HETEROCYCLES, Vol. 80, No. 2, 2010, pp. 1187 - 1196. © The Japan Institute of Heterocyclic Chemistry
Received, 3rd August, 2009, Accepted, 31st August, 2009, Published online, 4th September, 2009
DOI: 10.3987/COM-09-S(S)102

THERMAL BEHAVIOR OF BICYCLO[2.2.2]OCTADIENE-INSTALLED PRECURSORS FOR 2*H*-ANTHRA[2,3-*c*]PYRROLES AND ANTHRA[2,3-*c*]THIOPHENE

Hiroki Uoyama,[a] Cai Chenxin,[a,b] Hiroyuki Tahara,[a] Yusuke Shimizu,[a] Hideki Hagiwara,[c] Yasuaki Hanasaki,[c] Hiroko Yamada,[a,d] Tetsuo Okujima,[a] and Hidemitsu Uno[a,b]*

[a] Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan, [b] CREST, JST, [c] Tosoh Organic Chemical Co., Ltd., 4988 Kaisei-cho, Shunan 746-0006, Japan, [d] PRESTO, JST

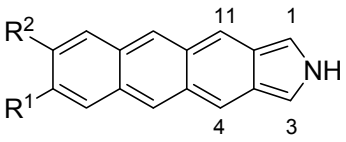
Abstract – 4,11-Ethano-4,11-dihydro-2*H*-anthra[2,3-*c*]pyrrole and 4,11-ethano-4,11-dihydroanthra[2,3-*c*]thiophene derivatives were prepared from the corresponding bicyclo[2.2.2]octadiene-fused five-membered heterocycles by the Diels-Alder reaction with *in situ* generated α,α'-dibromo-*o*-xylylene derivatives. Their thermogravimetric analyses showed evapolation without formation of 2*H*-anthra[2,3-*c*]pyrrole and anthra[2,3-*c*]thiophene derivatives under the atmospheric pressure.

Dedicated to Emeritus Professor Akira Suzuki on the occasion of his 80th birthday

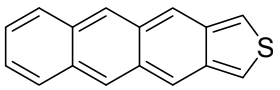
INTRODUCTION

Higher benzo analogs of [*c*]-fused five-membered heterocycles such as 2*H*-isoindole and isothianaphthene have attracted much attention from synthetic and theoretical chemists,[1] because these compounds showed clear contrast to the corresponding higher analogs of [*b*]-fused five-membered heterocycles (indoles and thianaphthenes) in the sense of aromaticity.[2] Local aromaticity is expected in addition to grobal aromaticity in [*b*]-fused five-membered heterocycles, while there is only grobal aromaticity in the [*c*]-fused five-membered hetrerocycles. These compounds are very unstable and readily decompose to form intractable resinous material. Moreover, existence of proton tautomerism in *N*-free isoindole analogs makes this problem worse. The 1- and 3-positions of 2*H*-isoindole are very reactive

toward electrophiles, while the 3-position of tautomeric isoindolenine (1*H*-isoindole) is highly electrophilic. Thus, self-condensation of isoindoles between the tautomers easily occurs especially in solution. Therefore, preparation of these compounds was limitted for the *N*-substituted derivatives such as naphtho[2,3-*c*]pyrrole and dibenzo[*e*,*g*]isoindoles.[3] However, the instability of isoindole, isothianaphthene, and their higher benzo analogs is not due to aromaticity,[1,2] but attributable to their high HOMO and low LUMO energy levels and very large coefficients at 1- and 3-positions in their HOMO and LUMO. In other words, these compounds must not be unstable if these molecules are separated from themselves in vacuum or in an inert matrix, because they have the similar heat formation energies to the corresponding [*b*]-fused heterocycles. During our continuous studies for the preparation and application of highly π-conjugated aromatics, we have explored the pericyclic cycloreversion method toward these highly reactive compounds either by thermal extrusion of ethylene from bicyclo[2.2.2]octadiene moiety (BCOD)[4] or by photo decomposition of an oxalo bridging moiety.[5] The latter method is proved to be extremely useful for the preparation of OTFT fabrication by a solution process[6] and for highly unstable π systems such as higher acenes.[7] However, this method has an inevitable drawback: difficult and tedious preparation of the precursors having the oxalo bridging moiety. Therefore, the thermal conversion method still deserves a certain advantage in order to roughly estimate fundamental stability and sensitivity of a new π system. In this paper, we will discuss about the results on our effort toward preparation of 2*H*-anthra[2,3-*c*]pyrroles (**1**) and anthra[2,3-c]thiophene (**2**) (Figure 1) by the thermal conversion of the BCOD-installed precursors.



