Selected Papers

Alkoxyphenyl-Substituted Symmetric Liquid Crystalline Diamantane Derivatives[#]

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Eleven novel thermotropic rod-shaped liquid crystals composed of alkoxyphenyl (methoxy to decyloxy) or hexanoyloxyphenyl groups on both ends of the diamantane core have been synthesized and their liquid crystalline properties investigated. All of them behaved as liquid crystals at considerably high temperatures. When the alkoxy side chains are propyloxy or shorter, the clearing points are over 300 °C. The clearing point of a liquid crystalline compound with two hexanoyloxy groups also exceeds 300 °C. When the alkoxy groups on both ends of the molecule are octyloxy or longer, they showed only smectic phases as the mesophase. When they are shorter than octyloxy, the compounds showed nematic phases just below their clearing points. A nematic phase was also observed for the hexanoyloxy compound as well as the smectic A and B phases. However, as the bent-shaped adamantane-derived hexyloxyphenyl molecule did not show any liquid crystalline properties, the linear structures of the diamantane-derived molecules were crucial in generating liquid crystalline phases.

Currently, liquid crystal displays (LCDs) are the major display devices for TVs, PCs, mobile phones, and other useful products. The liquid crystalline (LC) compounds for such devices should exhibit various significant properties before they are adopted for widespread use.[1] The required physical properties for any type of display are: 1) a wide nematic-phase temperature range, 2) high chemical and thermal stability, and 3) low viscosity to attain short switching times. Although numerous molecules have been synthesized and studied to improve performance, the development of a single compound that satisfies all of the required properties has not yet been achieved. Therefore, most liquid crystals (LCs) for LCDs are a mixture of several different LC compounds, however, the mixing of multiple LCs lowers the nematic–isotropic (N–I) phase-transition temperature. In order to maintain a practical LC temperature range which is as wide as possible, it is necessary that LCs which have high N–I phase transition temperatures be mixed together.[2]

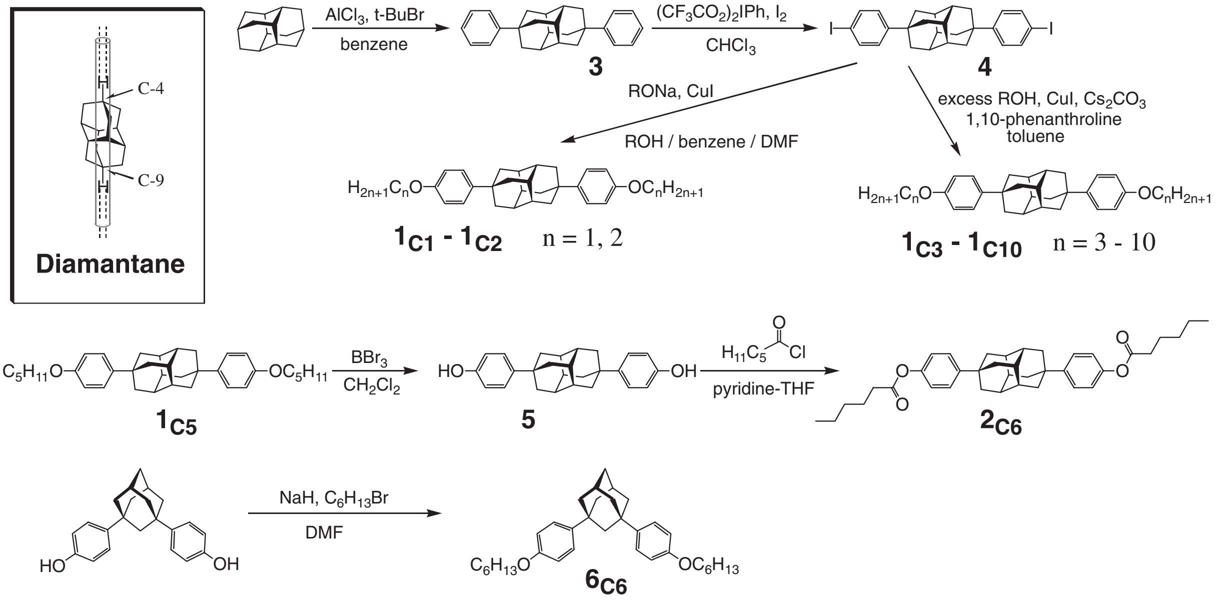
Most rod-like LC compounds have a rigid but flat core structure and one or two flexible side chains, and may also have a polar functional group.[3] The rigid core is made up of one or more hydrocarbon rings and heterocycles such as 1,4-disubstituted benzene, *trans*-1,4-disubstituted cyclohexane, 2,5-disubstituted pyrimidine, and *trans*-2,5-disubstituted 1,3-dioxane rings. However, some liquid crystalline compounds possessing barrel-like thick core structures, such as bicyclo[2.2.2]octanes,[4] hexasilabicyclo[2.2.2]octanes,[5] carboranes,[6] or other polycyclic hydrocarbon cores,[7] have been reported.

Recently, much attention has focused on the molecular nanodiamond family called diamondoids,[8] which was first discovered in the pitch of crude petroleum.[9] Diamondoids have a diamond-like saturated hydrocarbon skeleton based on three-dimensionally fused cyclohexanes whose smallest member is adamantane. They have been studied extensively because of their interesting structural as well as physical properties.[10–13] A number of their chemical modifications have also been reported.[14]

Diamantane, shown in Scheme 1, is the second smallest member of the diamondoid series. It has a C_{3v} symmetry axis along the line on which two C–H bonds on C-4 and C-9 are incorporated.[15] Therefore, when adequate straight-shaped substituents are introduced onto C-4 and C-9, a rod-like molecular framework which may show LC properties will be built up. We, therefore, undertook the construction of such molecules to see if they could work as LCs. Here, we report on the synthesis and LC properties of 4,9-bis(4-substituted phenyl)diamantanes.

Results and Discussion

Molecular Design and Synthetic Strategy. As the diamantane core is an aliphatic group, strong attractive interactions between the molecules which can induce an ordered arrangement are not expected. Although the concept of molecular design showing that diamantane could be the core part of liquid crystalline molecules was first suggested in our previous paper,[16] we have succeeded in extending this idea by the elaboration of molecular structures which can, in fact, display excellent liquid crystalline properties, as described in



Scheme 1. Synthetic route of $\mathbf{1}_{\mathbf{C}n}$, $\mathbf{2}_{\mathbf{C6}}$, and $\mathbf{6}_{\mathbf{C6}}$.

this paper. Thus, in order to increase attractive interactions, the phenylene groups on the C-4 and C-9 positions should be effective in realizing stable LC phases induced by π–π stacking. As flexible side chains on the C-4 of the phenyl groups, we chose alkoxy groups which can be introduced by the Ullmann reaction[17] or Buchwald protocol[18] to the iodophenyl moiety. The resulting alkoxyphenyl groups can be hydrolyzed to phenols, which in turn will be converted to other derivatives such as esters. The LC properties of an ester molecule are also described.

Synthesis. The 4,9-bis(alkoxyphenyl)diamantanes $\mathbf{1}_{\mathbf{C}n}$ ($n = 1$–10) and $\mathbf{2}_{\mathbf{C6}}$ were synthesized according to Scheme 1. The key intermediate **4** was prepared according to previous literature.[15,19] The coupling reaction of **4** with alcohols via the Buchwald protocol[18] afforded $\mathbf{1}_{\mathbf{C}n}$ ($n = 3$–10), whereas $\mathbf{1}_{\mathbf{C}n}$ ($n = 1$ and 2) were prepared by Ullmann-type reactions.[17] Hydrolysis of $\mathbf{1}_{\mathbf{C5}}$ afforded **5**, which was converted to $\mathbf{2}_{\mathbf{C6}}$ by treatment with hexanoyl chloride in the presence of pyridine. In order to see the effect of the molecular shape, an adamantane-derived alkoxy compound $\mathbf{6}_{\mathbf{C6}}$ was prepared by Williamson ether synthesis from 1,3-bis(4-hydroxyphenyl)adamantane and 1-bromohexane. The structures of the synthesized compounds were confirmed by ^{1}H NMR, FT-IR, and low- and high-resolution mass spectroscopy.

Investigation of the Liquid Crystalline Properties. The liquid crystalline properties of diamantane-based compounds $\mathbf{1}_{\mathbf{C}n}$, $\mathbf{2}_{\mathbf{C6}}$, and an adamantane derivative $\mathbf{6}_{\mathbf{C6}}$ were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) equipped with a hot stage. The X-ray diffractions (XRD) of the selected samples were measured at various temperatures. The phase-transition temperatures, enthalpy changes, and phase diagrams of $\mathbf{1}_{\mathbf{C}n}$, $\mathbf{2}_{\mathbf{C6}}$, and $\mathbf{6}_{\mathbf{C6}}$ determined by DSC and POM observations are summarized in Table 1.

As we have envisaged, all of the diamantane-derived compounds showed LC properties. Most are enantiotropic and their clearing points are surprisingly high, as shown in Table 1. On the other hand, crystals of the adamantane-derived compound $\mathbf{6}_{\mathbf{C6}}$ melted to give an isotropic liquid, showing no LC phases. Apparently, the bent-shape of $\mathbf{6}_{\mathbf{C6}}$ prevented the generation of any LC phases.

Bis(alkoxyphenyl) Derivatives $\mathbf{1}_{\mathbf{C}n}$: Most of the compounds belonging to $\mathbf{1}_{\mathbf{C}n}$ showed nematic, smectic A, and several anisotropic soft crystalline phases, though the behaviors depend on the length of the alkyl chains. First, we have described the LC behaviors of $\mathbf{1}_{\mathbf{C6}}$ as a typical example.

