SYNTHESIS OF OPTICALLY ACTIVE 9-METHOXY-9,10-DIHYDRO-9,10-ETHANOANTHRACENE-11,12-DICARBOXAMIDE DERIVATIVES *VIA* ASYMMETRIC DIELS-ALDER REACTION OF A CHIRAL SULFINYLMALEIMIDE WITH 9-METHOXYANTHRACENE†

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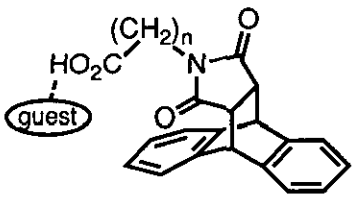
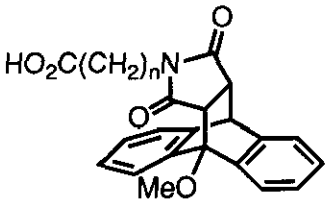
Abstract -- Optically active 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide derivatives (**1a-c**) were synthesized *via* an asymmetric Diels-Alder reaction of a chiral sulfinylmaleimide (**2**) with 9-methoxyanthracene (**3**).

Recently, Weber *et al.*[1] have reported that a characteristic 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide famework comprising an *N*-bonded lateral group showed the crystalline inclusion properties (Chart 1). The rigid tetracyclic framework is a favorable structural element for crystalline hosts. Moreover, the carboxylic acid unit in the *N*-bonded lateral group promotes clathrate formation by hydrogen bond interactions. To the best of our knowledge, there have been no reports on an asymmetric synthesis of 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide framework.[2] We thus designed an optically active 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide (**1**) (Chart 2).



