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Synthesis, Structure, and Mesomorphic Properties of Liquid Crystals with a Bitropone Core

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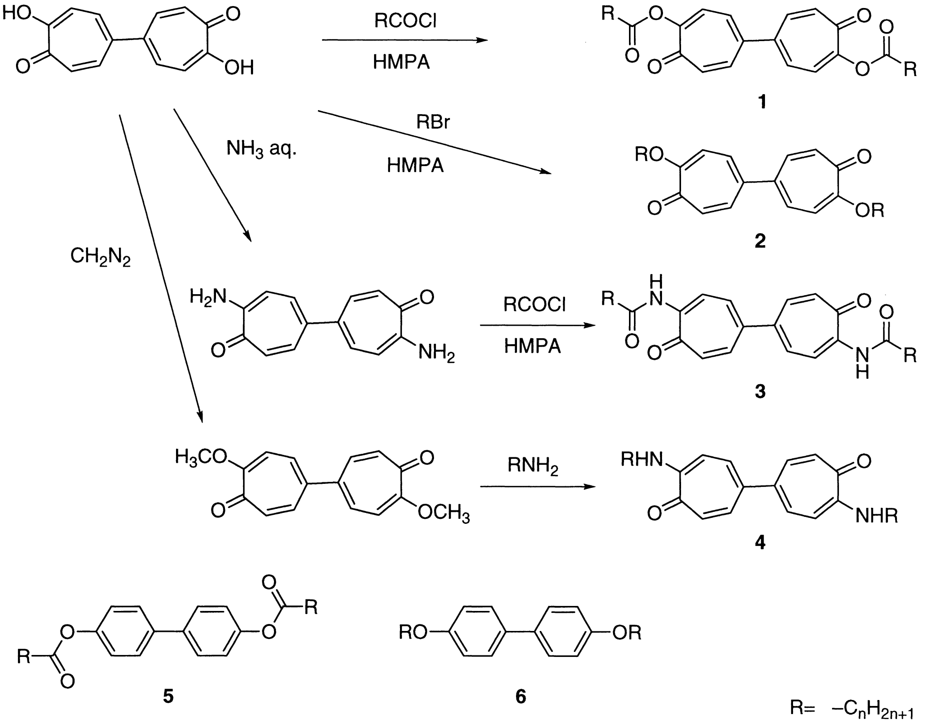
New troponoid liquid crystals (**1**–**4**) with a bitropone core were prepared. The ester derivatives (**1**) had enantiotropic smectic A and/or C phases with higher thermal stabilities than the corresponding benzenoid derivatives (**5**), which had a smectic B phase. The amide derivatives (**3**) had an enantiotropic smectic A phase, but the ether (**2**) and alkylamine (**4**) derivatives were not mesomorphic. The crystals of **1c** had a layer structure with an intermolecular π–π interaction between the bitropone cores. X-ray diffraction studies revealed that the layer spacings of the smectic A and C phases of **1i** were not very much different.

The typical structural units of rod-like liquid crystals possess a fairly rigid core, which generally consists of six-membered ring systems.[1] The preparation of new types of liquid-crystal materials with rings other than six-membered rings had received less attention. However, it is important to extend the molecular design of liquid crystals to involve other ring systems from not only theoretical, but also the practical, points of view. Recently we reported that monocyclic 2-alkanoyloxy-5-alkoxytropones showed a monotropic smectic A phase.[2] Furthermore, we prepared troponoid liquid crystals with a seven-membered core, such as 5-hydroxytropolone,[2] 5-aminotropolone,[3] 2-amino-5-hydroxytropone,[4] 5-cyanotropolone,[5] and 2-amino-5-phenyltropone.[6] The tropolone core has a large dipole moment (3.5 D),[7] which would help to form a layer structure. The cores enhanced the formation of smectic phases when compared with the corresponding benzenoids. In benzenoid liquid crystals, a biphenyl unit has been widely used as one of the most useful cores.[1] However, liquid crystals with a bitropone core have not been reported. In this paper, the crystal structures and mesomorphic properties of bitropone compounds are compared with those of the corresponding benzenoids.