On the DSC chart of $\mathbf{1}_{\mathbf{C6}}$ (Figure 1), four endothermic peaks were observed during heating, which correspond to, from lower to higher temperature, crystal 1 (Cr^{1}) to crystal 2 (Cr^{2}), Cr^{2} to smectic A (SmA), SmA to N, and N to I, respectively. Although a mesophase which did not appear during heating was observed at the lowest end of the temperature within a narrow range during measurement of cooling, its optical texture was indistinguishable from the Cr^{2} phase. The textures of $\mathbf{1}_{\mathbf{C6}}$ during cooling are shown in Figure 2. A mosaic texture (Cr^{2}), fan-shape texture (SmA), and schlieren texture (N) were observed in their corresponding temperature ranges.

In Figure 3a, the XRD profile of $\mathbf{1}_{\mathbf{C6}}$ at 176 °C is shown. It suggests that SmA appeared at this temperature from the observations of a sharp peak corresponding to the layer distance at the small angle region and only broad peaks at the wide angle region. On the other hand, the XRD pattern at 144 °C (Cr^{2}, Figure 3b) showed several sharp peaks at a wider angle, suggesting the generation of an ordered structure. Since a mosaic texture was observed at this temperature, Cr^{2} can be considered a soft crystal, though a rigorous assignment has not been done. As some of the compounds with different chain lengths belonging to the $\mathbf{1}_{\mathbf{C}n}$ family showed similar textures to Cr^{2} of $\mathbf{1}_{\mathbf{C6}}$, we tentatively assigned them as Cr^{2}.

The layer distance of SmA of $\mathbf{1}_{\mathbf{C6}}$ was calculated to be 2.8 nm from the value of 2θ (3.1°), which is slightly shorter than the molecular length of the extended shape calculated by PM3 calculations along the long axis (3.1 nm), suggesting that a slight interdigitation of the alkyl chains occurs.

Table 1. Phase-Transition Temperatures and Corresponding Enthalpy Values of $\mathbf{1}_{\mathrm{C}n}$, $\mathbf{2}_{\mathrm{C6}}$, and $\mathbf{6}_{\mathrm{C6}}$

Compound	Scan	Phase classification and phase transition temperature/°C [ΔH/kJ mol^{-1}]
$\mathbf{1}_{\mathrm{C1}}$	Heat	**Cr**^{1} 279.5 [22.4] **N** 345.3 [0.93] **I**
	Cool	**Cr**^{1} 274.4 [−12.1] **N** 326.1 [—] **I**
$\mathbf{1}_{\mathrm{C2}}$	Heat	**MCr** 130.9 [−19.2] **Cr**^{1} 217.6 [26.3] **Cr**^{2} 226.2 [29.3] **N** 342.4 [1.89] **I**
	Cool	**MCr** 216.1 [−32.2] **N** 336.2 [—] **I**
$\mathbf{1}_{\mathrm{C3}}$	Heat	**Cr**^{1} 154.9 [9.71] **Cr**^{3} 184.9 [1.71] **Cr**^{2} 199.0 [11.5] **N** 310.1 [0.71] **I**
	Cool	**Cr**^{1} 127.5 [−1.11] **Cr**^{5} 131.9 [−5.07] **Cr**^{4} 135.6 [−6.23] **Cr**^{2} 191.6 [−11.2] **N** 305.6 [−0.67] **I**
$\mathbf{1}_{\mathrm{C4}}$	Heat	**Cr**^{1} 132.9 [1.40] **Cr**^{5} 161.7 [11.4] **Cr**^{2} 172.7 [5.20] **N** 296.1 [1.23] **I**
	Cool	**Cr**^{1} 122.3 [−1.72] **Cr**^{5} 132.4 [−11.2] **Cr**^{2} 164.6 [−7.19] **N** 292.7 [−0.61] **I**
$\mathbf{1}_{\mathrm{C5}}$	Heat	**Cr**^{1} 94.8 [9.52] **Cr**^{4} 109.2 [7.91] **Cr**^{2} 180.9 [9.03] **SmA** 222.6 [0.12] **N** 279.6 [0.56] **I**
	Cool	**Cr**^{1} 69.6 [−8.82] **Cr**^{2} 175.1 [−8.88] **SmA** 211.6 [−0.05] **N** 276.0 [−0.68] **I**
$\mathbf{1}_{\mathrm{C6}}$	Heat	**Cr**^{1} 114.0 [11.5] **Cr**^{2} 160.5 [11.1] **SmA** 239.6 [0.28] **N** 266.0 [0.83] **I**
	Cool	**Cr**^{1} 80.6 [−7.38] **Cr**^{3} 83.6 [−5.17] **Cr**^{2} 155.3 [−11.5] **SmA** 232.0 [−0.21] **N** 262.2 [−0.76] **I**
$\mathbf{1}_{\mathrm{C7}}$	Heat	**Cr**^{1} 152.8 [5.30] **Cr**^{2} 156.2 [6.38] **SmA** 241.2 [2.08] **N** 248.1 [1.60] **I**
	Cool	**Cr**^{1} 82.6 [−0.67] **Cr**^{5} 143.9 [−6.08] **Cr**^{2} 153.1 [−5.05] **SmA** 238.5 [−1.64] **N** 245.9 [−1.45] **I**
$\mathbf{1}_{\mathrm{C8}}$	Heat	**Cr**^{1} 125.3 [5.52] **Cr**^{4} 132.1 [4.84] **Cr**^{3} 137.1 [3.57] **Cr**^{2} 142.0 [3.51] **SmA** 238.2 [3.82] **I**
	Cool	**Cr**^{1} 74.4 [−4.68] **Cr**^{4} 124.4 [−5.47] **Cr**^{3} 129.5 [−3.60] **Cr**^{2} 138.9 [−3.29] **SmA** 233.7 [−3.49] **I**
$\mathbf{1}_{\mathrm{C9}}$	Heat	**Cr**^{1} 115.7 [10.9] **Cr**^{4} 122.8 [6.88] **SmA** 228.0 [5.38] **I**
	Cool	**Cr**^{1} 84.0 [−8.94] **Cr**^{4} 114.9 [−6.48] **SmA** 223.8 [−5.16] **I**
$\mathbf{1}_{\mathrm{C10}}$	Heat	**Cr**^{1} 123.8 [21.8] **SmB** 149.8 [0.24] **SmA** 221.5 [6.04] **I**
	Cool	**Cr**^{1} 116.7 [−22.0] **SmB** 147.9 [−0.18] **SmA** 218.2 [−5.80] **I**
$\mathbf{2}_{\mathrm{C6}}$	Heat	**Cr**^{1} 115.2 [8.04] **Cr**^{2} 133.7 [1.14] **SmX** 141.7 [9.24] **SmB** 226.0 [0.96] **SmA** 283.5 [0.26] **N** 326.6 [1.02] **I**
	Cool	**Cr**^{1} 90.5 [−7.90] **Cr**^{2} 124.2 [−9.21] **SmB** 187.2 [−0.20] **SmA** 266.2 [−0.08] **N** 320.5 [−0.74] **I**
$\mathbf{6}_{\mathrm{C6}}$	Heat	**Cr**^{1} 13.6 [−19.2] **I**
	Cool	**Cr**^{1} 50.6 [23.2] **I**

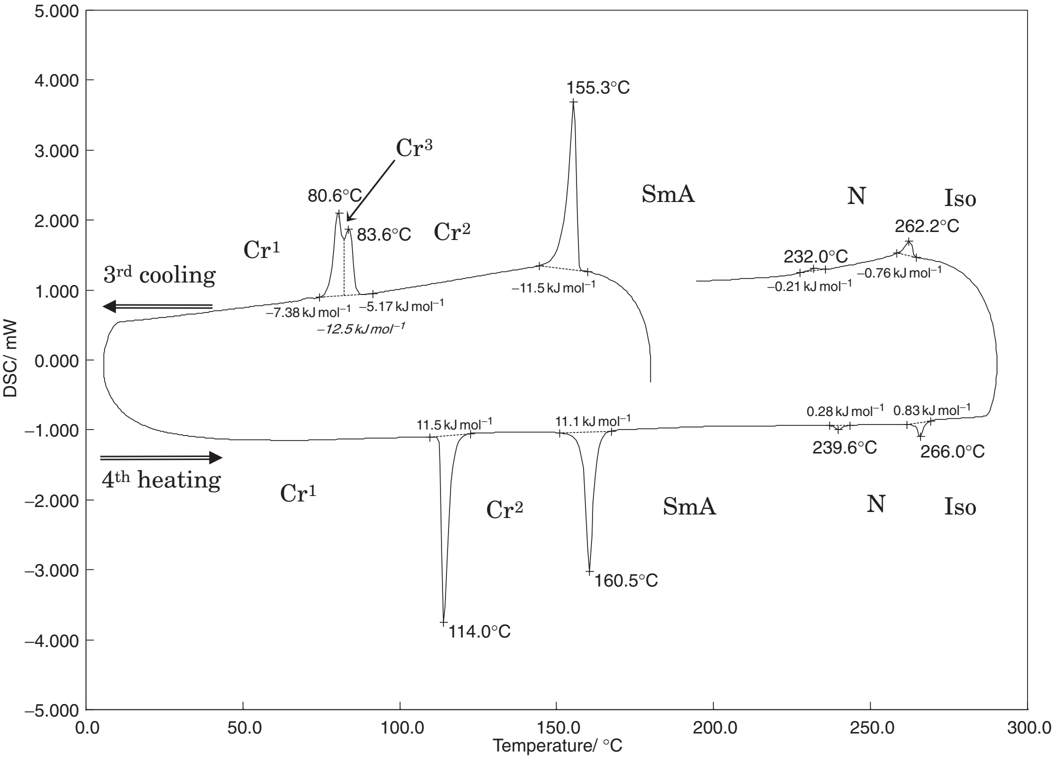


Figure 1. DSC chart of $\mathbf{1}_{\mathrm{C6}}$ (3rd cooling, 4th heating and cooling).