1a: $R^1 = R^2 = H$
1b: $R^1 = Br$; $R^2 = H$
1c: $R^1 = R^2 = Br$



2

Figure 1. 2*H*-Anthra[2,3-*c*]pyrrole and anthra[2,3-*c*]thiophene

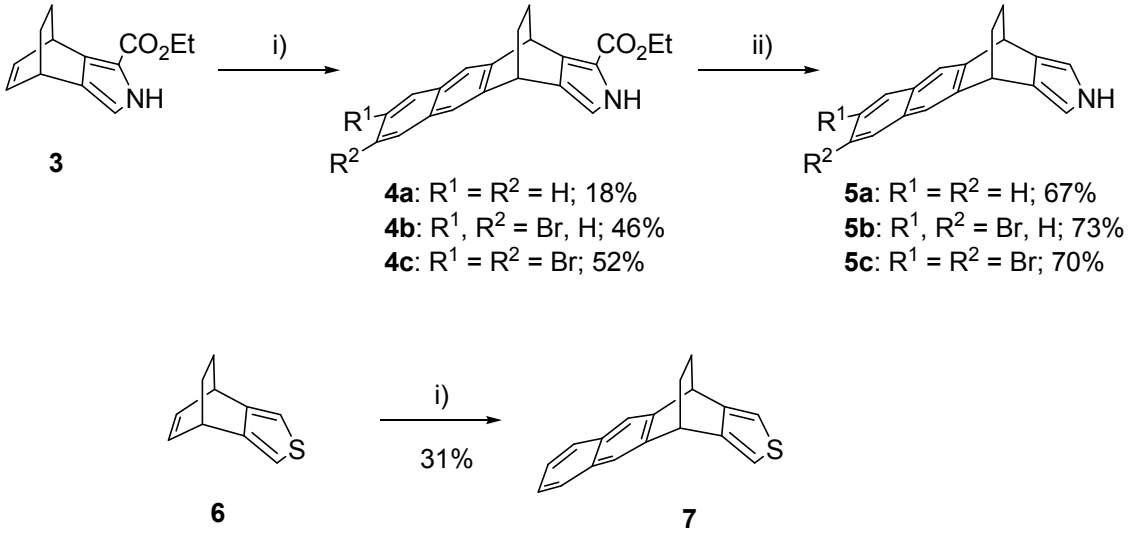
RESULTS AND DISCUSSION

Preparation of BCOD-installed Precursors

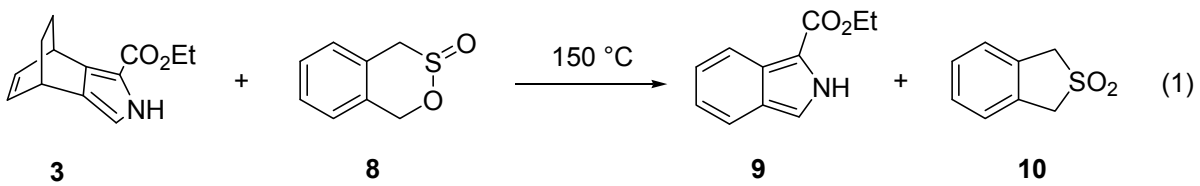
We successfully prepared the lower analog of anthra[2,3-*c*]pyrrole, namely naphtha[2,3-*c*]pyrrole, by construction of the pyrrole ring at an olefinic double bond of 1,4-ethano-1,4-dihydronaphthalene based on the modified Barton-Zard reaction.[8] In the case of anthra derivatives, however, preparation of hitherto unknown 1,4-ethano-1,4-dihydroanthracene is not thought to be easy due to the low reactivity of 1,3-cyclohexadiene toward dienophiles such as 2,3-naphthalyne.[9] Therefore, we decided to construct

the naphthalene ring at the double bonds of 4,7-ethano-4,7-dihydroisoindole[10] and 4,7-ethano-4,7-dihydroisothianaphthene[11] derivatives (Scheme 1).