Results and Discussion

5,5′-Bitropolone was obtained by homocoupling reactions of 5-iodotropolone in the presence of [Pd(PPh$_3$)$_4$].[8] The reaction of 5,5′-bitropolone with alkanoyl chlorides or alkyl bromides in a triethylamine-HMPA (hexamethylphosphoric triamide) solution afforded the ester and ether derivatives (**1** and **2**) in 13–40% and 11–22%, respectively, while 2,2′-diamino-5,5′-bitropone was prepared by the amination of 5,5′-bitropolone with aqueous NH$_3$. The amide derivatives (**3**) were obtained in 7–13% yield by the reaction of 2,2′-diamino-5,5′-bitropone with alkanoyl chlorides. On the other hand, the methylation of 5,5′-bitropolone with excess of diazomethane gave 2,2′-dimethoxy-5,5′-bitropone quantitatively. Finally, 2,2′-dimethoxy-5,5′-bitropone was reacted with various alkylamines to give 2-alkylaminotropone derivatives (**4**) in 15–43% yield. The low yields of **1**–**4** are attributed to the poor solubility of the starting materials, such as 5,5′-bitropolone, 2,2′-dimethoxy-5,5′-bitropone, and 2,2′-diamino-5,5′-bitropone. The starting materials could not be recovered. The benzenoid derivatives (**5**,**6**)[9] were prepared by the esterification and alkylation of 4,4′-biphenol with alkanoyl chlorides and alkyl bromides (Scheme 1). The structure and purity of **1** and **2** were ascertained by NMR spectroscopy and elemental analysis. The transition temperatures and thermal behaviors of the textures were determined using a differential scanning calorimeter and a polarizing microscope equipped with a hot stage as well as by an X-ray diffraction study.

Mesomorphic Properties. The thermal behaviors of bitropones (**1**–**4**) and the corresponding benzenoids (**5**,**6**) are summarized in Table 1. Troponoids (**1**) and benzenoids (**5**) have different mesomorphic sequences. The former series had a phase sequence of crystals–smectic A–isotropic for *n* = 7 and crystals–smectic C–smectic A–isotropic for *n* = 8–15, while the latter series have a phase sequence of crystals–smectic B–isotropic. The smectic phases were determined from a following observation as well as from X-ray diffraction studies, i.e., bâtonnets, focal-conic fan, and homeotropic textures for the smectic A phase; broken-fan and schlieren textures for the smectic C phase; homeotropic and mosaic textures for the smectic B phase. As shown in Table 1, troponoids (**1**) showed smectic phases with higher thermal stabilities than the corresponding benzenoids (**5**). This is due to the presence of the carbonyl group of a tropone core. The ether and amine deriva-



Scheme 1.

Table 1. Transition Temperatures of **1**–**6**

	n	Transition temp/°C		*n*	Transition temp/°C
1a	5	Cr·143.0·I	**4b**	6	Cr·144.3·I
1b	6	Cr·138.0·I	**4f**	10	Cr·145.3·I
1c	7	Cr·129.6·$\mathrm{S_A}$·132.2·I	**4i**	14	Cr·140.1·I
1d	8	Cr·117.2·$\mathrm{S_C}$·119.8·$\mathrm{S_A}$·148.3·I	**5a**	5	Cr·117.0·$\mathrm{S_B}$·118.0·I
1e	9	Cr·120.9·$\mathrm{S_C}$·126.6·$\mathrm{S_A}$·155.2·I	**5b**	6	Cr·105.0·$\mathrm{S_B}$·118.0·I
1f	10	Cr·119.2·$\mathrm{S_C}$·129.8·$\mathrm{S_A}$·156.7·I	**5c**	7	Cr·95.0·$\mathrm{S_B}$·122.0·I
1g	11	Cr·124.3·$\mathrm{S_C}$·128.2·$\mathrm{S_A}$·157.2·I	**5d**	8	Cr·95.0·$\mathrm{S_B}$·121.0·I
1h	12	Cr·110.0·$\mathrm{S_C}$·123.3·$\mathrm{S_A}$·152.5·I	**5e**	9	Cr·98.0·$\mathrm{S_B}$·122.0·I
1i	13	Cr·110.2·$\mathrm{S_C}$·125.2·$\mathrm{S_A}$·146.1·I	**5f**	10	Cr·100.0·$\mathrm{S_B}$·121.4·I
1j	14	Cr·115.0·$\mathrm{S_C}$·131.8·$\mathrm{S_A}$·151.6·I	**5g**	11	Cr·101.1·$\mathrm{S_B}$·120.8·I
1k	15	Cr·118.2·$\mathrm{S_C}$·131.6·$\mathrm{S_A}$·153.4·I	**5h**	12	Cr·102.1·$\mathrm{S_B}$·120.4·I
2b	6	Cr·141.3·I	**5i**	13	Cr·102.0·$\mathrm{S_B}$·118.2·I
2f	10	Cr·141.4·I	**5j**	14	Cr·105.3·$\mathrm{S_B}$·118.9·I
2i	14	Cr·138.5·I	**5k**	15	Cr·119.0·I
3a	5	Cr·160.0·I	**6b**	6	Cr·124.0·N·130.0·I
3e	9	Cr·149.6·($\mathrm{S_A}$·142.7·) I	**6f**	10	Cr·113.0·I
3i	13	Cr·138.3·$\mathrm{S_A}$·144.5·I	**6i**	14	Cr·115.1·I