When the alkoxy chains become longer, the clearing point becomes lower and the nematic range narrower. When the alkoxy group is octyloxy or longer, only smectic LC phases are observed. The DSC charts and POM textures of $\mathbf{1}_{\mathrm{C8}}$ during cooling are shown in Figures 4 and 5, respectively. Four intermediate phases were observed during heating, though three of them were observed within a narrow temperature range of 120–140 °C. The crystal phase 4 was assigned to a phase which

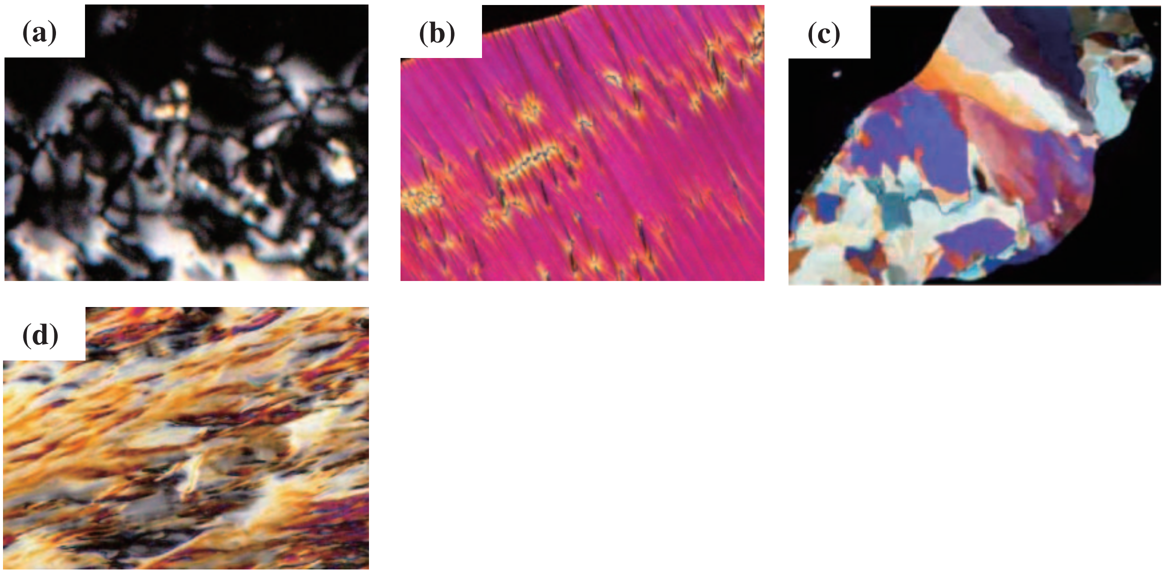


Figure 2. Polarized optical microscopic textures of $\mathbf{1}_{\mathbf{C6}}$. (a) 231 °C (cooling, nonsurface treated), (b) 156 °C (cooling, rubbing treated), (c) 155 °C (cooling, rubbing treated), and (d) 101 °C (cooling, rubbing treated).

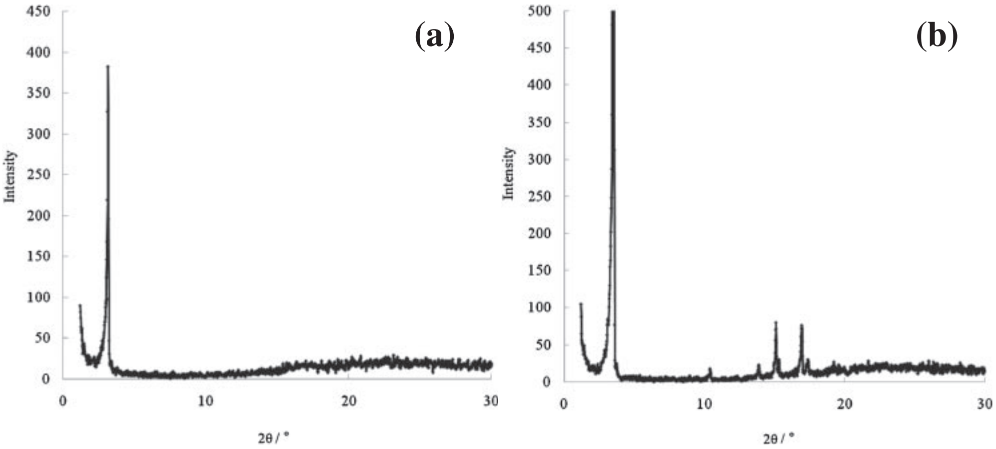


Figure 3. X-ray diffractograms of $\mathbf{1}_{\mathbf{C6}}$. (a) 176 and (b) 144 °C.

appeared at a much lower temperature range during cooling than the heating due to supercooling, since (1) the numbers of crystalline states for the cooling and heating processes are the same, and (2) their phase transition enthalpy values are similar.

When $\mathbf{1}_{\mathbf{C8}}$ was cooled down from the isotropic liquid, a batonnet-like fine texture appeared just below the clearing point, which then changed to a fan-shape texture at around 220 °C (Figure 5a), and it changed to a mosaic texture (Figure 5b) while cooling down further. As its XRD pattern at 180 °C (Figure 6a) at a wide angle showed only a broad peak, it was assigned to the SmA phase. On the other hand, several sharp peaks are observed in a wide angle region at 137 °C, which is similar to that of the crystal 2 phase of $\mathbf{1}_{\mathbf{C6}}$ (Figure 6b).

For $\mathbf{1}_{\mathbf{C10}}$ which possesses the longest alkyl chains examined in this study, the SmB phase was observed. Its DSC chart (Figure 7) showed three phase transition peaks for both cooling and heating. The phase change with a small phase-transition enthalpy at around 149 °C was assigned to that between SmA and SmB, as concluded from XRD measurements. As the POM observations at 191 and 141 °C showed similar fan-shape textures (Figure 8), it was difficult to distinguish between them. From the XRD chart at 160 °C, only a broad peak at a wide angle region was observed, suggesting the formation of SmA (Figure 9a), while at 134 °C a relatively sharp diffraction peak was observed at 17.7° (Figure 9b). These results showed the existence of a long-distance order within a layer. Judging from the similarity of the POM textures and the small enthalpy change between them, it was concluded that SmB is generated at the lower temperature range.

Figure 10 shows the DSC chart of $\mathbf{1}_{\mathbf{C4}}$. During both the heating and cooling processes, four phase transition peaks were observed. Although the corresponding transition temperatures at the lower temperature range are different, it was concluded that the same mesophases appeared during both processes since the corresponding phase-transition enthalpies are similar. When the isotropic phase was cooled down, a schlieren texture of the nematic phase (Figure 11a) appeared, and the mosaic Cr^2 phase was observed upon further cooling (Figure 11b).

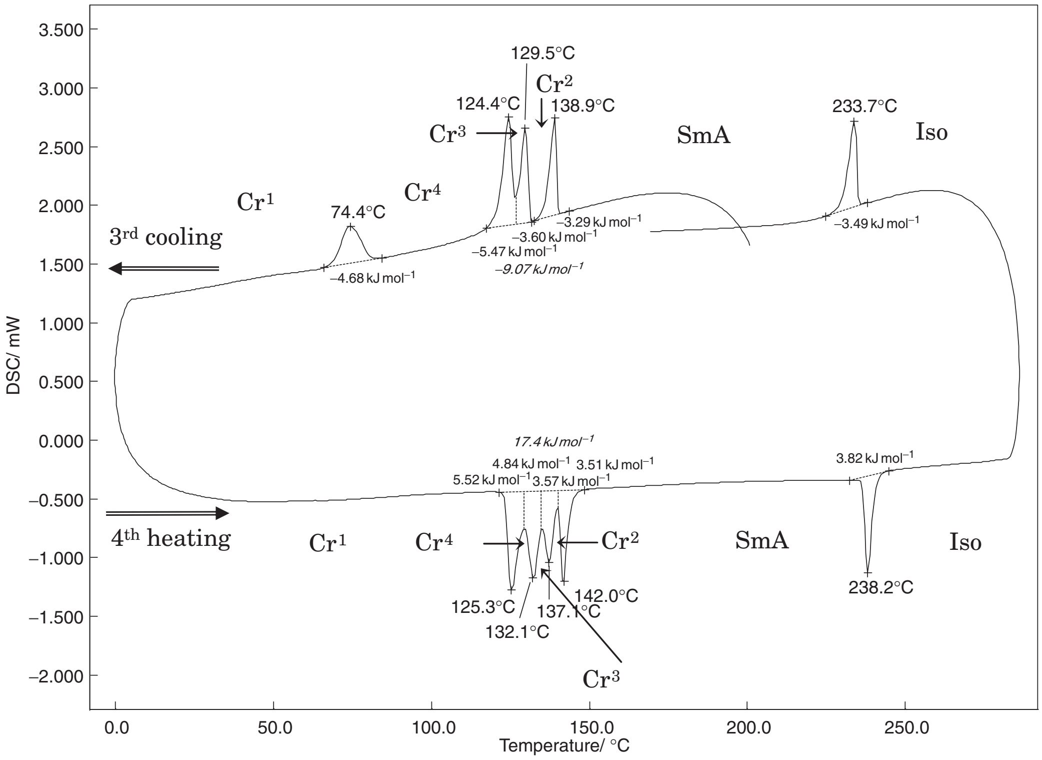


Figure 4. DSC chart of $\mathbf{1}_{\mathbf{C8}}$ (3rd cooling, 4th heating and cooling).

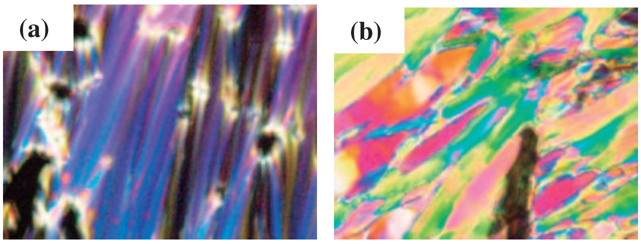


Figure 5. Polarized optical microscopic textures of $\mathbf{1}_{\mathbf{C8}}$. (a) 223 °C (cooling, rubbing treated) and (b) 134 °C (cooling, rubbing treated).

The DSC chart of $\mathbf{1}_{\mathbf{C2}}$ during heating showed three endothermic peaks (Figure 12) which correspond to the transitions from Cr^1 to Cr^2, Cr^2 to N, and N to I, respectively. In addition, an exothermic peak was observed at 130 °C. While the corresponding peak was not observed during cooling, it was concluded that a phase transition from an LC phase to a metastable crystalline phase occurred. This phase-transition behavior was observed only for $\mathbf{1}_{\mathbf{C2}}$.