The reactions of ethyl 4,7-ethano-4,7-dihydroisoindole-1-carboxylate (**3**) with *o*-xylylene generated from some precursors were examined. Since BCOD-fused pyrrole **3** gradually decomposed to the corresponding isoindole over 180 °C in solution, a precursor which generated *o*-xylylene at the lower temperature must be required. 1,3-Dihydroisothianaphthene S,S-dioxide (**10**) was reported as a thermal precursor for *o*-xylylene.[12] BCOD-fused pyrrole **3** and sulfone **10** were heated at 100 °C for several hours and the reaction was monitored by TLC. As no other compound than the starting materials was observed, the temperature was gradually raised finally to 170 °C. The desired Diels-Alder product was not formed at all and the presence of isoindole **9** was detected. Sultine derivative **8** prepared from the reaction of α,α'-dibromoxylene with Longalite ($HOCH_2SO_2Na\cdot 2H_2O$) was reported to be a good precursor for *o*-xylylene.[12,13] The reaction of **3** with sultine **8** was conducted at 150 °C and the reaction was stopped after disappearance of **3**. The identifiable products were, however, isoindole **9** and sulfone **10**, and none of the desired Diels-Alder product was obtained (Eq 1). In order to suppress the undesired retro-Diels-Alder reaction of **3**, the reaction temperature was lowered. However, decomposition prior to the desired Diels-Alder reaction or no reaction took place.



Scheme 1. Preparation of BCOD-installed precursors. *Reagents and conditions*: i) $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene, NaI, DMF, 65 °C; ii) KOH, ethylene glycol, 175 °C.



After several trials for the construction of the naphthalene ring, α,α'-dibromoxylylene *in situ* generated from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene and NaI was proved to be a good reagent for this purpose.[14] Preparation of the BCOD-installed precursors for anthra[2,3-*c*]pyrroles and anthra[2,3-*c*]thiophene is shown in Scheme 1. BCOD-fused pyrrole **3** was reacted with $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene in DMF at 65 °C with the aid of NaI to give ethanoanthra[2,3-*c*]pyrrole **4a** in a 18% yield.[15] Similarly, brominated ethanoanthra[2,3-*c*]pyrroles **4b** and **4c** were obtained by using 4,$\alpha,\alpha,\alpha',\alpha'$-pentabromo-*o*-xylene and 4,5,$\alpha,\alpha,\alpha',\alpha'$-hexabromo-*o*-xylene in 46% and 52% yields, respectively. The ester moiety of these compounds was easily removed by the alkaline treatment in ethylene glycol at 175 °C to afford α-free pyrroles **5a**, **5b**, and **5c** in good yields. BCOD-installed thiophene **7** was also obtained from 4,7-ethano-4,7-dihydroisothianaphthene (**6**)[11] in a 31% yield.

Thermal Behavior of the BCOD-installed Precursors

The sample compositions of precursors were first examined by combustion and X-ray analyses. The combusion analysis showed that a tiny amount of water was included in the purified samples of **4a**, **4b**, **5a**, and **7** (see experimental section). In the cases of **5a** and **7**, single crystals for the X-ray analysis were obtained by slow diffusion of methanol into solutions of **5a** and **7** in chlorobenzene.[16] In both crystals, no solvent molecule was found. Figure 2 shows the Ortep drawings of **5a** and **7**. In the asymmetric unit cell of **5a**, two crystallographically independent molecules were found. Dihedral angles of the BCOD moiety in **5a** and **7** (plane[C3a,C4,C11,C11a] vs plane[C4,C4a,C10a,C11]) were 120.23(17)°, 121.12(17)° and 122.05(13)°. These values were quite similar to those obverved in ethanoisoindoles (121.1(1)°~122.8(2)°).[17] Interestingly, the angles between the mean planes of pyrrole and naphthalene moieties were narrowed to be 113.86(9)° and 119.09(9)°, while that of thiophene and naphthalene was widened to be 123.97(5)°. This difference would be ascribed to the crystal packing effect.