Cr: crystals, $\mathrm{S_A}$: smectic A phase, $\mathrm{S_C}$: smectic C phase, $\mathrm{S_B}$: smectic B phase, N: nematic phase, I: isotropic liquid.

tives (**2** and **4**), however, were not mesomorphic. Compared with the melting points of compounds **1** and **2**, it was confirmed that the ester groups at C-2 and C-2′ of **1** assisted in the appearance of the mesophase through a sigmatropic rearrangement.[2] The amide derivatives (**3**) had a monotropic and an enantiotropic $\mathrm{S_A}$ phase, respectively, when the alkyl chains were $n = 9$ and 13, though the melting points of the compounds **3** were higher than those of **1**. This means that the hydrogen bonds between a NH and tropone carbonyl group make the intermolecular interaction stronger.

X-ray Crystal-Structure Analysis of 1c and 5a. Two single crystals of **1c** and **5a** were obtained by recrystallization from chloroform. The molecular structure of **1c** is shown in Fig. 1. The planarity of the seven-membered ring of **1c** is fairly good. The C–C bond lengths of the seven-membered ring of **1c** are similar to those of tropone[10] and distinct from 2-butoxy-5-nitrotropone.[11]

The intersection angle between two tropolone rings, A [defined by C1/C2/C3/C4/C5/C6/C7/O1/O2] and B [defined by C8/C9/C10/C11/C12/C13/C14/O3/O4], is 51.0°, which is distinct from that [0°] of biphenyl.[12] While the intersection angles between the tropolone ring A and the ester plane [defined by O2/O5/C15] and between the tropolone ring B and the ester plane [defined by O4/O6/C23] are 76.9° and 79.5°, respectively, which are similar to those [71.5° and 71.8°] of tropolonyl *p*-chlorobenzoate[13] and 2-butanoyl-5-nitrotropone.[11] The paraffin chains all have *trans* conformations, except for one *gauche* conformation (C25–C26–C27–C28).

Intermolecular π–π interactions between the bitropone cores (head-to-tail) of **1c** were observed, as shown in Fig. 2. The distance between the intermolecular tropolone planes is 3.46(3) Å for C8–C10$^{\mathrm{i}}$ (symmetry codes i: $2-x$, $-y$, $1-z$), which is similar to that [3.399 Å] for C1–C5$^{\mathrm{ii}}$ (ii: $-x$, $1-y$, $1-z$) of 2-butoxy-5-nitrotropone.[11]

The molecular structure of **5a** is shown in Fig. 3. The intersection angle between two benzene rings, A′ [defined by C1/C2/C3/C4/C5/C6] and B′ [defined by C7/C8/C9/C10/C11/C12], is 18.8°, which is distinct from that [0°] of biphenyl.[12] On the other hand, the intersection angles between plane A and the ester plane [defined by O1/O2/C13] and between plane B and the ester plane [defined by O3/O4/C19] are 57.1° and 28.9°. The paraffin chains all have *trans* conformations.

Intermolecular π–π interactions between the phenyl planes of **5a** were observed (Fig. 4). The distance between the intermolecular phenyl planes is 3.42 Å for C2–C5$^{\mathrm{iii}}$ (iii: x, y, $1+z$), which is within the range of the intermolecular π–π interaction.[14] The crystals of **1c** and **5a** have distinct layer structures, such as smectic phases (Fig. 5). The troponoids (**1**) showed smectic phases with higher thermal stabilities than the corresponding benzenoids (**5**). This suggests that the intermolecular π–π interaction between the bitropone cores is stronger than that between the biphenyl cores.

X-ray Diffraction Study. We measured the X-ray diffraction pattern of the mesophases. The smectic layer spacings (*d*)

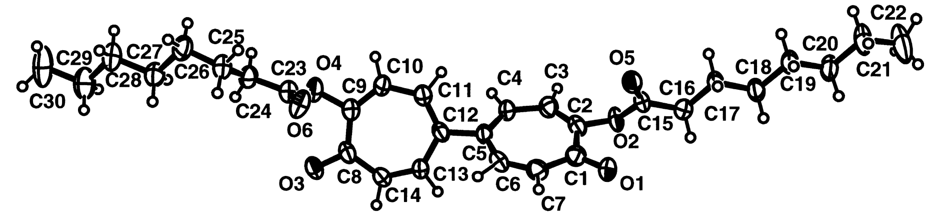


Fig. 1. ORTEP drawing of **1c** with the numbering. Thermal ellipsoids are drawn with 50% probabilities.