Due to the rapid degradation of the compound at temperatures for the isotropic phase, the clearing point of $\mathbf{1}_{\mathbf{C2}}$ during cooling was not observed by DSC. However, the I to N phase transition was observed by POM. When the isotropic phase was cooled down, a schlieren texture appeared at 336 °C (Figure 13a), confirming that the phase transition from I to N

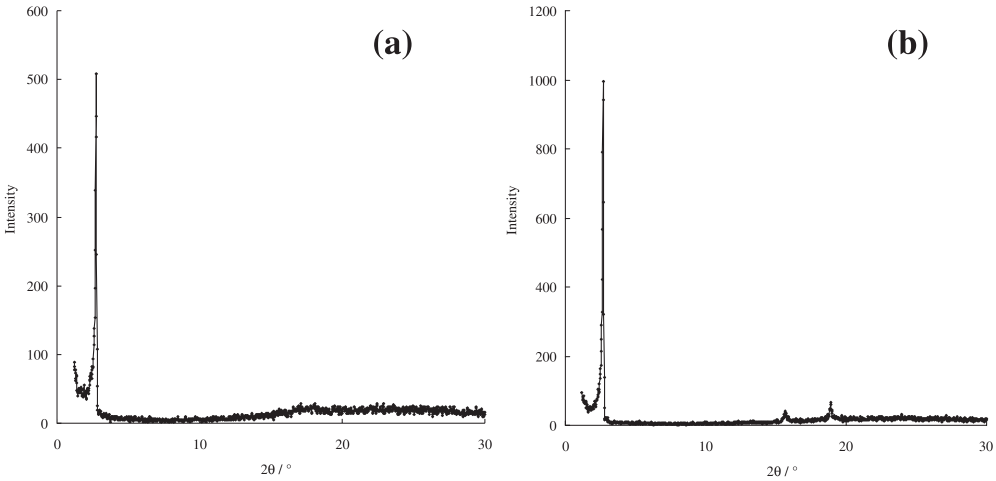


Figure 6. X-ray diffractograms of $\mathbf{1}_{\mathbf{C8}}$. (a) 180 and (b) 137 °C.

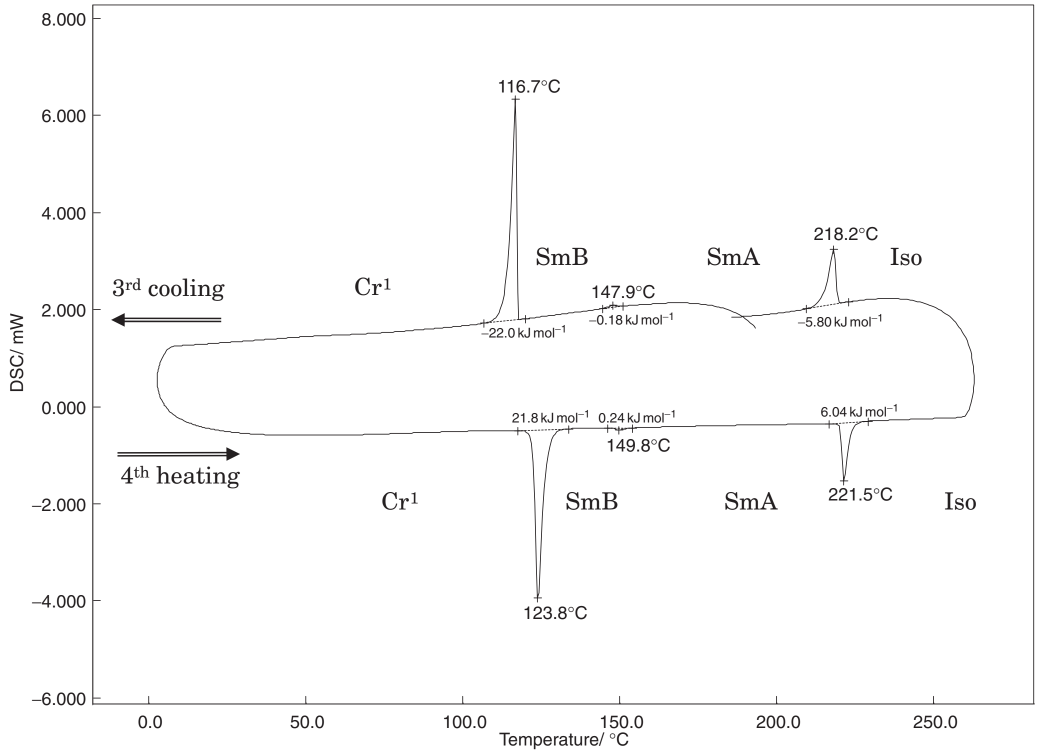


Figure 7. DSC chart of $\mathbf{1}_{\mathbf{C10}}$ (3rd cooling, 4th heating and processes).

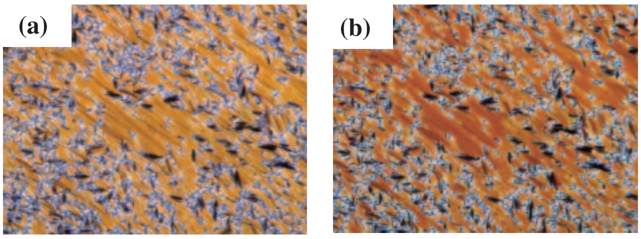


Figure 8. Polarized optical microscopic textures of $\mathbf{1}_{\mathbf{C10}}$. (a) 191 °C (cooling, rubbing treated) and (b) 141 °C (cooling, rubbing treated).

occurred. Upon further cooling from the nematic phase, the nonfluid texture shown in Figure 13b was observed at a temperature range lower than 217 °C. Although this phase is considered to be a crystalline phase, the exothermic peak during heating suggests that it is a metastable crystalline phase.

The relationship between the length of the alkyl chains and the properties of the LCs prepared and examined in this study can be understood by the well-known tendencies of the LCs. Upon an increase in the length of the side chains, the temperature of the clearing point decreased and the smectic property was enhanced. These tendencies are common to general rod-like thermotropic LCs.[1]

The layer distances of the SmA phases for $\mathbf{1}_{\mathbf{C6}}$, $\mathbf{1}_{\mathbf{C8}}$, and $\mathbf{1}_{\mathbf{C10}}$ calculated from the X-ray diffraction patterns and molecular

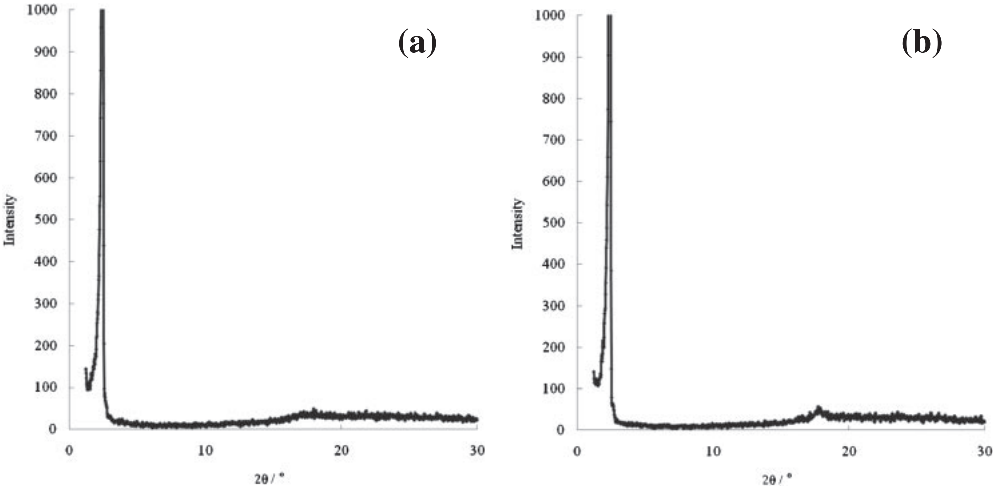


Figure 9. X-ray diffractograms of $\mathbf{1}_{\mathbf{C10}}$. (a) 160 and (b) 134 °C.

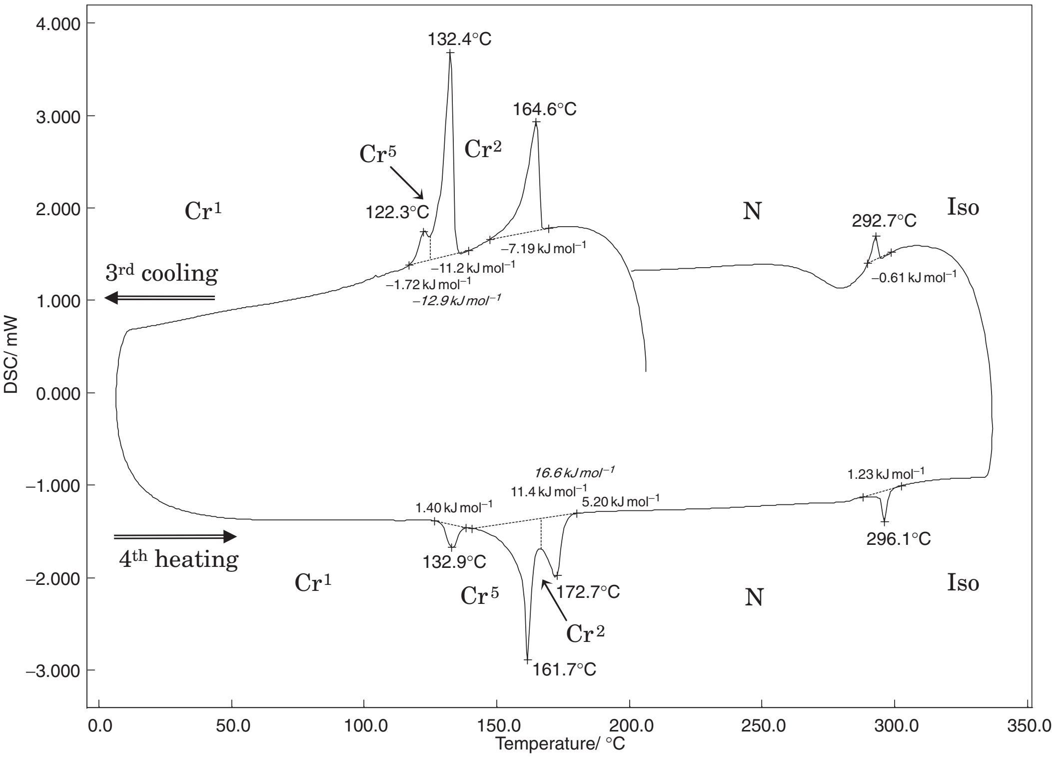


Figure 10. DSC chart of $\mathbf{1_{C4}}$ (3rd cooling, 4th heating and cooling). A broad band appeared at around 300 °C upon cooling is due to the overheating up to 350 °C and not an endothermic peak.