n = 1-5

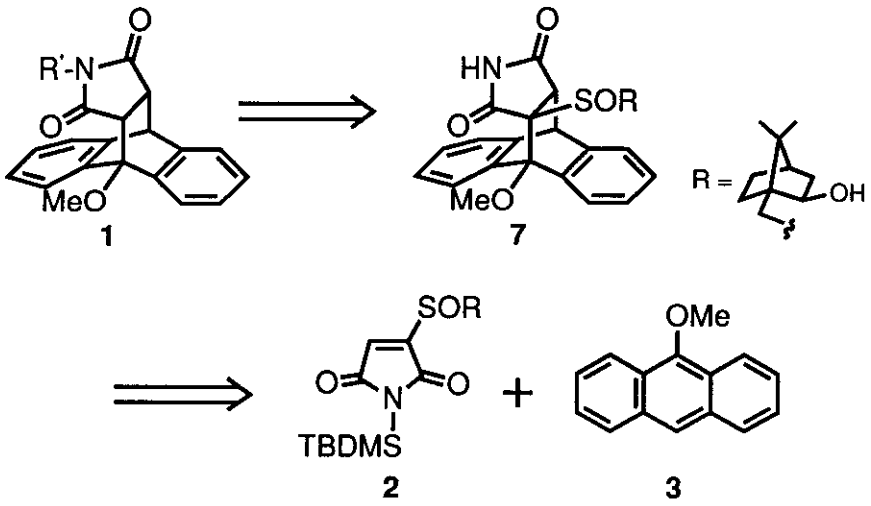
Chart 1



1: n = 1-3

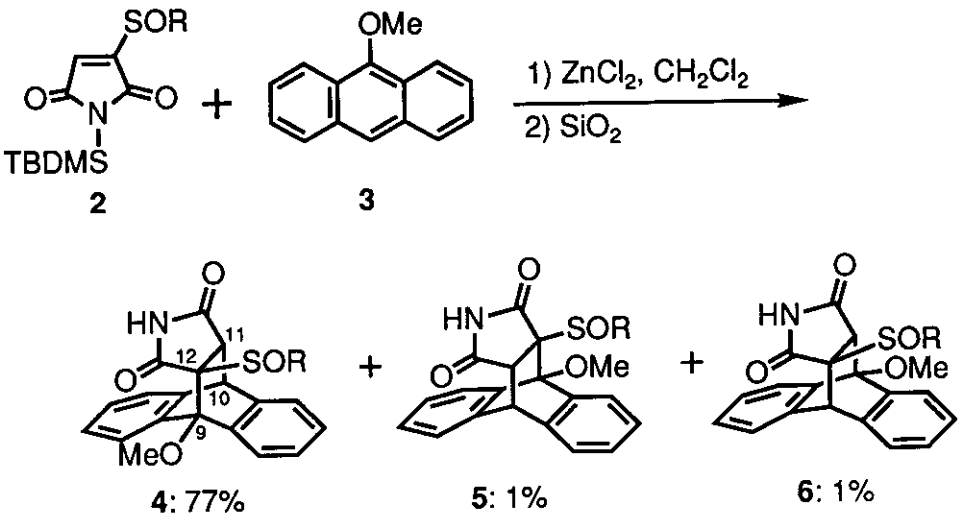
Chart 2

Synthesis of this roof-shaped compound (**1**) involves an asymmetric Diels-Alder (D-A) addition of a chiral sulfinylmaleimide (**2**)[3] to 9-methoxyanthracene (**3**)[4] as the principal synthetic step (Scheme 1). The merits of using 9-methoxyanthracene (**3**) compared with utilizing 1- or 2-methoxyanthracene and anthracene are as follows: (i) C_{2v} symmetry structure of **3** would reduce the number of possible isomers in half in the asymmetric D-A reaction; (ii) association of methoxy group with a Lewis acid would cause high regioselectivity in the asymmetric D-A reaction; (iii) the cycloadduct maintains chirality after removal of the chiral auxiliary.



Scheme 1

Asymmetric D-A reaction of the sulfinylmaleimide (R_S)-(**2**) with 1.3 equivalents of 9-methoxyanthracene (**3**) in the presence of zinc chloride at -15 °C followed by deprotection of *N*-TBDMS group gave 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamides (**4-6**) in 77%, 1%, and 1% yield, respectively (Scheme 2). In the ^{1}H nmr spectra of **4** and **5**, each couple of doublets (J = 3.4 Hz) at δ 3.57 and 4.82, and at δ 3.55 and 4.80, respectively, showed the presence of two vicinal bridge head protons, implying that the sulfinyl group locates on C-12. In the ^{1}H nmr spectrum of **6**, a couple of singlets at δ 3.29 and 5.11 showed the presence of 11-sulfinyl group. The absolute configuration of the cycloadducts (**4-6**) was assigned as depicted in Scheme 2. This assignment is based on the mechanistic consideration as shown in Chart 3 by analogy with that of the asymmetric D-A reaction of sulfinylmaleimides with cyclopentadiene in the presence of a Lewis acid.[3,5] The diastereoselectivity (d. e.) was calculated to be 98% for **4** and 100% for **6**. As expected, this D-A reaction showed high regioselectivity (78:1). The major cycloadduct (**4**) was subjected to a chiral synthesis of the



