **5** (Scheme 1).[7]

In contrast, photoirradiation of **1** in the solid state afforded head-to-tail dimer **3** alone. X-ray analysis of **1** reveals that the distances between the bond-forming carbons are both 3.772 Å, which is short enough to indicate dimerization of anthracene in the solid state.[12] Selective formation of **3** reflects the topology of the crystal phase. The photoadducts **3**, **4**, and **5** underwent thermal reversal to **1** almost quantitatively. When neat samples of dimers **3** and **4** were heated at 200 °C in the dark for 30 min, **1** was cleanly obtained.

Finally, we examined nucleophilic addition reactions of **1**. Treatment of **1** with *n*-BuLi afforded a complex mixture, probably due to competitive reactions caused by electron transfer. The reaction with phenyllithium, however, gave the corresponding alcohol **6** in 53% yield as well as the 8-phenyl substituted derivative **7** in 26% yield (Scheme 1).[7] Compound **7** does not dimerize upon irradiation either in solution or in the solid state, probably owing to steric hindrance. X-ray analysis shows that the intermolecular distance between the anthracene rings is 4.59 Å, which is too far to undergo [4 + 4] cycloaddition.[7,9]

In conclusion, we have prepared a new anthracene-containing triptycene derivative **1** and characterized its structure and photophysical and photochemical properties. Easy [4 + 4] photodimerization, which can be conducted under visible light, is the most noteworthy feature of **1**; this is probably due to its stained structure. The fluorescent properties of **1**, in combination with the property of selective cross-adduct formation with anthracene, results in a potential switching or sensing system with emission-based detection.

References and Notes

1 a) G. Yamamoto, Y. Kobayashi, K. Ono, E. Yano, M. Minoura, Y. Mazaki, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1293. b) C. Zhang, C.-F. Chen, *J. Org. Chem.* **2006**, *71*, 6626. c) E. M. Veen, P. M. Postma, H. T. Jonkman, A. L. Spek, B. L. Feringa, *Chem. Commun.* **1999**, 1709. d) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 11864. e) T. M. Long, T. M. Swager, *J. Am. Chem. Soc.* **2003**, *125*, 14113.

2 a) G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* **2005**, *105*, 1281. b) T. R. Kelly, R. A. Silva, H. D. Silva, S. Jasmin, Y. Zhao, *J. Am. Chem. Soc.* **2000**, *122*, 6935. c) C. E. Godinez, G. Zepeda, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 4701.

3 a) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.* **2000**, *29*, 43. b) H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, *Chem. Soc. Rev.* **2001**, *30*, 248.

4 a) H.-D. Becker, K. Sandros, K. Andersson, *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 495. b) H.-D. Becker, K. Andersson, *Tetrahedron Lett.* **1983**, *24*, 3273. c) H.-D. Becker, H. Sörensen, E. Hammarberg, *Tetrahedron Lett.* **1989**, *30*, 989. d) H. Sakurai, K. Sakamoto, A. Nakamura, M. Kira, *Chem. Lett.* **1985**, 497. e) J. Luo, H. Hart, *J. Org. Chem.* **1987**, *52*, 3631.

5 Y. Nishimae, H. Kurata, M. Oda, *Angew. Chem. Int. Ed.* **2004**, *43*, 4947.

6 H.-D. Becker, L. Hansen, K. Andersson, *J. Org. Chem.* **1986**, *51*, 2956.

7 Spectroscopic data and ^{1}H NMR spectra of all new compounds and crystallographic data and structures of **1**, **3**, and **7** are summerized in Supporting Information, which is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/.

8 UV–vis data of 9-acetylanthracene in CH_2Cl_2: λ_{max}/nm ($\log \varepsilon$) 384 (3.85), 364(3.89), 347(3.71), 331(3.42), 256(5.18).

9 Crystallographic data of **1**, **3**, and **7** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-637053, 637054, and 637055, respectively.

10 There should be four isomers for the dimer of **1**; however, two of them are excluded because of steric hindrance (see Supporting Information, which is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/).

11 Examples of approaches to selective formation of anthracene cross-dimers: a) H. Bouas-Laurent, R. Lapouyade, *J. Chem. Soc. D* **1969**, 817. b) D. Bailey, V. E. Williams, *Chem. Commun.* **2005**, 2569. c) D. Bailey, V. E. Williams, *J. Org. Chem.* **2006**, *71*, 5778.

12 V. Ramamurthy, K. Vekatesan, *Chem. Rev.* **1987**, *87*, 433.