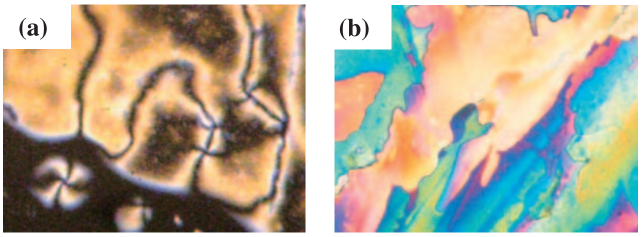


Figure 11. Polarized optical microscopic textures of $\mathbf{1_{C4}}$. (a) 277 °C (cooling, nonsurface treated) and (b) 150 °C (cooling, nonsurface treated).

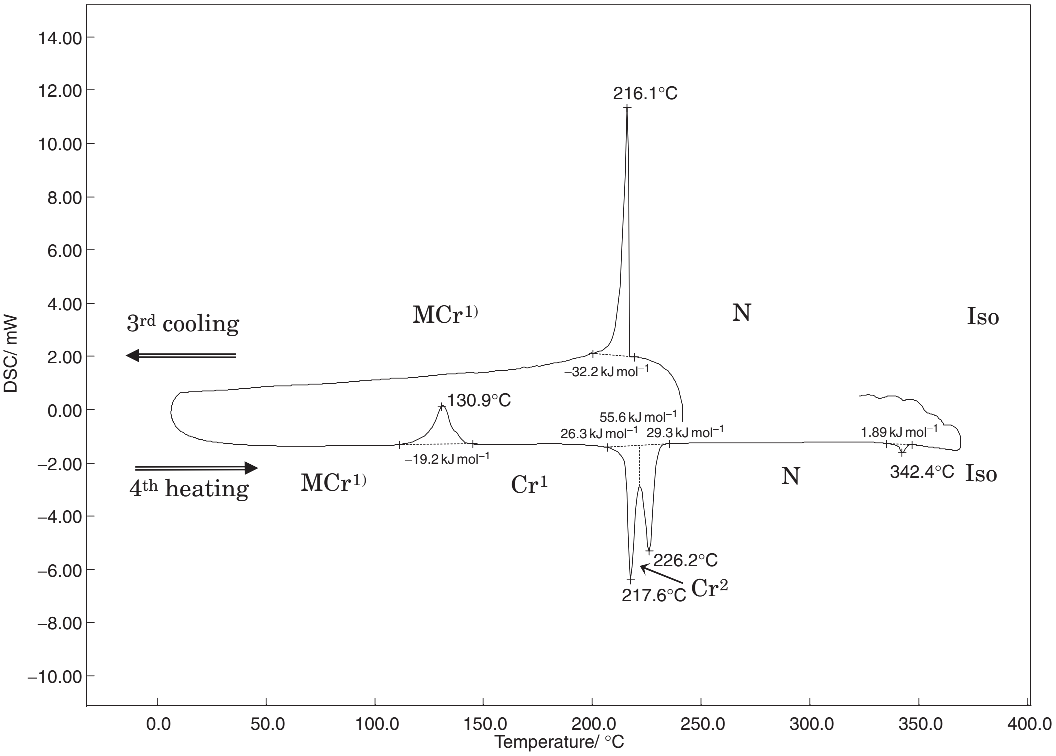
lengths of $\mathbf{1_{C6}}$, $\mathbf{1_{C8}}$, and $\mathbf{1_{C10}}$ obtained by PM3 molecular orbital calculations are summarized in Table 2. The layer distances of the SmA phases are slightly shorter than the calculated molecular lengths, suggesting that interdigitation of the alkyl chains between the layers are occurring. The discrepancy between the layer spacing and the molecular length, the $l - d$ value, becomes larger when the alkoxy chains become longer. Therefore, interdigitation is larger for the longer alkoxy chains.

We have compared the liquid crystalline properties of $\mathbf{1_{C7}}$, having two 4-C_7H_{15}O-phenylene moiety at both ends of the molecule, with the liquid crystalline molecules whose core parts are 1,12-dicarba-*closo*-dodecaborane (**A**), 1,10-dicarba-*closo*-decaborane (**B**), bicyclo[2.2.2]octane (**C**), and 1,4-phenylene (**D**), which have the same 4-C_7H_{15}O-phenylene end groups.

The transition temperatures are summarized in Table 3.[20] Although **A** and **B**, possessing a *p*-carborane core, exhibit only the nematic phase, their thermal stability is inferior to that of $\mathbf{1_{C7}}$, **C**, and **D**. This is in good accordance with the report of Kaszynski and co-workers that *p*-carborane derivatives usually exhibit only the nematic phase as their liquid crystalline phases.[6b,6c,6f,6g,6i,20,21] On the other hand, **C** and **D**, possessing a bicyclo[2.2.2]octane ring system and a 1,4-phenylene system as their cores, respectively, exhibit only smectic phases. While **C** exhibits orthogonal smectic phases such as SmA and SmB, **D** mainly exhibits tilted smectic phases such as SmF, SmI, and SmC. Because $\mathbf{1_{C7}}$ displays orthogonal SmA and N phases in addition to a soft crystal phase, $\mathbf{1_{C7}}$ shows rather similar properties to bicyclo[2.2.2]octane derivatives with regard to the nature of smectic phases they exhibit.

The clearing point of these compounds increases in the order of $\mathbf{A} \approx \mathbf{B} < \mathbf{C} < \mathbf{D} < \mathbf{1_{C7}}$ (Table 3). In addition, $\mathbf{1_{C7}}$ have the widest liquid crystalline range of 91.9 °C. These observations suggest that the introduction of the diamantane ring system as the mesogen core afforded an excellent thermal stability of liquid crystalline phases. Moreover, from the viewpoint of thermal stability of the liquid crystalline phases, $\mathbf{1_{C7}}$ resembles **D** which possesses a phenylene ring.

Bis(hexanoyloxyphenyl) Derivative $\mathbf{2_{C6}}$: The DSC chart and POM textures of the hexanoyloxy derivative $\mathbf{2_{C6}}$ are shown in Figures 14 and 15, respectively. As shown in Figure 15a, the N phase appeared just beneath the clearing point, and further cooling gave the SmA phase which was confirmed by the fan-shape POM texture (Figure 15b). Upon cooling, another smectic phase (SmB) appeared with a small exothermic transition. During heating, an ordered texture with slight fluidity was observed at a narrow temperature range (134–142 °C). This is assigned to the third smectic phase (SmX). When the behavior of $\mathbf{2_{C6}}$ is compared with that of $\mathbf{1_{C6}}$ having



1) MCr: Metastable crystalline phase

Figure 12. DSC chart of $\mathbf{1_{C2}}$ (3rd cooling, 4th heating and cooling).

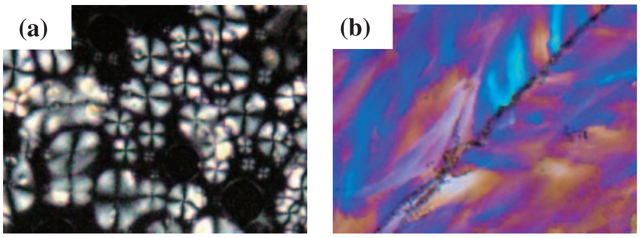


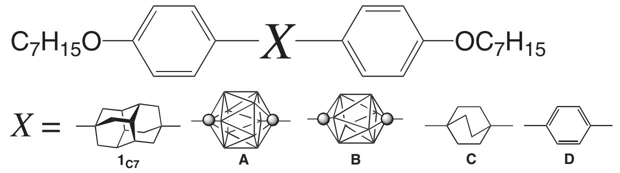
Figure 13. Polarized microscopic textures of $\mathbf{1_{C2}}$. (a) 334 °C (cooling, nonsurface treated) and (b) 196 °C (cooling, rubbing treated).

Table 2. Layer Spacings and Calculated Molecular Lengths of SmA of $\mathbf{1_{C6}}$, $\mathbf{1_{C8}}$, and $\mathbf{1_{C10}}$

Compound	Layer spacing[a] d/nm	Calculated molecular length[b] l/nm	$l - d$/nm
$\mathbf{1_{C6}}$	2.82	3.31	0.49
$\mathbf{1_{C8}}$	3.23	3.77	0.54
$\mathbf{1_{C10}}$	3.65	4.27	0.62

a) Calculated from XRD patterns. b) Obtained by PM3 calculations.