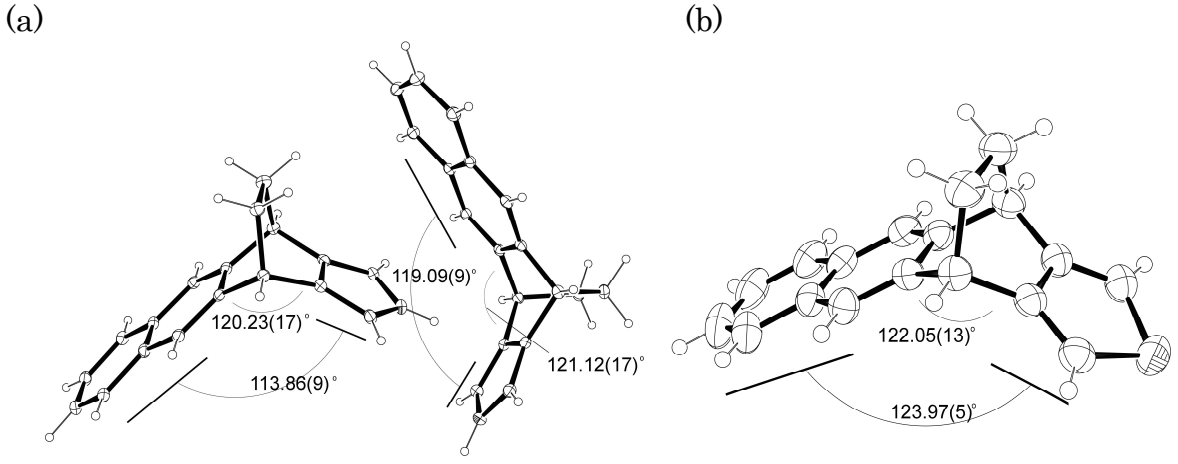


Figure 2. Ortep drawings of (a): **5a** and (b): **7** with plane angles

The thermal behaviors of the BCOD-installed compounds were examined by thermogravimetric analysis (TG), conditions of which were as follows: About 2 mg of the sample were weighed and placed on an aluminium pan, and the temperature was slowly raised to 450 °C at a rate of 10 °C/min under a stream of nitrogen. The TG curves of ethyl anthra[2,3-*c*]pyrrole-1-carbonylates were shown in Figure 3-a. In all cases, weight losses started at *ca*. 230 °C and stopped at *ca*. 300 °C for **4b**, 325 °C for **4a**, and 350 °C for **4c**. The total weight losses of **4a**, **4b**, and **4c** were 65-95%. Simultaneous differential thermal analysis (DTA) revealed the existence of isotropic phase transition during the weight losses. The peak temperatures of DTA in **4a**, **4b**, and **4c** were 245 °C, 213 °C, and 279 °C, respectively. The lowest isotropic phase transition temperature recorded in **4b** was ascribed to the diastereomeric nature of this sample. Almost all amounts of the samples were lost in the cases of **4a** and **4b**, while some amounts of a decomposed material remained in **4c**. As the decomposition of the ethyl ester moiety at the 2-position of pyrroles started at *ca*. 250 °C,[17] the retro-Diels-Alder reaction of the BCOD moiety would not take place and the compounds would evapolate simultaneously with the ester decomposition during this temperature range. This was proved by the TG experiment of BCOD-installed α-free pyrrole derivatives **5** and thiophene **7**. The TG results are shown in Figure 3-b. The weight losses started at *ca*. 180 °C for **5a**, 230 °C for **5b**, 280 °C for **5c**, and 180 °C for **7**. From DTA, the temperatures of isotropic phase transition in **5a**, **5b**, **5c**, and **7** were 220 °C, 197 °C, 213 °C, and 240 °C, respectively. Since the BCOD moiety fused to [*c*]thiophene decomposed at the higher temperature than that fused to [*c*]pyrrole,[11,17,18] these heterocycles were concluded to evapolate without forming anthra[2,3-*c*] five-membered heterocycles **1** and **2**.

In conclusion, we prepared 4,11-ethano-4,11-dihydro-2*H*-anthra[2,3-*c*]pyrrole and 4,11-ethano-4,11-dihydroanthra[2,3-*c*]thiophene derivatives from the corresponding bicyclo[2.2.2]octadiene-fused five-membered heterocycles by the Diels-Alder reaction of