Scheme 2

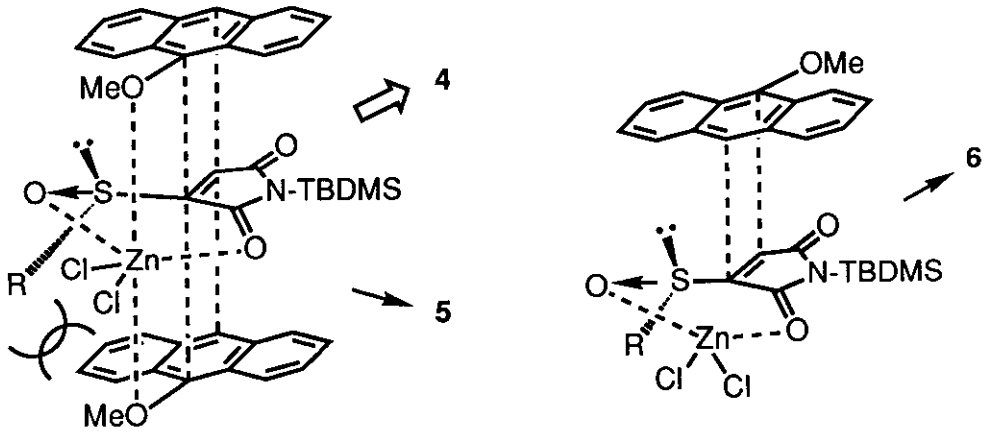
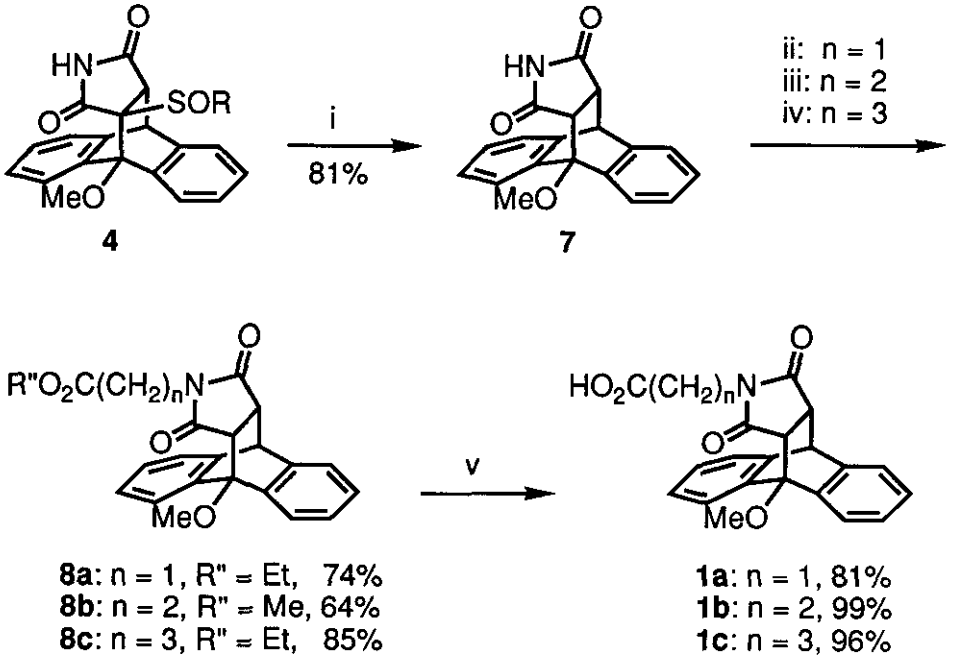


Chart 3

optically active host compound (**1**) (Scheme 3). Reductive desulfinylation of **4** with SmI_2 in the presence of ^tBuOH gave the imide (**7**) in 81% yield. *N*-Alkylation of the imide (**7**) proceeded with NaH and the corresponding bromoesters or methyl acrylate to afford the esters (**8a-c**) in 74, 64, and 85% yield, respectively. Hydrolysis of **8a-c** with 2% NaOH in THF-MeOH gave the optically active 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-carboxylic acids (**1a-c**) in quantitative yield.



i) SmI_2, ^tBuOH, THF; ii) NaH, THF, $BrCH_2CO_2Et$; iii) NaH, THF, $CH_2{=}CHCO_2Me$; iv) NaH, THF, HMPA, $Br(CH_2)_3CO_2Et$; v) 2% aqueous NaOH, MeOH, THF

Scheme 3

The optically active host compounds (**1a-c**) thus obtained were subjected to the formation of crystalline inclusion compounds according to the procedure of Weber *et al.*[1] In the preliminary experiments, when the acid (**1a**) was recrystallized from dimethylacetamide (DMA), a 1:1 solvated species of **1a** containing DMA were formed. Compound (**1b**) gave crystalline inclusion compound with DMA, DMF, and pyridine in a 1:1, 1:1, and 1:2 stoichiometry, respectively. Acid (**1c**) formed a 1:2 clathrate with pyridine. Host-guest stoichiometry was determined by elemental analyses and / or ^1H nmr integration.

Thus, we developed the first chiral synthesis of 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide derivatives (**1**) in high diastereo- and regioselectivity. Moreover, these carboxylic acids (**1**) were proved to form crystalline inclusion compounds with some solvents. These carboxylic acids (**1**) may be used for optical resolution of enantiomeric guests. Studies along this line are in progress in our group.