Table 3. Phase-Transition Temperatures of $\mathbf{1_{C7}}$ and **A**–**D**



Compounds	Phase classification and phase transition temperature/°C[a]
$\mathbf{1_{C7}}$	**Cr**^{1} 152.8 **Cr**^{2} 156.2 **SmA** 241.2 **N** 248.1 **I**
A[b]	**Cr** 96 **N** 98 **I**
B[b]	**Cr** 73 **N** 105 **I**
C[b]	**Cr** 98 **SmB** 161 **SmA** 179 **I**
D[b]	**Cr**[c] 182 **SmF** 218 **SmI** 219 **SmC** 232 **SmA** 235 **I**

a) Obtained in heating process; Cr: crystal, Sm: smectic, N: nematic, I: isotropic. b) Ref. 20. c) Cr–Cr transition at 108 °C.

the same side chain lengths, the clearing point of $\mathbf{2_{C6}}$ is higher by 60 °C than that of $\mathbf{1_{C6}}$. This is interpreted by the stabilization of the LC phase of $\mathbf{2_{C6}}$ with the larger intermolecular interactions enhanced by the large dipole moment of the carbonyl groups.

Conclusion

In conclusion, we have synthesized LC molecules possessing a bulky barrel-shaped diamantane as the core group. The linear-shaped diamantane derivatives with 4-alkoxyphenyl or 4-acyloxyphenyl groups on both ends of the diamantane group formed LC states with enhanced thermal stability. The clearing points of $\mathbf{1_{C1}}$–$\mathbf{1_{C3}}$ with shorter alkoxy chains and $\mathbf{2_{C6}}$ with the hexanoyloxy chains are high at temperatures above 300 °C. While compounds $\mathbf{1_{C8}}$–$\mathbf{1_{C10}}$ with octyloxy or longer chains exhibited only smectic phases, the compounds with shorter chains than octyloxy formed nematic phases. On the other hand, the bent-shaped adamantane-derivative $\mathbf{6_{C6}}$ did not show any LC properties.

The diamantane-derived compounds examined in this study are easily accessible and exhibit stable LC properties at

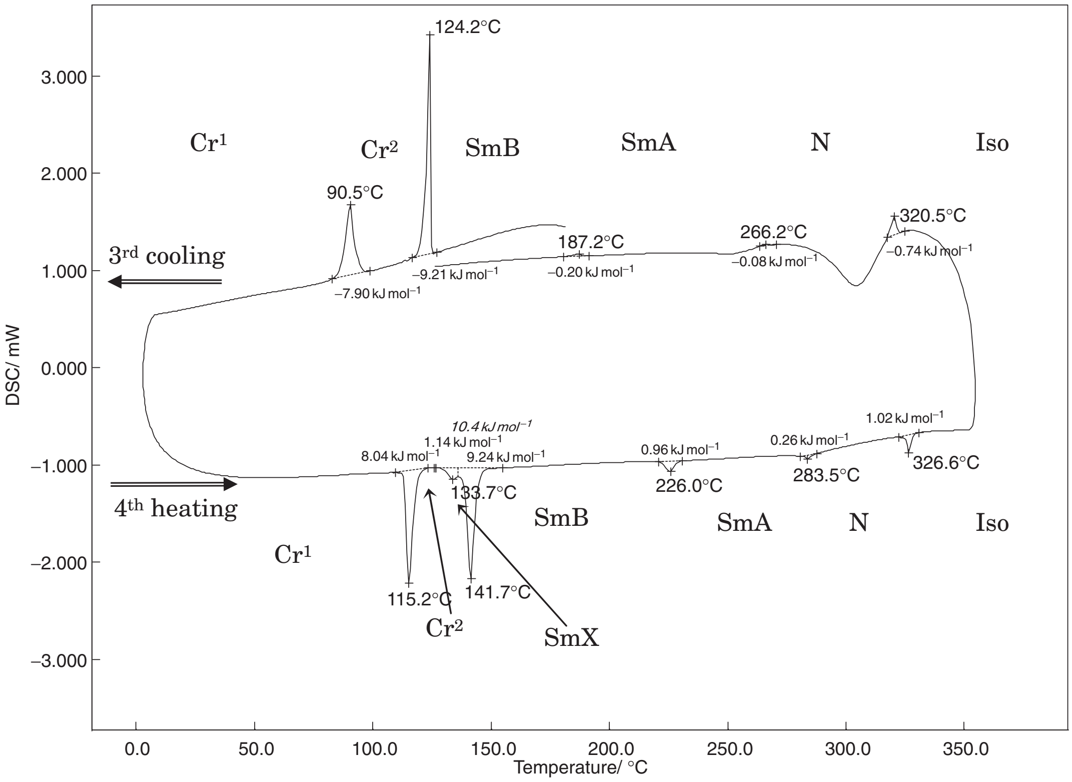


Figure 14. DSC chart of $\mathbf{2}_{\mathbf{C6}}$ (3rd cooling, 4th heating and cooling). A broad band appeared at around 300 °C upon cooling is due to overheating up to 350 °C and not an endothermic peak.

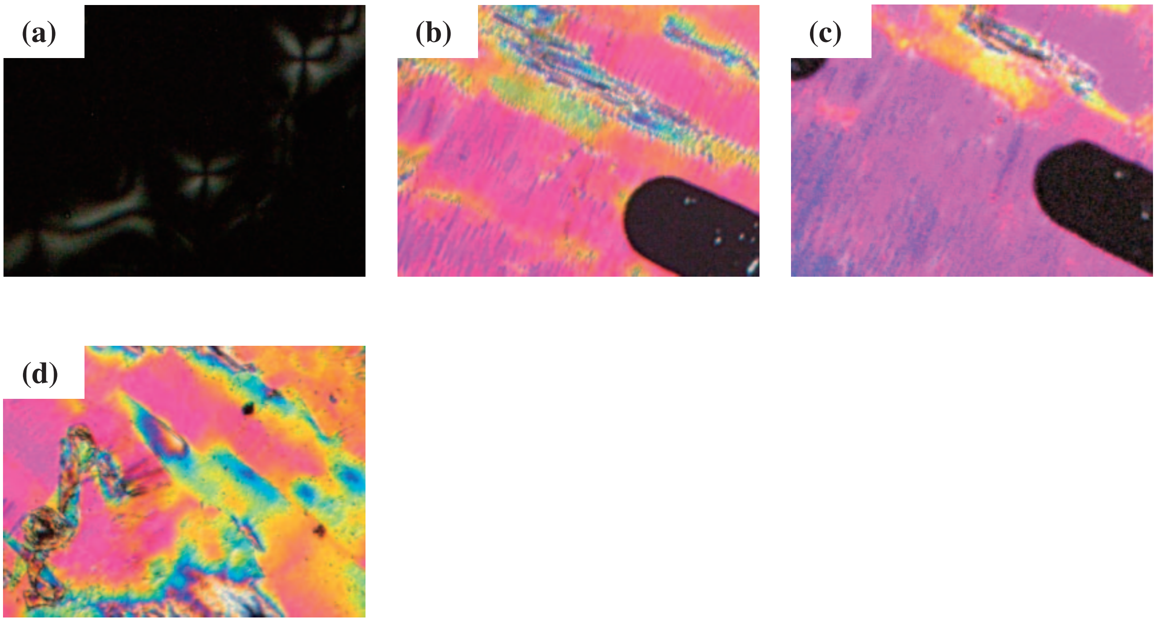


Figure 15. Polarized microscopic textures of $\mathbf{2}_{\mathbf{C6}}$. (a) 272 °C (cooling, nonsurface treated), (b) 218 °C (cooling, rubbing treated), (c) 135 °C (cooling, rubbing treated), and (d) 136 °C (heating, rubbing treated).

elevated temperatures so that they can be used alone or as a mixture with other components for LC materials for use at high temperatures such as displays in automobiles. Moreover, the diamantane is useful as a component of a mesogenic core so that the introduction of diamantane can lead to the development of novel liquid crystalline materials.

Experimental

Materials. Dry tetrahydrofuran (THF) was purchased and used as is. Benzene, methanol, ethanol, dichloromethane, and dimethylformamide were dried by distillation from calcium hydride. Pyridine was dried by distillation from potassium hydroxide. All other chemicals were used as received without further purification. Glass-backed TLC plates coated wth silica gel (60 F_{254} Merck) was used to monitor the progress of reactions. Flash column chromatography was carried out with Merck silica gel 60 (230–400 mesh).

Characterizations. ^{1}H NMR spectra were recorded on a Bruker DRX-300 spectrometer with resonance frequency of 300.15 MHz and samples were dissolved in $CDCl_3$, with tetramethylsilane (TMS) as the internal reference. Infrared (IR) spectra were recorded on JASCO FT/IR-4100 FT-IR spectrometer equipped with an attenuated total reflection attachment. Low- and high-resolution mass spectra were measured by electron impact mass spectrometry (70 eV) using a JEOL JMS-AX-600 mass spectrometer. Melting points were measured using Yazawa BY-2 hot stage microscope, and those were uncorrected. Differential scanning calorimetry (DSC) data of the final compounds were obtained with a SEIKO Instruments Inc. DSC6100 in connection with Extra6000 instrument controller or a Shimadzu DSC60 equipped with a TAC-60i temperature controller. The measurements were carried out under nitrogen atmosphere with heating and cooling rate of 10 °C min^{-1}. The cycle was repeated for rather lower temperature (ca. 50 to 200 °C) 3 times, and the temperature was finally raised up to 250–400 °C to measure the clearing point, because samples are often degraded when temperature was raised up to 250–400 °C, and they do no more show the same phase transition behaviors. For polarized optical microscopy, an OLYMPUS BX50 polarized-light microscope combined with a Mettler Toledo FP90-FP82HT hot stage or a Nikon ECLIPSE LV100POL equipped with a Mettler Toledo FP90-FP82HT hot stage were used. X-ray diffraction (XRD) patterns of compound $\mathbf{1_{C6}}$, $\mathbf{1_{C8}}$, and $\mathbf{1_{C10}}$ were recorded with a Shimadzu XRD-6100 using Cu Kα radiation equipped with an Anton Paar TTK450 temperature controller.