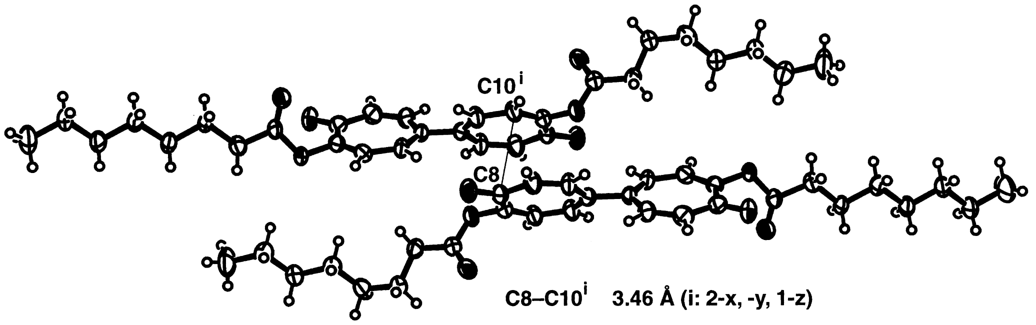


Fig. 2. π–π interaction of head-to-tail dimer of **1c.**

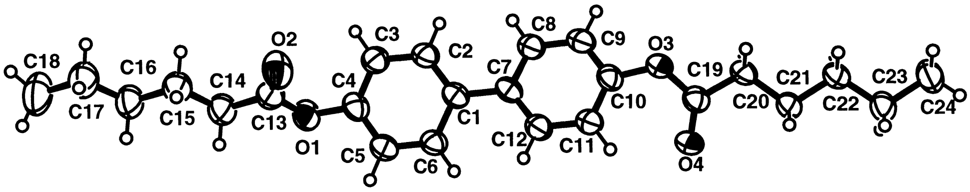


Fig. 3. ORTEP drawing of **5a** with the numbering. Thermal ellipsoids are drawn with 50% probabilities.

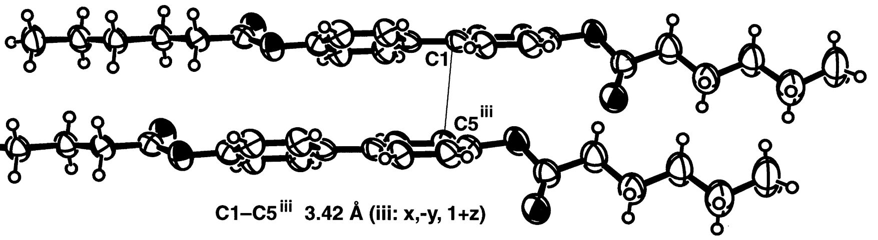


Fig. 4. π–π interaction of **5a** showing benzene–benzene stacking arrangement.

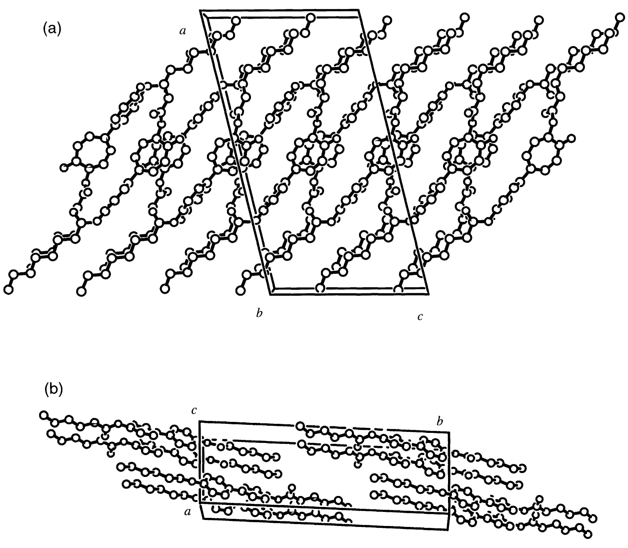


Fig. 5. Crystal structures of (a) **1c** viewed down the *b* axis and (b) **5a** viewd down the *c* axis.