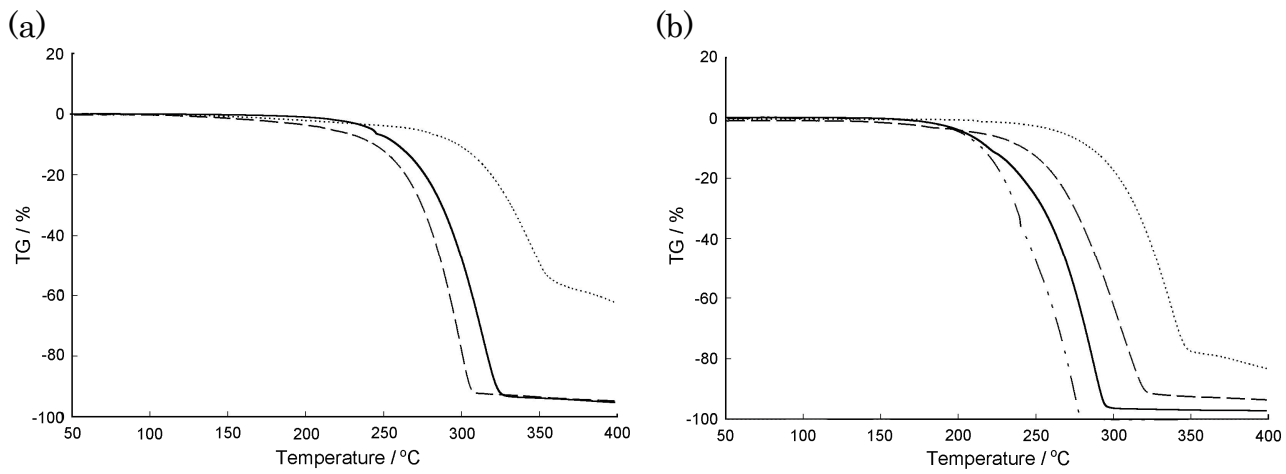


Figure 3. Thermogravimetric curves of (a): **4a** (solid line), **4b** (broken line), and **4c** (dotted line); and (b): **5a** (solid line), **5b** (broken line), **5c** (dotted line), and **7** (dotted broken line).

α,α'-dibromo-*o*-xylylenes, which were *in situ* generated from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene derivatives and NaI in DMF at 65 °C. By TG and DTA analyses, no conversion to fully conjugated 2*H*-anthra[2,3-*c*]pyrrole and anthra[2,3-*c*]thiophene derivatives was observed. The precursors bearing an ethano bridge are proved to be insufficient for the preparation of 2*H*-anthra[2,3-*c*]pyrrole and anthra[2,3-*c*]thiophene. Precursors with an oxalo bridge are necessary for this purpose. Further studies along this line are underway.

EXPERIMENTAL

General

Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using tetramethylsilane as an internal standard for ^{1}H and ^{13}C. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. EI MS spectra were measured with a JEOL JMS-700. Elemental analysis was performed with a Yanaco MT-5 elemental analyzer. TG analysis was preformed with JII EXSTAR 6000 TD/DTA6200. X-Ray diffraction was measured with a Rigaku AFC5R (for **7**) or Rigaku AFC8S Mercury-CCD (for **5a**) diffractometor. All solvents and chemicals were reagent grade quality, obtained commercially, and used without further purification except for otherwise noted. Dry DMF was distilled under a reduced pressure and then stored on Molecular Sieves 13X. Solvents for chromatography were purified by distillation. Thin-layer (TLC) and column chromatography with silica gel was performed on Art. 5554 (Merck KGaA) or Silica Gel 60N (Kanto Chemical Co.). BCOD-fused pyrrole[10] and thiophene[11] were prepared according to the literatures.

General procedure for construction of a naphthalene moiety with *α,α,α',α'*-tetrabromo-*o*-xylene

Sodium iodide (24 mmol) was added to a stirred solution of *α,α,α',α'*-tetrabromo-*o*-xylene derivative (4 mmol) and BCOD-fused pyrrole or thiophene (3 mmol) in dry DMF (20 mL) under N_2. The mixture was heated at 65 °C for 8 h. After cooling, saturated aqueous $NaHSO_3$ was added to the reaction mixture until the color turned to light yellow. The resulted white solid was collected by filtration. Recrystallization of the crude product from $CHCl_3$/hexane afforded an analytically pure sample.

Ethyl 1,4-dihydro-1,4-ethanoanthra[2,3-*c*]pyrrole-1-carboxylate (4a):[15] Yield 18%, white powder, mp 249-252 °C, R_f = 0.25 ($CHCl_3$/hexane: 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (3H, t, J = 7.2 Hz), 1.78-1.85 (4H, m), 4.35 (2H, q, J = 7.2 Hz), 4.40 (1H, m), 4.91 (1H, m), 6.70 (1H, d, J = 2.4 Hz), 7.38 (2H, m), 7.61 (1H, s), 7.68 (1H, s), 7.74 (2H, m), and 8.45 (1H, br s). Anal. Calcd for $C_{21}H_{19}NO_2$+1/8H_2O: C, 78.91; H, 6.07; N, 4.38. Found: C, 79.01; H, 6.08; N, 4.45%.