Synthesis of 4,9-Diphenyldiamantane (3). To a stirred mixture of diamantane (3.04 g, 16.13 mmol) and aluminum chloride (218.4 mg, 1.64 mmol) in 35 mL benzene was added dropwise *t*-butyl bromide (5.5 mL, 49.0 mmol) at 0 °C under a nitrogen atmosphere. The resulting mixture was stirred at rt for 2 h. The gasses generated were quenched with sat. aq. sodium bicarbonate solution. The reaction was quenched by adding 0.5 mol dm^{-3} hydrochloric acid, and the resultant mixture was extracted with chloroform three times. The combined organic layer was washed with sat. brine, and the solvent was evaporated. To the residue was added hexane and the resulting mixture was stirred vigorously. The powder material formed was collected by filtration to give 4,9-diphenyldiamantane (**3**) as a colorless powder (4.60 g, 84%). Mp 264.5–265.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.98 (18H, s), 7.19 (2H, tt, $J = 7.2$, 1.6 Hz), 7.34 (4H, t, $J = 7.6$ Hz), 7.42 (4H, dt, $J = 8.4$, 1.2 Hz). IR (ATR, neat): ν/cm^{-1} 3079 (w), 3052 (w), 3014 (w), 2914 (s), 2888 (s), 2849 (s), 1600 (w), 1492 (m), 1461 (w), 1441 (w), 1378 (w), 1350 (w), 1316 (w), 1271 (w), 1248 (w), 1157 (w), 1067 (w), 1049 (w), 1031 (w), 1001 (w), 987 (w), 966 (w), 906 (w), 761 (s), 699 (s), 682 (w), 530 (m). LRMS (EI, 70 eV): *m*/*z*, 342 ((M + 2)$^+$, 4.1), 341 ((M + 1)$^+$, 28.6), 340 (M$^+$, 100), 263 (3.6). Found: *m*/*z* 340.22106. Calcd for $C_{26}H_{28}$: M, 340.21910.

Synthesis of 4,9-Bis(4-iodophenyl)diamantane (4). A solution of 4,9-diphenyldiamantane (**3**) (2.14 g, 6.29 mmol), iodine (1.815 g, 7.15 mmol), $(CF_3CO_2)_2IPh$ (5.808 g, 13.0 mmol) in chloroform (42 mL) was stirred for 30 min at rt, when a solid material precipitated. The resulting mixture was transferred to a beaker containing water (200 mL) which was vigorously stirred. Sodium dithionite was added until the purple color disappeared. The resulting biphasic mixture was extracted with chloroform. The combined organic layer was washed with sat. brine, and the solvent evaporated. To the residue was added hexane and stirred vigorously. The solid material thus formed was collected by filtration to give 4,9-bis(4-iodophenyl)diamantane (**4**) as a faint pink powder (2.92 g, 74%). Mp >360 °C (higher than the measurement limit). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.92 (12H, br s), 1.96 (6H, br s), 7.15 (4H, d(AA′BB′), $J = 8.7$ Hz), 7.64 (4H, d(AA′BB′), $J = 8.7$ Hz). IR (ATR, neat): ν/cm^{-1} 2911 (s), 2874 (s), 2849 (s), 1488 (m), 1461 (w), 1437 (w), 1391 (m), 1243 (w), 1108 (w), 1073 (m), 1048 (m), 1003 (m), 984 (m), 893 (w), 821 (s), 796 (m), 760 (w), 716 (w), 699 (w), 526 (s). LRMS (EI, 70 eV): *m*/*z*, 593 ((M + 1)$^+$, 59.1), 592 (M$^+$, 100), 466 (54.2), 389 (7.4). Found: *m*/*z* 592.01233. Calcd for $C_{26}H_{26}I_2$: M, 592.01245.

Synthesis of 4,9-Bis(4-methoxyphenyl)diamantane ($\mathbf{1_{C1}}$). To a mixture of 4,9-bis(4-iodophenyl)diamantane (**4**) (198.9 mg, 0.336 mmol), 4.9 mol dm^{-3} sodium methoxide methanol solution (12 mL, 58.8 mmol), dry benzene (8 mL), and dry DMF (2 mL) was added copper(I) iodide (31.2 mg, 0.164 mmol) at the refluxing temperature under nitrogen atmosphere. The resulting mixture was refluxed for 8.5 h continuously. After cooling to rt, the reaction was quenched by adding water. The resulting mixture was extracted with ethyl acetate–benzene (9:1). The combined organic layer was washed with water and sat. brine, and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using chloroform as an eluent, to give a colorless powder. The powder was recrystallized from chloroform to give $\mathbf{1_{C1}}$ as colorless needle crystals (42.9 mg, 31%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.93 (18H, br s), 3.80 (6H, s), 6.88 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.33 (4H, d(AA′BB′), $J = 8.2$ Hz). IR (ATR, neat): ν/cm^{-1} 3031 (w), 3004 (w), 2953 (w), 2911 (s), 2875 (s), 2851 (m), 1606 (m), 1509 (s), 1463 (m), 1437 (m), 1301 (m), 1250 (s), 1181 (s), 1115 (w), 1076 (w), 1047 (w), 1033 (m), 984 (s), 825 (s), 795 (m), 671 (w), 653 (w), 582 (m), 540 (s). LRMS (EI, 70 eV): *m*/*z*, 401 ((M + 1)$^+$, 53), 400 (M$^+$, 100). Found: *m*/*z* 400.23957. Calcd for $C_{28}H_{32}O_2$: M, 400.24023.

Synthesis of 4,9-Bis(4-ethoxyphenyl)diamantane ($\mathbf{1_{C2}}$). To a mixture of 4,9-bis(4-iodophenyl)diamantane (**4**) (200.9 mg, 0.339 mmol) and sodium hydride (2.30 g, 57.5 mmol) was added dry ethanol (17 mL) under nitrogen atmosphere. After stirring vigorously at rt, dry benzene (5 mL) and dry DMF (2 mL) was added, and the mixture was heated to reflux, then copper(I) iodide (31.7 mg 0.166 mmol) was added. This mixture was refluxed for 20.5 h continuously. After cooling to rt, the reaction was quenched by adding 3 mol dm^{-3} hydrochloric acid. The resulting mixture was extracted with chloroform three times. The combined organic layer was washed with water and sat. brine, and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using hexane–chloroform (4:1) as an eluent, to give colorless powder. The powder was recrystallized from chloroform to give $\mathbf{1_{C2}}$ as colorless needle crystals (15.3 mg, 10%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.41 (6H, t, $J = 7.0$ Hz), 1.93 (18H, br s), 4.03 (4H, q, $J = 7.1$ Hz), 6.87 (4H, d(AA′BB′), $J = 9.0$ Hz), 7.32 (4H, d(AA′BB′), $J = 9.0$ Hz). IR (ATR, neat): ν/cm^{-1} 3081 (w), 3031 (w), 2952 (m), 2914 (m), 2882 (m), 2848 (m), 1509 (m), 1458 (m), 1439 (m), 1404 (w), 1349 (w), 1302 (w), 1286 (w), 1269 (w), 1253 (w), 1114 (w), 1075 (m), 1049 (m), 1017 (w), 985 (m), 965 (w), 830 (s), 798 (m), 727 (w), 551 (s). LRMS (EI, 70 eV): *m*/*z*, 429 ($(M + 1)^+$, 57), 428 (M^+, 100), 400 (6), 186 (9). Found: *m*/*z* 428.27549. Calcd for $C_{30}H_{36}O_2$: M, 428.27153.

General Procedures for the Synthesis of 4,9-Bis(4-alkoxyphenyl)diamantanes ($\mathbf{1_{C3}}$–$\mathbf{1_{C10}}$). Synthesis of 4,9-Bis(4-propyloxyphenyl)diamantane ($\mathbf{1_{C3}}$): To a mixture of 4,9-bis(4-iodophenyl)diamantane (**4**) (199.8 mg, 0.337 mmol), copper(I) iodide (29.1 mg, 0.153 mmol), 1,10-phenanthroline (anhydrous, 24.3 mg, 0.135 mmol), and cesium carbonate (449.1 mg, 1.38 mmol), was added 1-propanol (0.5 mL, 6.72 mmol) and toluene (2.0 mL), and the resulting mixture was refluxed for 38 h with vigorous stirring. After cooling to rt, chloroform was added. Insoluble material was filtered off and the solvent evaporated. The residue was purified by column chromatography on silica gel using hexane–chloroform (7:3) as an eluent, to give a colorless powder. The powder was recrystallized from chloroform–hexane to give $\mathbf{1_{C3}}$ as colorless plate crystals (67.9 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.03 (6H, t, $J = 7.4$ Hz), 1.80 (4H, sext, $J = 7.1$ Hz), 1.93 (18H, br s), 3.91 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 9.0$ Hz), 7.32 (4H, d(AA′BB′), $J = 9.0$ Hz). IR (ATR, neat): ν/cm^{-1} 3033 (w), 2910 (s), 2870 (s), 1607 (m), 1510 (s), 1465 (m), 1439 (w), 1378 (w), 1299 (m), 1252 (s), 1179 (s), 1119 (w), 1074 (w), 1039 (m), 1012 (w), 974 (w), 826 (m), 795 (m), 753 (w), 618 (m), 540 (m). LRMS (EI, 70 eV): *m*/*z*, 457 ($(M + 1)^+$, 60), 456 (M^+, 100), 414 (12), 372 (25), 186 (18). Found: *m*/*z* 456.29724. Calcd for $C_{32}H_{40}O_2$: M, 456.30283.

Synthesis of 4,9-Bis(4-butyloxyphenyl)diamantane ($\mathbf{1_{C4}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$, using 4,9-bis(4-iodophenyl)diamantane (**4**) (201.8 mg, 0.341 mmol), copper(I) iodide (29.1 mg, 0.153 mmol), 1,10-phenanthroline (anhydrous, 27.3 mg, 0.11 mmol), cesium carbonate (432.8 mg, 1.33 mmol), 1-butanol (1.5 mL, 16.4 mmol), and toluene (3 mL). The reflux time was 46 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (7:3) as an eluent and recrystallization from chloroform–hexane to give $\mathbf{1_{C4}}$ as colorless needle crystals (105.8 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.97 (6H, t, $J = 7.4$ Hz), 1.42–1.54 (4H, m), 1.71–1.81 (4H, m), 1.93 (18H, br s), 3.95 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.32 (4H, d(AA′BB′), $J = 8.9$ Hz). IR (ATR, neat): ν/cm^{-1} 3033 (w), 2910 (s), 2871 (s), 1607 (m), 1465 (s), 1378 (m), 1299 (w), 1252 (s), 1179 (m), 1119 (w), 1074 (m), 1039 (w), 1012 (m), 974 (m), 826 (m), 795 (m), 757 (w), 618 (w), 540 (m). LRMS (EI, 70 eV): *m*/*z*, 485 ($(M + 1)^+$, 59), 484 (M^+, 100), 428 (12), 372 (25), 186 (18). Found: *m*/*z* 484.33124. Calcd for $C_{34}H_{44}O_2$: M, 484.33413.