of **1i** were observed to be 35.6 Å (140 °C) for the smectic A phase and 36.5 Å (120, 125, and 130 °C) for the smectic C phase, respectively. The *d* of **5d** was observed to be 28.3 Å (105 and 110 °C) for the smectic B phase. The calculated molecular lengths (*l*) of **1i** and **5d** by the MM2 method were found to be 43.6 Å and 31.4 Å, respectively. The *d*/*l* ratios of the smectic A and C phases of **1i** are 0.82 and 0.84, respectively. Although it seems to be unusual that both are almost the same and the former smectic A has rather a smaller *d*/*l* ratio than the latter, the *d*/*l* value (0.82) is typical for smectic A phases,[14] where terminal chains deform and the cores randomly tilt to make molecules orthogonal to the layer planes, as shown in Fig. 6. In the case of the smectic C phase, the molecules had an organized tilt direction to the normal of the layer planes, where the mobility of the terminal chains would be reduced. As a result, the layer spacings between the smectic A and C phases were not very different from each other. On the other hand, the layer spacing of the smectic B phase is almost identical with the calculated molecular length.

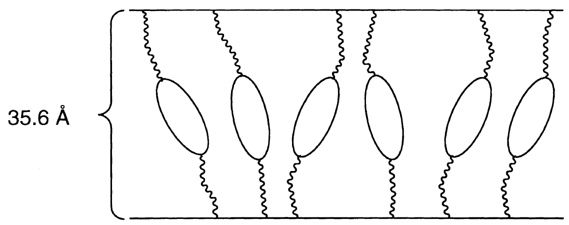


Fig. 6. Packing model of **1i** in the smectic A phase. Terminal alkyl chains deformed and bitropolone cores randomly tilted.

The X-ray diffraction pattern of **3i** was taken at 137 °C (on cooling), when a S_A phase appeared obtained from a powder sample of **3i**. The layer spacing of **3i** was 35.8 Å, whereas the calculated molecular length from MM2 calculations is 45.1Å. The *d*/*l* ratio of the smectic A phase of **3i** is 0.79, which is similar to that of **1i**.

In conclusion, the mesogenic properties of liquid crystals with a bitropone core were investigated. The ester derivatives (**1**) had enantiotropic smectic A and C phases. From a comparison of the transition temperatures of compounds **1** and **5**, a bitropone core should be more useful to enhance the thermal stabilities of the liquid–crystalline states than a biphenyl core. The molecules of **1c** and **5a** form layer structures with intermolecular π–π interactions. Packing models of compounds **1** and **5** in the smectic phases were consistent with the observation of single crystallographic analyses. Thus, a bitropone core should be useful to form a tilted layer structure.

Experimental

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. The melting points were obtained using a Yanagimoto micro-melting-point apparatus and are uncorrected. The NMR spectra were recorded using JEOL Lambda 400 and 600 spectrometers and solutions in $CDCl_3$ at room temperature; the chemical shifts are expressed in δ units. The mass spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. The stationary phase used in column chromatography was Wakogel C-300. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage). X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-$K\alpha$ radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

Preparation of Bitropolone. A mixture of 5-iodotropolone (300 mg, 1.21 mmol), $[Pd(PPh_3)_4]$ (71 mg, 0.061 mmol), and triethylamine (0.48 cm^3) in THF (6 cm^3) was heated at 80 °C under nitrogen. Acidification of the alkaline solution with 6 M HCl yielded brownish-yellow precipitates, which were collected by filtration, and washed with ethyl acetate (30 cm^3) to give yellow powders (91 mg, 69%) of 5,5′-bitropolone; mp 260 °C (decomp) [lit.,[8] 260 °C (decomp)], ^{1}H NMR (DMSO-d_6) δ 7.25 (4H, d, J = 11.5 Hz) and 7.56 (4H, d, J = 11.5 Hz); ^{13}C NMR (DMSO-d_6) δ 124.7 (4C), 136.9 (4C), 141.6 (4C), and 171.1 (2C).