Ethyl 7-bromo-4,11-dihydro-4,11-ethanoanthra[2,3-*c*]pyrrole-1-carboxylate and ethyl

8-bromo-4,11-dihydro-4,11-ethanoanthra[2,3-*c*]pyrrole-1-carboxylate (4b): Yield 46%, white powder, mp 210.5-213.5 °C, R_f = 0.4 ($CHCl_3$/hexane: 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (3H, t, J = 7.4 Hz), 1.78-1.84 (4H, m), 4.33-4.39 (3H, m), 4.90 (1H, m), 4.90 (1H, m), 6.70 (m, 1H), 7.43-7.51 (2H, m), 7.56-7.64 (2H, m), 7.90 (1H, m), and 8.49 (1H, br s,). ^{13}C NMR (100 MHz, $CDCl_3$, typical signals) δ 14.59, 27.43, 28.02, 37.41, 37.69, 60.13, 113.76, 113.84, 115.00, 115.04, 118.81, 118.87, 119.95, 120.60, 120.73, 121.39, 128.34, 128.38, 128.38, 129.34, 129.41, 129.72, 130.54, 133.28, 133.30, 134.58, 142.89, 143.51, 143.54, 144.17, and 161.35; IR (KBr) ν_{max} 3325, 1680, 1421, 1319, 1292, and 1143 cm^{-1}; MS (EI$^+$) 398 for $C_{21}H_{19}O_2N^{81}Br$. Anal. Calcd for $C_{21}H_{19}BrNO_2$+1/4H_2O: C, 62.93; H, 4.65; N, 3.49. Found: C, 62.95; H, 4.86; N, 3.46%.

Ethyl 7,8-dibromo-4,11-dihydro-4,11-ethanoanthra[2,3-*c*]pyrrole-1-carboxylate (4c): Yield 52%, white powder, mp 211-214 °C, R_f = 0.45 ($CHCl_3$/hexane: 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (3H, t, J = 7.4 Hz), 1.79 (4H, m), 4.35 (2H, q, J = 7.4 Hz), 4.39 (1H, m) 4.89 (1H, m), 6.71 (1H, d, J = 2.7 Hz), 7.48 (1H, s), 7.56 (1H, s), 8.02 (2H, d, J = 6.1 Hz), and 8.49 (br. s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.72, 27.23, 27.89, 37.30, 37.68, 60.07, 113.70, 115.02, 119.66, 120.33, 120.71, 120.77, 129.37, 131.50, 131.59, 131.81, 131.83, 143.83, 144.48, and 161.16; IR (KBr) v_{max} 3309, 1676, 1421, 1319, 1294, 1142, 1190, and 1043 cm^{-1}; MS (EI$^+$) 475 for $C_{21}H_{17}{}^{79}Br^{81}BrNO_2$. Anal. Calcd for $C_{21}H_{19}Br_2NO_2$: C, 53.08; H, 3.61; N, 2.95. Found: C, 52.96; H, 3.70; N, 2.94%.

4,11-Dihydro-4,11-ethanoanthra[2,3-*c*]thiophene (7): Yield 31%, white powder, mp 244-245 °C, R_f = 0.40 ($CHCl_3$/hexane: 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (4H, m), 4.44 (2H, m), 6.92 (2H, s), 7.39 (2H, m), 7.63 (s, 2H), and 7.74 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.36, 40.69, 114.27, 121.24, 125.12, 127.30, 132.15, 141.71, and 144.61; IR (KBr) v_{max} 1697, 1647, 1558, 1541, 1496, 1458, and 1386 cm^{-1}. MS (EI$^+$) 262. Anal. Calcd for $C_{18}H_{14}S$+1/8H_2O: C, 81.70; H, 5.43. Found: C, 81.72; H, 5.68%. The single crystals were obtained by slow vapor diffusion of methanol into a solution of **7** in chlorobenzene. Crystal formula: $C_{18}H_{14}S$, 0.30 x 0.25 x 0.25 mm, *monoclinic*, space group $P2_1/c$, a = 6.301(5), b = 7.872(5), c = 26.269(4) Å, β = 93.81(4)º, V = 1300.0(13) Å^3, Mo $K\alpha$, T = 298 K, Z = 4, ρ_{calcd} = 1.340 g·cm^{-3}, μ = 0.230 mm^{-1}, $F(000)$ = 552. 3244 diffractions measured, 2976 unique, 1980 observed [$I > 2\sigma(I)$]; R_{equiv} = 0.0281, R_1 = 0.0459 [$I > 2\sigma(I)$], wR_2 = 0.1215 (all); GOF = 1.017. CCDC No. 739265.

General procedure for removal of an ester moiety

A stirring mixture of an ester (1.00 mmol) and KOH (5 mmol) in ethylene glycol (10 mL) was heated at 175 °C under N_2 in the dark. After 2 h, the reaction mixture was cooled to room temperature, and then extracted with CH_2Cl_2 (50 mL). The organic extract was washed with saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica-gel

chromatography and recrystallization to give the targeted compound.