EXPERIMENTAL

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Microanalyses were performed by Microanalysis Center of Toyama Medical & Pharmaceutical University. Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO DIP-140 digital polarimeter; ir, Perkin-Elmer 1600 Series FTIR; ^{1}H-nmr, JEOL JNM-GX 270 (270 MHz) for solutions in $CDCl_3$ with Me_4Si as internal standard; mass spectra (ms), JEOL JMS D-200. Column chromatography, flash column chromatography, and preparative tlc (plc) were performed on Kieselgel 60 (Merck, Art. 7734, Art. 9385 and Art. 7748, respectively).

Asymmetric Diels-Alder Reaction of Sulfoxide (2) and 9-Methoxyanthracene (3) $ZnCl_2$ (257 mg, 1.89 mmol) was added to a solution of the sulfoxide[3] (**2**) (519 mg, 1.26 mmol) in dry CH_2Cl_2 (20 ml) and the mixture was stirred at 0 °C for 1.5 h under argon. To this was added dropwise a solution of 9-methoxyanthracene[4] (**3**) (342 mg, 1.64 mmol) in dry CH_2Cl_2 (40 ml) over a period of 40 min at -15 °C. After the reaction temperature was raised to ambient temperature, cold 1 N HCl (20 ml) and water (40 ml) were added to the mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (80 ml x 2). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was adsorbed on a column of silica gel (50 g) and was set aside overnight. This was eluted with hexane / AcOEt (6:1) followed by hexane / AcOEt (1:2) to give a mixture of diastereomers (621 mg). The mixture was recrystallized from AcOEt / hexane to give the major cycloadduct (**4**) (478 mg). The mother liquor was separated by plc (hexane / AcOEt = 1:1) to give the cycloadduct (**4**) (15 mg), the minor adduct (**5**) (5 mg, 1%), and the minor adduct (**6**) (6 mg, 1%). Total yield of the adduct (**4**) was 493 mg (77%).

(11*S*,12*S*,*R*$_S$)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-12-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-11,12-dicarboxamide (4): Amorphous powder. mp 199-201 °C. $[\alpha]_D^{24}$ +10.8° (*c* 1.03, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3454, 3201, 1777, 1733, 1706, 1047. ^{1}H-Nmr δ: 0.56 and 0.79 (each 3H, s), 1.05-1.85 (7H, m), 1.55 (1H, d, *J* = 12.9 Hz), 2.33 (1H, d, *J* =

12.7 Hz), 3.40 (1H, br s), 3.57 (1H, d, J = 3.4 Hz), 3.75-3.88 (1H, m), 4.17 (3H, s), 4.82 (1H, d, J = 3.2 Hz), 7.2-7.5 (5H, m), 7.5-7.8 (3H, m), 7.73 (1H, s). Ms *m/z*: 304 (M^+ - $C_{10}H_{17}O_2S$), 208 ($C_{15}H_{12}O$). *Anal.* Calcd for $C_{29}H_{31}NO_5S$: C, 68.88; H, 6.18; N, 2.77. Found: C, 68.68; H, 6.35; N, 2.7.

(11*R*,12*R*,*R*$_S$)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-12-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-11,12-dicarboxamide (**5**): Columns. mp 174-177 °C (AcOEt / hexane). $[\alpha]_D^{23}$ -47.4° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3388, 1778, 1729, 1032. ^{1}H-Nmr δ: 0.55 and 0.78 (each 3H, s), 1.0-1.8 (7H, m), 1.53 (1H, d, J = 12.7 Hz), 2.35 (1H, d, J = 12.7 Hz), 3.43 (1H, br s), 3.55 (1H, d, J = 3.4 Hz), 3.7-3.85 (1H, m), 4.14 (3H, s), 4.80 (1H, d, J = 3.4 Hz), 7.15-7.4 (5H, m), 7.4-7.7 (3H, m), 8.36 (1H, s). Ms *m/z*: 304 (M^+ - $C_{10}H_{17}O_2S$), 303 (M^+ - $C_{10}H_{18}O_2S$), 208 ($C_{15}H_{12}O$). *Anal.* Calcd for $C_{29}H_{31}NO_5S$: C, 68.88; H, 6.18; N, 2.77. Found: C, 68.76; H, 6.50; N, 2.81.