Preparation of Ester Derivatives (1). Decanoyl chloride (626 mg, 3.28 mmol) was added to an HMPA (2 cm^3) solution of 5,5′-bitropolone (100 mg, 0.41 mmol) and triethylamine (1 cm^3). The reaction mixture was stirred at room temperature for 3 h. The mixture was poured into a 2 M HCl solution and extracted with ethyl acetate. The organic layer was washed with a saturated NaCl solution and dried over Na_2SO_4. The organic layer was evaporated in vacuo to leave a residue which was chromatographed in hexane–ethyl acetate or hexane–chloroform mixture on a silica-gel column to give crystals. The crystals were recrystallized with hexane–benzene (1:1 v/v) to give colorless crystals (**1e**, 91 mg, 40%). **1a** (18%); ^{1}H NMR ($CDCl_3$) δ 0.93 (6H, t, J = 7.5 Hz), 1.34–1.47 (8H, m), 1.79 (4H, quit, J = 7.5 Hz), 2.64 (4H, t, J = 7.5 Hz), 7.20 (4H, d, J = 11.4 Hz), and 7.27 (4H, d, J = 11.4 Hz); FAB-MS *m*/*z* 439 (M + H^+); Found: C, 70.99; H, 6.87%. Calcd for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90%. **1b** (28%); Found: C, 71.87; H, 7.33%. Calcd for $C_{28}H_{34}O_6$: C, 72.08; H, 7.35%. **1c** (35%); Found: C, 72.65; H, 7.65%. Calcd for $C_{30}H_{38}O_6$: C, 72.85; H, 7.74%. **1d** (21%); Found: C, 73.42; H, 8.05%. Calcd for $C_{32}H_{42}O_6$: C, 73.53; H, 8.10%. **1e** (40%); Found: C, 74.12; H, 8.35%. Calcd for $C_{34}H_{46}O_6$: C, 74.15; H, 8.42%. **1f** (17%); Found: C, 74.52; H, 8.67%. Calcd for $C_{36}H_{50}O_6$: C, 74.71; H, 8.71%. **1g** (22%); Found: C, 75.11; H, 8.90%. Calcd for

$C_{38}H_{54}O_6$: C, 75.21; H, 8.97%. **1h** (25%); Found: C, 75.68; H, 9.22%. Calcd for $C_{40}H_{58}O_6$: C, 75.67; H, 9.21%. **1i** (24%); Found: C, 75.92; H, 9.37%. Calcd for $C_{42}H_{62}O_6$: C, 76.09; H, 9.43%. **1j** (18%); Found: C, 76.44; H, 9.65%. Calcd for $C_{44}H_{66}O_6$: C, 76.48; H, 9.63%. **1k** (13%); Found: C, 76.68; H, 9.79%. Calcd for $C_{46}H_{70}O_6$: C, 76.84; H, 9.81%.

Preparation of Ether Derivatives (2). 1-Bromodecane (626 mg, 3.28 mmol) was added to a HMPA (1 cm^3) solution of 5,5′-bitropolone (50 mg, 0.21 mmol) and triethylamine (1 cm^3). The reaction mixture was stirred at 60 °C for 7 h. The mixture was poured into 2 M HCl, and organic matter was extracted with ethyl acetate. The organic layer was washed with a saturated NaCl solution and dried over Na_2SO_4. The organic layer was evaporated in vacuo to leave a residue, which was chromatographed in hexane–ethyl acetate or hexane–chloroform mixture on a silica-gel column to give crystals. The crystals were recrystallized with hexane–benzene (1:1 v/v) to give pale-yellow crystals (18 mg, 20%). **2b** (19%); ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, t, J = 7.0 Hz), 1.28–1.53 (12H, m), 1.94 (4H, quit, J = 7.0 Hz), 4.09 (4H, t, J = 7.0 Hz), 6.79 (2H, d, J = 10.5 Hz), 7.12 (2H, dd, J = 12.3, 1.9 Hz), 7.27 (2H, d, J = 10.5 Hz), and 7.34 (2H, dd, J = 12.3, 1.9 Hz) ; ^{13}C NMR ($CDCl_3$) δ 14.0 (2C), 22.5 (2C), 25.6 (2C), 28.6 (2C), 31.5 (2C), 69.7 (2C), 112.9 (2C), 131.7 (2C), 136.8 (2C), 137.0 (2C), 141.9 (2C), 164.5 (2C), and 179.7 (2C); FAB-MS m/z 411 (M+H$^+$); Found: C, 75.98; H, 8.34%. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35%. **2f** (20%); Found: C, 77.89; H, 9.65%. Calcd for $C_{34}H_{50}O_4$: C, 78.12; H, 9.64%. **2i** (11%); Found: C, 79.26; H, 10.40%. Calcd for $C_{42}H_{66}O_4$: C, 79.44; H, 10.48%.

Preparation of 2,2′-Diamino-5,5′-bitropone. A mixture of 5,5′-bitropolone (693 mg, 2.87 mmol), NH_3 aq (50 cm^3), and methanol (50 cm^3) was heated at 150 °C in a sealed tube for 12 h. The yellow precipitates were collected by filtration and recrystallized with methanol to give yellow crystals (425 mg, 63%); mp > 300 °C, ^{1}H NMR (DMSO-d_6) δ 6.97 (2H, d, J = 12.1 Hz), 7.00 (2H, d, J = 11.1 Hz), 7,34 (2H, d, J = 11.1 Hz), and 7.41 (2H, d, J = 12.1 Hz); ^{13}C NMR (DMSO-d_6) δ 111.7 (2C), 128.5 (2C), 135.5 (2C), 136.4 (2C), 136.8 (2C), 157.3 (2C), and 174.5 (2C); HR EI-MS Found: m/z 240.0900. Calcd for $C_{14}H_{12}N_2O_2$: 240.0899.