4,11-Dihydro-4,11-ethanoanthra[2,3-*c*]pyrrole (5a):[15] Yield 67%, white powder, mp 220-223 °C, R_f = 0.15 ($CHCl_3$/hexane: 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (4H, m), 4.39 (2H, m), 6.70 (1H, d, J = 2.0 Hz), 7.36 (2H, m), 7.61 (2H, s), 7.73 (2H, m), and 7.59 (1H, br s). Anal. Calcd for $C_{18}H_{15}N$+1/4H_2O: C, 86.54; H, 6.25; N, 5.61. Found: C, 86.36; H, 6.36; N, 5.66%. The single crystals were obtained by slow vapor diffusion of methanol into a solution of **5a** in chlorobenzene. Crystal formula, $C_{18}H_{15}N$, 0.60 x 0.20 x 0.04 mm, *monoclinic*, space group *C2/c*, a = 35.039(6), b = 6.1755(8), c = 28.703(5) Å, β = 125.559(3)º, V = 5052.6(14) Å^3, Mo $K\alpha$, T = 100 K, Z = 16, ρ_{calcd} = 1.290 g·cm^{-3}, μ = 0.075 mm^{-1}, *F(000)* = 2080. 13006 diffractions measured, 5685 unique, 3655 observed [$I > 2\sigma(I)$]; R_{equiv} = 0.0444, R_1 = 0.0665 [$I > 2\sigma(I)$], wR_2 = 0.1953 (all); GOF = 1.049. CCDC No. 742678.

7-Bromo-4,11-dihydro-4,11-ethanoanthra[2,3-*c*]pyrrole (5b): Yield 73%, white powder, mp 182-184 °C; R_f = 0.2 ($CHCl_3$/hexane: 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (4H, m), 4.38 (2H, m), 6.59 (2H, m), 7.45 (1H, m), 7.50 (2H, m), 7.59 (2H, m), and 7.89 (1H, br s,); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.44, 37.42, 108.99, 109.07, 118.55, 119.84, 120.62, 127.45, 127.49, 128.08, 128.93, 129.29, 130.53, 133.29, 136.21, 144.33, 144.95, and one carbon signal was not identified probably due to overlap; IR (KBr) ν_{max} 3365, 1592, 1520, 1487, 1047, and 895 cm^{-1}; MS (EI$^+$) 325 for $C_{18}H_{14}N^{81}Br$. Anal. Calcd for $C_{18}H_{14}BrN$: C, 66.68; H, 4.35; N, 4.32. Found: C, 66.70; H, 4.74; N, 4.17%.

7,8-Dibromo-4,11-dihydro-4,11-ethanoanthra[2,3-*c*]pyrrole (5c): Yield 70%, white powder, mp 207-209 °C. R_f = 0.2 ($CHCl_3$/hexane: 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (4H, m), 4.39 (2H, m), 6.59 (2H, d, J = 2.4 Hz), 7.48 (2H, s), 7.64 (1H, br s), and 8.01(2H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.31, 37.42, 109.06, 119.64, 120.38, 127.22, 131.53, 131.93, and 145.21; IR (KBr) ν_{max} 3435, 1466, 1394, 1099, and 1030 cm^{-1}; MS (EI$^+$) 403 for $C_{18}H_{13}N^{79}Br^{81}Br$. Anal. Calcd for $C_{18}H_{13}Br_2N$: C, 53.63; H, 3.25; N, 3.47. Found: C, 53.72; H, 3.27; N, 3.83%.

ACKNOWLEDGEMENTS

This work was partially supported by Grant-in-Aid for Scientific Research C (20550047) from Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES AND NOTES

1. For reviews, see: *"Comprehensive Heterocyclic Chemistry*," ed. by A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, Vol. 4; *"Comprehensive Heterocyclic Chemistry II*," ed. by A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, Pergamon, Oxford, 1996. Vol. 2.
2. T. L. Gilchrist and S. J. Higgins, "*Benzo[c]thiophenes,*" in "*Hetarenes and Related Ring Systems,*

Fused Five-Membered Hetarenes with One Heteroatom," E. J. Thomas, ed in a series of "*Science of Synthesis*," George Thieme Verlag, Stuttgart, 2000, **10.5**, 185.