(11*R*,12*S*,*R*$_S$)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylsulfinyl)-11,12-dicarboxamide (**6**): Amorphous powder. mp 177-179 °C (AcOEt / hexane). $[\alpha]_D^{23}$ +19.2° (*c* 0.54, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3483, 3226, 1775, 1720, 1045. ^{1}H-Nmr δ: 0.74 and 1.04 (each 3H, s), 0.8-1.9 (8H, m), 2.14 (1H, d, J = 12.5 Hz), 3.29 (1H, s), 3.36 (1H, d, J = 3.4 Hz), 3.85-3.95 (1H, m), 4.13 (3H, s), 5.11 (1H, s), 7.15-7.4 (5H, m), 7.4-7.7 (4H, m). Ms *m/z*: 506 (M^+ + 1), 304 (M^+ - $C_{10}H_{17}O_2S$), 208 ($C_{15}H_{12}O$). *Anal.* Calcd for $C_{29}H_{31}NO_5S$: C, 68.88; H, 6.18; N, 2.77. Found: C, 68.56; H, 6.39; N, 2.83.

(11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide (**7**) ^{t}BuOH (1.95 ml, 20.7 mmol) was added to a solution of the adduct (**4**) (1.05 g, 2.08 mmol) in dry THF (10 ml) at room temperature under argon. After being stirred for 10 min, a 0.1 M-solution of SmI_2 in THF (104 ml, 10.4 mmol) was added and the mixture was stirred for 5 min. The reaction mixture was worked up with cold water (30 ml) and 1 N HCl (10 ml), and extracted with $CHCl_3$ (80 ml x 3). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was recrystallized from MeOH to give the imide (**7**) as an amorphous powder (514 mg, 81%). mp > 300 °C. $[\alpha]_D^{23}$ +3.5° (*c* 1.00, acetone). Ir ν_{max} (KBr) cm^{-1}: 3187, 3073, 1778, 1708. ^{1}H-Nmr δ: 3.40 (1H, dd, J = 3.2, 8.8 Hz), 3.65 (1H, d, J = 8.8 Hz), 4.10 (3H, s), 4.69 (1H, d, J = 3.2 Hz), 7.1-7.3 (5H, m), 7.39 (1H, d, J = 6.8 Hz), 7.40 (1H, br s), 7.51 (1H, d, J = 7.1 Hz), 7.59 (1H, d, J = 7.3 Hz). Ms *m/z*: 305 (M^+). *Anal.* Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.77; H, 4.82; N, 4.47.

A Typical Precedure for Alkylation of Imide (7) A solution of the imide (**7**) (50 mg, 0.16 mmol) in THF (3 ml) was added to a suspension of NaH (60%, 8.5 mg, 0.21 mmol) in THF (2 ml) at 0 °C under argon. After being stirred at 0 °C for 1.5 h, ethyl bromoacetate (36 μl, 0.33 mmol) was added and whole mixture was refluxed for 2 h. Cold 1 N HCl (3 ml) and water (12 ml) were added to the mixture and the whole mixture was extracted with $CHCl_3$ (30 ml x 3). The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was recrystallized from MeOH to give the ester (**8a**) as colorless prisms (48 mg, 74%). Transformation of **7** into **8b** and **8c** was also performed similarly.

Ethyl (11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-acetate (8a): mp 193-195 °C. $[\alpha]_D^{23}$ -8.6° (*c* 1.01, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 1780, 1735, 1708. ^{1}H-Nmr δ: 1.19 (3H, t, *J* = 7.1 Hz), 3.46 (1H, dd, *J* = 3.3 and 8.7 Hz), 3.71 (1H, d, *J* = 8.7 Hz), 3.72 (2H, s), 4.09 (2H, q, *J* = 7.1 Hz), 4.13 (3H, s), 4.71 (1H, d, *J* = 3.2 Hz), 7.05-7.3 (5H, m), 7.39 (1H, d, *J* = 7.3 Hz), 7.51 (1H, d, *J* = 7.3 Hz), 7.55 (1H, d, *J* = 8.5 Hz). Ms *m/z*: 392 (M^+ + 1), 346 (M^+ - C_2H_5O). *Anal.* Calcd for $C_{23}H_{21}NO_5$: C, 70.57; H, 5.41; N, 3.58. Found: C, 70.32; H, 5.33; N, 3.50.