Preparation of Amide Derivatives (3). Tetradecanoyl chloride (0.40 mL, 1.47 mmol) was added to a HMPA (1 cm^3) solution of 2,2′-diamino-5,5′-bitropone (50 mg, 0.21 mmol) and triethylamine (0.5 cm^3). The reaction mixture was stirred at room temperature for 8 h. The mixture was poured into 2 M HCl, and organic matter was extracted with ethyl acetate. The organic layer was washed with a saturated NaCl solution and dried over Na_2SO_4. The organic layer was evaporated in vacuo to leave a residue, which was chromatographed in hexane-ethyl acetate or a hexane–chloroform mixture on a silica-gel column to give crystals. The crystals were recrystallized with hexane–benzene (1:1 v/v) to give pale-yellow crystals (19 mg, 13%). **3a** (7%); ^{1}H NMR ($CDCl_3$) δ 0.92 (6H, t, J = 7.2 Hz), 1.30–1.46 (8H, m), 1.76 (4H, quit, J = 7.2 Hz), 2.56 (4H, t, J = 7.2 Hz), 7.34 (2H, dd, J = 10.7, 2.0 Hz), 7.41 (2H, d, J = 12.6 Hz), 7.50 (2H, dd, J = 12.6, 2.0 Hz), 9.10 (2H, d, J = 10.7 Hz), and 9.39 (2H, s); ^{13}C NMR ($CDCl_3$) δ 13.9 (2C), 22.3 (2C), 25.0 (2C), 31.3 (2C), 38.7 (2C), 120.5 (2C), 135.2 (2C), 136.1 (2C), 138.3 (2C), 144.6 (2C), 146.5 (2C), 173.5 (2C), and 178.3 (2C); EI MS: m/z 436 (M$^+$), 240 (base peak); Found: C, 71.61; H, 7.40; N, 6.46%. Calcd for $C_{26}H_{32}N_2O_4$: C, 71.53; H, 7.39; N, 6.42%. **3e** (19%); Found: C, 74.21; H, 8.77; N, 5.07%. Calcd for $C_{34}H_{48}N_2O_4$: C, 74.42; H, 8.82; N, 5.10%. **3i** (13%); Found: C, 76.09; H, 9.72; N, 4.18%. Calcd for $C_{42}H_{64}N_2O_4$: C, 76.32; H, 9.76; N, 4.24%.

Preparation of Amine Derivatives (4). 2,2′-Dimethoxy-5,5′-bitropone was prepared by the methylation of 5,5′-bitropolone with diazomethane, as reported before. A mixture of 2,2′-dimethoxy-5,5′-bitropone (50 mg, 0.21 mmol) and 1-hexylamine (4 cm^3) was stirred at 120 °C for 24 h. The mixture was evaporated in vacuo to leave a residue, which was chromatographed in hexane-ethyl acetate or hexane-chloroform mixture on a silica-gel column to give crystals. The crystals were recrystallized with hexane–benzene (1:1 v/v) to give yellow crystals (**4b**, 36 mg, 43%).

4b (43%); ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, t, J = 7.3 Hz), 1.24–1.42 (8H, m), 1.46 (4H, quit, J = 7.3 Hz), 1.77 (4H, quit, J = 7.3 Hz), 3.34 (4H, q, J = 7.3 Hz), 6.60 (2H, d, J = 11.1 Hz), 7.19 (2H, d, J = 12.0 Hz), 7.25 (2H, brs), 7.35 (2H, dd, J = 11.1, 2.0 Hz), and 7.34 (2H, dd, J = 12.0, 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.4 (2C), 22.2 (2C), 27.2 (2C), 28.8 (2C), 31.8 (2C), 43.2 (2C), 109.1 (2C), 128.6 (2C), 136.1 (2C), 138.1 (2C), 154.9 (2C), and 176.1 (2C); Found: C, 76.46; H, 8.83; N, 6.79%. Calcd for $C_{26}H_{36}N_2O_2$: C, 76.43; H, 8.88; N, 6.86%. **4f** (34%); Found: C, 78.23; H, 10.11; N, 5.45%. Calcd for $C_{34}H_{52}N_2O_2$: C, 78.41; H, 10.06; N, 5.38%. **4i** (15%); Found: C, 79.42; H, 10.82; N, 4.42%. Calcd for $C_{42}H_{68}N_2O_2$: C, 79.69; H, 10.83; N, 4.43%.