3. R. P. Kreher and G. Use, *Heterocycles*, 1982, **19**, 637; R. P. Kreher and T. Hildebrand, *Chem. Ber.*, 1988, **121**, 81.
4. For recent examples, see: T. Akiyama, H. Uoyama, T. Okujima, H. Yamada, N. Ono, and H. Uno, *Tetrahedron*, 2009, **65**, 4345; H. Uoyama, T. Takiue, K. Tominaga, N. Ono, and H. Uno, *J. Porphyrins Phthalocyanines*, 2009, **13**, 122; H. Uno, M. Hashimoto, and A. Fujimoto, *Heterocycles*, 2009, **77**, 887.
5. H. Uno, Y. Yamashita, M. Kikuchi, H. Watanabe, H. Yamada, T, Okujima, T. Ogawa, and N. Ono, *Tetrahedron Lett*., 2005, **46**, 1981; H. Yamada, Y. Yamashita, M. Kikuchi, H. Watanabe, T. Okujima, H. Uno, T. Ogawa, K. Ohara, and N. Ono, *Chem. Eur. J*., 2005, **11**, 6212.
6. H. Yamada, E. Kawamura, S. Sakamoto, Y. Yamashita, T. Okujima, H. Uno, and N. Ono, *Tetrahedron Lett*., 2006, **47**, 7501; A. Masumoto, Y. Yamashita, S. Go, T. Kikuchi, H. Yamada, T. Okujima, N. Ono, and H. Uno, *Jpn. J. Appl. Phys.*, 2009, 051505/1.
7. R. Mondal, B. K. Shah, and D. C. Neckers, *J. Am. Chem. Soc.*, 2006, **128**, 9612; R. Mondal, R. M. Adhikari, B. K. Shah, and D. C. Neckers, *Org. Lett.*, 2007, **9**, 2505.
8. S. Ito, N. Ochi, H. Uno, T. Murashima, and N. Ono, *Chem Commun*., 2000, 893.
9. C. S. LeHoullier and G. W. Gribble, *J. Org. Chem.*, 1983, **48**, 2364.
10. S. Ito, T. Murashima, H. Uno, and N. Ono, *Chem. Comunn.,* 1998, 1661; S. Ito, N. Ochi, T. Murashima, H. Uno, and N. Ono, *Heterocycles,* 2000, **52**, 399.
11. Y. Shimizu, Z. Shen, T. Okujima, H. Uno, and N. Ono, *Tetrahedron Lett.,* 2002, **43**, 8485; H. Uno, Y. Shimizu, H. Uoyama, Y. Tanaka, T. Okujima, and N. Ono, *Eur. J. Org. Chem.,* 2008, 87.
12. B. Rickborn, "*The retro-Diels-Alder reaction. Part II. Dienophiles with one or more heteroatom*," in "*Organic Reactions*," John Wiley&Sons, Inc., (1998) Vol. 53.
13. M. D. Hoey and D. C. Dittmer, *J. Org. Chem*., 1991, **56**, 1947.
14. M. P. Cava and A. A. Dana, *J. Am. Chem. Soc.*, 1959, **81**, 6458; M. N. Paddon-Row and H. K. Patney, *Synthesis*, 1986, 328.
15. H. Yamada, D. Kuzuhara, T. Takahashi, Y. Shimizu, K. Uota, T. Okujima, H. Uno, and N. Ono, *Org. Lett.,* 2008, **10**, 2947.
16. X-Ray data were processed by CrystalClear Ver. 1.3.6 and CrystalStructure Ver. 3.8.2. The processed data were treated with the CrystalStructure and WinGX programs. Structures were solved by SIR-97 or SIR2004, and then refined by SHELXL-97. The final structures were validated by the PLATON cif check. WinGX 1.80.03: Suite for small-molecule single-crystal crystallography, University of Glasgow, L. J. Farrugia, *J. Appl. Cryst.,* 1999, **32**, 837. CrystalClear Ver. 1.3.6 and

CrystalStructure Ver. 3.8.2: Rigaku (3-9-12 Akishima, Tokyo, Japan) and Rigaku/MSC (9009 New Trails Dr., The Woodlands, TX 77381 USA), (2006). SIR-97 and SIR2004: A package for crystal structure solution and refinement, Istituto di Gristallografia, Italy; A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Cryst*., 1999, **32**, 115. SHELXL-97: Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany; G. M. Sheldrick and T. Schneider, *Methods Enzymol.*, 1997, **277**, 319; *"A short history of SHELX"*. G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112. PLATON, A. L. Spek (2003), A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherland; A. L. Spek, *J. Appl. Cryst*., 2003, **36**, 7.

17. H. Uno, S. Ito, M. Wada, H. Watanabe, M. Nagai, A. Hayashi, T. Murashima, and N. Ono, *J. Chem. Soc., Perkin Trans. 1*, 2000, 4347.
18. J. Mack, M. Bunya, Y. Shimizu, H. Uoyama, N. Komobuchi, T. Okujima, H. Uno, S. Ito, M. J. Stillman, N. Ono, and N. Kobayashi, *Chem. Eur. J.,* 2008, **14**, 5001.