Methyl (11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-propionate (8b): From the imide (**7**) (100 mg, 0.33 mmol), NaH (60%, 16 mg, 0.39 mmol), and methyl acrylate (148 μl, 1.64 mmol) in THF (10 ml) was obtained **8b** (83 mg, 64%) as colorless prisms. mp 172-174 °C (MeOH). $[\alpha]_D^{23}$ -13.2° (*c* 1.07, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 1778, 1735, 1708. ^{1}H-Nmr δ: 1.55-1.8 (2H, m), 3.35 (1H, dd, *J* = 3.4 and 8.3 Hz), 3.39 (2H, t, *J* = 8.2 Hz), 3.58 (1H, d, *J* = 8.3 Hz), 3.61 (3H, s), 4.13 (3H, s), 4.70 (1H, d, *J* = 3.2 Hz), 7.1-7.3 (5H, m), 7.39 (1H, d, *J* = 6.8 Hz), 7.52 (1H, d, *J* = 7.8 Hz), 7.57 (1H, d, *J* = 7.6 Hz). Ms *m/z*: 392 (M^+ + 1), 360 (M^+ - CH_4O). *Anal.* Calcd for $C_{23}H_{21}NO_5$: C, 70.57; H, 5.41; N, 3.58. Found: C, 70.56; H, 5.19; N, 3.33.

Ethyl (11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-butyrate (8c): From the imide (**7**) (2.51 g, 8.22 mmol), NaH (60%, 0.559 g, 14.0 mmol), and ethyl γ-bromo-*n*-butyrate (2.35 ml, 16.4 mmol) in THF (200 ml) and HMPA (10 ml) was obtained **8c** (2.75 g, 85%) as colorless columns. mp 114-117 °C (AcOEt / hexane). $[\alpha]_D^{23}$ -12.9° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 1770, 1729, 1695. ^{1}H-Nmr δ: 1.1-1.35 (2H, m), 1.26 (3H, t, *J* = 7.2 Hz), 1.6-1.85 (2H, m), 3.18 (2H, t, *J* = 6.8 Hz), 3.33 (1H, dd, *J* = 3.3 and 8.7 Hz), 3.58 (1H, d, *J* = 8.8 Hz), 4.09 (2H, q, *J* = 7.1 Hz), 4.13 (3H, s), 4.70 (1H, d, *J* = 3.2 Hz), 7.05-7.3 (5H, m), 7.38 (1H, d, *J* = 6.6 Hz), 7.51 (1H, d, *J* = 7.1 Hz), 7.58 (1H, d,

J = 7.3 Hz). Ms *m/z*: 420 (M^+ + 1), 375 (M^+ - C_2H_5O). *Anal.* Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34. Found: C, 71.70; H, 5.96; N, 3.22.

A Typical Procedure for Hydrolysis of Esters (8a-c) To a solution of the ester **(8a)** (2.70 g, 6.92 mmol) in THF (20 ml) and MeOH (43 ml) was added 2% aqueous NaOH (20 ml) and the mixture was stirred at room temperature for 5 min. 1N HCl (50 ml) and water (100 ml) were added to the mixture and the whole mixture was extracted with $CHCl_3$ (50 ml x 3). The organic layer was dried over $MgSO_4$ and concentrated. The residue was recrystallized from hexane / AcOEt to give the carboxylic acid **(1a)** as an amorphous powder (2.04 mg, 81%). Reactions with **8b** and **8c** were also performed similarly.