Preparation of Benzenoid Derivatives (5,6). The benzenoid derivatives (**5**,**6**) were prepared by the esterification and etherification of 4,4′-biphenol with alkanoyl chloride or alkyl bromide, as reported in a previous paper.[9]

5i; ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, J = 7.4 Hz), 1.20–1.47 (40H, m), 1.77 (4H, quit, J = 7.4 Hz), 2.58 (4H, t, J = 7.4 Hz), 7.14 (4H, d, J = 8.7 Hz), and 7.55 (4H, d, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1 (2C), 22.7 (2C), 25.0 (2C), 29.1 (2C), 29.3 (2C), 29.4 (2C), 29.5 (2C), 29.61 (4C), 29.66 (2C), 29.69 (2C), 31.9 (2C), 34.4 (2C), 121.9 (4C), 128.1 (4C), 138.1 (2C), 150.2 (2C), and 172.4 (2C); FAB-MS m/z 607 (M+H$^+$); Found: C, 79.21; H, 10.30%. Calcd for $C_{40}H_{62}O_4$: C, 79.16; H, 10.30%. **5j**; Found: C, 79.46; H, 10.45%. Calcd for $C_{42}H_{66}O_4$: C, 79.44; H, 10.48%.

6i; ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, J = 6.9 Hz), 1.20–1.41 (40H, m), 1.46 (4H, quit, J = 6.9 Hz), 1.80 (4H, quit, J = 6.9 Hz), 3.98 (4H, t, J = 6.9 Hz), 6.94 (4H, d, J = 8.7 Hz), and 7.46 (4H, d, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1 (2C), 22.7 (2C), 26.1 (2C), 29.31 (2C), 29.37 (2C), 29.42 (2C), 29.59 (2C), 29.61 (2C), 29.66 (2C), 29.67 (2C), 29.68 (2C), 29.70 (2C), 31.9 (2C), 68.1 (2C), 114.7 (4C), 127.6 (4C), 133.3 (2C), and 158.2 (2C); FAB-MS m/z 579 (M+H$^+$); Found: C, 83.02; H, 11.50%. Calcd for $C_{40}H_{66}O_2$: C, 82.98; H, 11.49%.

X-ray Crystallographic Analyses of 1c and 5a. Single crystals of **1c** and **5a** for X-ray analysis were grown in a chloroform solution at room temperature. Two colorless crystals of **1c** and **5a** having approximate dimensions of 0.10 × 0.10 × 0.05 mm and 0.35 × 0.30 × 0.06 mm were mounted on a glass fiber in a random orientation, respectively. A preliminary examination and data collection were performed with Mo $K\alpha$ radiation (λ = 0.71069 Å) on a Rigaku RAXIS-RAPID equipped with an imaging plate. Data collection and cell refinement: MSC/AFC diffractometer control. Data reduction: *teXsan for windows version 1.06*.[16] Structure solution: *SIR92*.[17] Refinement: S*HELXL97*.[18] Molecular graphics: *ORTEP-III*.[19] All H atoms were fixed at ideal positions and restrained with U_{iso} held fixed to $1.2U_{\mathrm{eq}}$ of the parent atoms. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers 180991 and 180992. The data also were deposited as Document No. 75029 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Crystal data for **1c**: $C_{30}H_{38}O_6$, monoclinic, $P2_1/a$, a = 13.770(1) Å, b = 8.2007(6) Å, c = 25.362(2) Å, β = 103.688(3)°, V = 2782.6(4) Å^3, Z = 4, M_r = 494.63, D_x = 1.181 Mg m^{-3}, μ = 0.081 mm^{-1}, T = 223(2) K, refinement on F^2 (SHELXL97),[18] $R[F^2 > 2\sigma(F^2)] = 0.1011$, $wR(F^2) = 0.2820$, S = 1.025.

Crystal data for **5a**: $C_{24}H_{30}O_4$, triclinic, $P\bar{1}$, a = 8.085 (2) Å, b = 24.996(5) Å, c = 5.5008(9)Å, α = 93.80(1)°, β = 107.634(5)°, γ = 87.325(2)°, V = 1056.6(3) Å^3, Z = 2, M_r = 382.50, D_x = 1.202 Mg m^{-3}, μ = 0.080 mm^{-1}, T = 223(2) K, refinement on F^2 (SHELXL97),[18] $R[F^2 > 2\sigma(F^2)] = 0.0938$, wR $(F^2) = 0.2920$, S = 1.038.

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