(11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-acetic acid (1a): mp 136-138 °C. $[\alpha]_D^{23}$ -7.6° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 1780, 1732, 1713. ^{1}H-Nmr δ: 3.45 (1H, dd, *J* = 3.3 and 8.7 Hz), 3.69 (1H, d, *J* = 8.8 Hz), 3.83 (2H, s), 4.13 (3H, s), 4.71 (1H, d, *J* = 3.2 Hz), 4.9-6.2 (1H, br), 7.05-7.3 (5H, m), 7.39 (1H, d, *J* = 6.6 Hz), 7.51 (1H, d, *J* = 6.8 Hz), 7.54 (1H, d, *J* = 7.3 Hz). Ms *m/z*: 363 (M^+), 346 (M^+ - OH). *Anal.* Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.86. Found: C, 69.50; H, 5.17; N, 3.68.

(11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-propionic acid (1b): From the ester **(8b)** (381 mg, 0.974 mmol) was obtained **1b** (364 mg, 99%) as colorless prisms. mp 261-262 °C (AcOEt / hexane). $[\alpha]_D^{23}$ -9.6° (*c* 1.00, acetone). Ir ν_{max} (KBr) cm^{-1}: 1771, 1739, 1704, 1682. ^{1}H-Nmr δ: 1.6-1.85 (2H, m), 3.36 (1H, dd, *J* = 3.7 and 8.3 Hz), 3.39 (2H, t, *J* = 7.8 Hz), 3.59 (1H, d, *J* = 8.3 Hz), 4.13 (3H, s), 4.71 (1H, d, *J* = 2.9 Hz), 7.05-7.3 (5H, m), 7.39 (1H, d, *J* = 7.3 Hz), 7.52 (1H, d, *J* = 6.8 Hz), 7.57 (1H, d, *J* = 7.3 Hz). Ms *m/z*: 377 (M^+), 304 (M^+ - $C_3H_5O_2$). *Anal.* Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 69.98; H, 5.19; N, 3.58.

(11*R*,12*R*)-9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide-*N*-butyric acid (1c): From the ester **(8c)** (2.46 g, 5.86 mmol) was obtained **1c** (2.21 g, 96%) as an amorphous powder. mp 174-176 °C (AcOEt / hexane). $[\alpha]_D^{23}$ -19.8° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 1770, 1737, 1694. ^{1}H-Nmr δ: 1.1-1.25 (2H, m), 1.65-1.85 (2H, m), 3.19 (2H, t, *J* = 6.8 Hz), 3.34 (1H, dd, *J* = 3.2 and 8.5 Hz), 3.59 (1H, d, *J* = 8.8 Hz), 4.14 (3H, s), 4.71 (1H, d, *J* = 3.4 Hz), 7.05-7.3 (5H, m), 7.39 (1H, d, *J* = 6.4 Hz), 7.51 (1H, d, *J* = 6.8 Hz), 7.58 (1H, d, *J* = 7.3 Hz). Ms *m/z*: 374 (M^+ - OH). *Anal.* Calcd for $C_{23}H_{21}NO_5$: C, 70.57; H, 5.41; N, 3.58. Found: C, 70.65; H, 5.60; N, 3.41.

Preparation of the Crystalline Inclusion Compounds. General Procedure The host compound (**1a-c**) (100 mg) was dissolved by heating in a minimum amount of the guest solvent. After storage for 1 to 10 days at room temperature, the crystals formed were collected by suction filtration and dried (under reduced pressure at room temperature). Host-guest stoichiometry was determined by elemental analyses and / or ^{1}H NMR integration.

1a•DMA (1:1): Columns. mp 103-104 °C. Ir ν_{max} (KBr) cm^{-1}: 1775, 1709, 1603. ^{1}H-Nmr δ: 2.08, 2.93, and 3.01 (each 3H, s), 3.44 (1H, dd, *J* = 3.2, 8.8 Hz), 3.69 (1H, d, *J* = 8.8 Hz), 3.77 (2H, s), 4.12 (3H, s), 4.71 (1H, d, *J* = 3.2 Hz), 7.05-7.3 (5H, m), 7.39 (1H, d, *J* = 6.6 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.54 (1H, d, *J* = 7.3 Hz). Ms *m/z*: 364 (carboxylic acid + 1), 87 (DMA). *Anal.* Calcd for $C_{25}H_{26}N_2O_6$: C, 66.65; H, 5.82; N, 6.22. Found: C, 66.68; H, 5.74; N, 6.39.

1b•DMA (1:1): Needles. mp 127-128 °C. Ir ν_{max} (KBr) cm^{-1}: 1771, 1704, 1602. ^{1}H-Nmr δ: 1.6-1.8 (2H, m), 2.09, 2.94, and 3.01 (each 3H, s), 3.35 (1H, dd, *J* = 3.3, 8.7 Hz), 3.39 (2H, t, *J* = 8.2 Hz), 3.59 (1H, d, *J* = 8.5 Hz), 4.13 (3H, s), 4.71 (1H, d, *J* = 3.2 Hz), 7.1-7.3 (5H, m), 7.39 (1H, d, *J* = 6.1 Hz), 7.52 (1H, d, *J* = 7.1 Hz), 7.57 (1H, d, *J* = 7.3 Hz). Ms *m/z*: 377 (carboxylic acid), 87 (DMA). *Anal.* Calcd for $C_{26}H_{28}N_2O_6$: C, 67.22; H, 6.08; N, 6.03. Found: C, 67.12; H, 6.30; N, 5.86.

1b•DMF (1:1): Prisms. mp 111-114 °C. Ir ν_{max} (KBr) cm^{-1}: 1774, 1725, 1703, 1650. ^{1}H-Nmr δ: 1.6-1.85 (2H, m), 2.89 and 2.97 (each 3H, s), 3.36 (1H, dd, *J* = 3.4, 8.6 Hz), 3.40 (2H, t, *J* = 8.1 Hz), 3.59 (1H, d, *J* = 8.5 Hz), 4.13 (3H, s), 4.71 (1H, d, *J* = 3.2 Hz), 7.1-7.3 (5H, m), 7.40 (1H, d, *J* = 6.6 Hz), 7.52 (1H, d, *J* = 6.8 Hz), 7.57 (1H, d, *J* = 7.3 Hz), 8.02 (1H, s). Ms *m/z*: 377 (carboxylic acid). *Anal.* Calcd for $C_{25}H_{26}N_2O_6$: C, 66.65; H, 5.82; N, 6.22. Found: C, 66.35; H, 5.72; N, 6.15.

1b•pyridine (1:2): Needles. mp 241-247 °C. Ir ν_{max} (KBr) cm^{-1}: 1771, 1738, 1704, 1682, 1584. ^{1}H-Nmr δ: 1.6-1.85 (2H, m), 3.34 (1H, dd, *J* = 3.3, 8.7 Hz), 3.41 (2H, t, *J* = 8.1 Hz), 3.57 (1H, d, *J* = 8.6 Hz), 4.12 (3H, s), 4.70 (1H, d, *J* = 3.4 Hz), 7.05-7.4 (10H, m), 7.50 (1H, d, *J* = 6.8 Hz), 7.56 (1H, d, *J* = 7.3 Hz), 7.69 (1H, d, *J* = 7.8 Hz), 7.72 (1H, d, *J* = 7.6 Hz), 8.60 (4H, d, *J* = 4.4 Hz). Ms *m/z*: 377 (carboxylic acid), 79 (pyridine). Pyridine was readily removed from **1b**•pyridine (1:2) under reduced pressure at room temperature.

1c•pyridine (1:2): Needles. mp 80-82 °C. Ir ν_{max} (KBr) cm^{-1}: 1770, 1700, 1597, 1580. ^{1}H-Nmr δ: 1.15-1.3 (2H, m), 1.75-1.9 (2H, m), 3.23 (2H, t, *J* = 6.8 Hz), 3.35 (1H, dd, *J* = 3.4, 8.6 Hz), 3.59 (1H, d, *J* = 8.5 Hz), 4.11 (3H, s), 4.72 (1H, d, *J* = 3.4 Hz), 7.1-7.45 (10H, m), 7.52 (1H, d, *J* = 7.1 Hz), 7.60 (1H, d, *J* = 7.1 Hz), 7.71 (1H, d, *J* = 7.6 Hz), 7.74 (1H, d, *J* = 7.6 Hz). Ms *m/z*: 391 (carboxylic acid). Pyridine was readily removed from **1c**•pyridine (1:2) under reduced pressure at room temperature.

REFERENCES AND NOTES

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