Synthesis of 4,9-Bis(4-pentyloxyphenyl)diamantane ($\mathbf{1_{C5}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$ using 4,9-bis(4-iodophenyl)diamantane (**4**) (192.4 mg, 0.325 mmol), copper(I) iodide (26.3 mg, 0.138 mmol), 1,10-phenanthroline (anhydrous, 24.9 mg, 0.138 mmol), cesium carbonate (441.8 mg, 1.35 mmol), 1-pentanol (2.0 mL, 18.5 mmol), and toluene (2 mL). The reflux time was 43 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (7:3) as an eluent and recrystallization from chloroform–hexane to give $\mathbf{1_{C5}}$ as colorless needle crystals (129.1 mg, 61.2%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.93 (6H, t, $J = 7.1$ Hz), 1.31–1.49 (8H, m), 1.77 (4H, quint, $J = 6.6$ Hz), 1.93 (18H, br s), 3.94 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.32 (4H, d(AA′BB′), $J = 8.9$ Hz). IR (ATR, neat): ν/cm^{-1} 3046 (w), 3030 (w), 2952 (m), 2931 (s), 2907 (s), 2885 (s), 2867 (s), 1607 (m), 1577 (w), 1510 (s), 1474 (m), 1440 (w), 1394 (w), 1377 (w), 1351 (w), 1299 (w), 1252 (s), 1239 (s), 1184 (s), 1119 (w), 1051 (m), 1028 (m), 984 (w), 835 (m), 798 (w), 729 (w), 620 (m), 542 (m). LRMS (EI, 70 eV): *m*/*z*, 513 ($(M + 1)^+$, 62), 512 (M^+, 100), 442 (14), 372 (36), 186 (13). Found: *m*/*z* 512.36650. Calcd for $C_{36}H_{48}O_2$: M, 512.36543.

Synthesis of 4,9-Bis(4-hexyloxyphenyl)diamantane ($\mathbf{1_{C6}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$ using 4,9-bis(4-iodophenyl)diamantane (**4**) (166 mg, 0.28 mmol), copper(I) iodide (27.0 mg, 0.14 mmol), 1,10-phenanthroline (anhydrous, 19.4 mg, 0.11 mmol), cesium carbonate (368.5 mg, 1.13 mmol), 1-hexanol (0.3 mL, 2.38 mmol), and toluene (2 mL). The reflux time was 69 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (7:3) as an eluent and recrystallization from chloroform–hexane to give $\mathbf{1_{C6}}$ as colorless needle crystals (99.3 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.90 (6H, t, $J = 6.9$ Hz), 1.30–1.35 (8H, m), 1.41–1.47 (4H, m), 1.77 (4H, quint, $J = 6.8$ Hz), 1.93 (18H, br s), 3.94 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.32 (4H, d(AA′BB′), $J = 8.9$ Hz). IR (ATR, neat): ν/cm^{-1} 3033 (w), 2916 (s), 2879 (s), 2850 (s), 1607 (m), 1577 (w), 1509 (s), 1467 (m), 1393 (w), 1297 (w), 1250 (s), 1180 (s), 1118 (w), 1048 (w), 983 (w), 825 (s), 795 (m), 727 (w), 619 (w), 540 (m). LRMS (EI, 70 eV): *m*/*z*, 542 ($(M + 1)^+$, 62), 541 (M^+, 100), 456 (14), 372 (36), 186 (10). Found: *m*/*z* 540.39976. Calcd for $C_{38}H_{52}O_2$: M, 540.39673.

Synthesis of 4,9-Bis(4-heptyloxyphenyl)diamantane ($\mathbf{1_{C7}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$ using 4,9-bis(4-iodophenyl)diamantane (**4**) (102.1 mg, 0.172 mmol), copper(I) iodide (14.9 mg, 0.078 mmol), 1,10-phenanthroline (anhydrous, 14.6 mg, 0.081 mol), cesium carbonate (230.7 mg, 0.708 mmol), 1-heptanol (1.0 mL, 7.07 mmol), and toluene (5 mL). The reflux time was 38 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (3:2) as an eluent and recrystallization from methanol–chloroform to give $\mathbf{1_{C7}}$ as colorless plate crystals (55.1 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.89 (6H, t, $J = 6.5$ Hz), 1.28–1.48 (16H, m), 1.77 (4H, quint, $J = 6.6$ Hz), 1.93 (18H, br s), 3.94

(4H, t, $J = 6.6$ Hz), 6.87 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.31 (4H, d(AA′BB′), $J = 8.9$ Hz). IR (ATR, neat): ν/cm^{-1} 3097 (w), 3055 (w), 3036 (w), 2915 (s), 2884 (s), 2851 (s), 1610 (m), 1577 (w), 1510 (s), 1475 (m), 1467 (m), 1437 (w), 1390 (w), 1351 (w), 1300 (w), 1254 (s), 1237 (s), 1182 (s), 1115 (w), 1044 (w), 1022 (m), 984 (w), 825 (s), 796 (m), 726 (w), 620 (w), 542 (m). LRMS (EI, 70 eV): m/z, 570 ((M + 2)$^+$, 11), 569 ((M + 1)$^+$, 45), 568 (M$^+$, 100), 470 (16), 372 (42), 186 (10). Found: m/z 568.42758. Calcd for $C_{40}H_{56}O_2$: M, 568.42803.

Synthesis of 4,9-Bis(4-octyloxyphenyl)diamantane ($\mathbf{1_{C8}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$ using 4,9-bis(4-iodophenyl)diamantane (**4**) (203.5 mg, 0.344 mmol), copper(I) iodide (28.5 mg, 0.149 mmol), 1,10-phenanthroline (anhydrous, 26.0 mg, 0.144 mmol), cesium carbonate (456.2 mg, 1.40 mmol), 1-octanol (0.5 mL, 3.17 mmol), and toluene (3 mL). The reflux time was 69 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (3:1) as an eluent and recrystallization from chloroform–hexane to give $\mathbf{1_{C8}}$ as colorless needle crystals (104.4 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.89 (6H, t, $J = 7.4$ Hz), 1.29–1.48 (20H, m), 1.77 (4H, quint, $J = 6.4$ Hz), 1.93 (18H, br s), 3.94 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 9.0$ Hz), 7.31 (4H, d(AA′BB′), $J = 9.0$ Hz). IR (ATR, neat): ν/cm^{-1} 3041 (w), 2952 (m), 2918 (s), 2887 (s), 2848 (s), 1608 (m), 1577 (w), 1475 (m), 1439 (w), 1392 (w), 1306 (m), 1294 (m), 1251 (s), 1240 (s), 1181 (s), 1117 (m), 1047 (s), 1025 (s), 1014 (m), 1003 (w), 984 (w), 828 (s), 796 (m), 757 (w), 725 (m), 541 (s). LRMS (EI, 70 eV): m/z, 598 ((M + 1)$^+$, 73), 597 (M$^+$, 100), 484 (14), 372 (33), 186 (7.5). Found: m/z 596.45637. Calcd for $C_{42}H_{60}O_2$: M, 596.45933.

Synthesis of 4,9-Bis(4-nonyloxyphenyl)diamantane ($\mathbf{1_{C9}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$ using 4,9-bis(4-iodophenyl)diamantane (**4**) (200.7 mg, 0.339 mmol), copper(I) iodide (29.4 mg, 0.154 mmol), 1,10-phenanthroline (anhydrous, 29.9 mg, 0.166 mmol), cesium carbonate (436.2 mg, 1.33 mmol), 1-nonanol (1.5 mL, 8.60 mmol), and toluene (4.5 mL). The reflux time was 44 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (7:3) as an eluent and recrystallization from methanol–chloroform to give $\mathbf{1_{C8}}$ as a colorless powder (124.9 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.88 (6H, t, $J = 6.8$ Hz), 1.23–1.48 (24H, m), 1.72–1.88 (4H, m), 1.93 (18H, br s), 3.94 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 9.6$ Hz), 7.31 (4H, d(AA′BB′), $J = 9.6$ Hz). IR (ATR, neat): ν/cm^{-1} 3097 (w), 3056 (w), 3034 (w), 2919 (s), 2883 (s), 2851 (s), 1611 (m), 1578 (w), 1510 (s), 1468 (m), 1437 (w), 1390 (w), 1300 (w), 1254 (s), 1237 (s), 1180 (s), 1114 (w), 1041 (w), 984 (w), 824 (s), 797 (m), 725 (w), 621 (w), 542 (m). LRMS (EI, 70 eV): m/z, 626 ((M + 2)$^+$, 13), 625 ((M + 1)$^+$, 49), 624 (M$^+$, 100), 498 (12), 372 (32). Found: m/z 624.49016. Calcd for $C_{44}H_{64}O_2$: M, 624.49063.

Synthesis of 4,9-Bis(4-decyloxyphenyl)diamantane ($\mathbf{1_{C10}}$): This compound was prepared by following the procedures described for compound $\mathbf{1_{C3}}$ using 4,9-bis(4-iodophenyl)diamantane (**4**) (210.0 mg, 0.356 mmol), copper(I) iodide (31.7 mg, 0.166 mmol), 1,10-phenanthroline (anhydrous, 30.7 mg, 0.170 mmol), cesium carbonate (456.9 mg, 1.40 mmol), 1-decanol (0.5 mL, 3.17 mmol), and toluene (3 mL). The reflux time was 57 h. The crude product was purified by column chromatography on silica gel using hexane–chloroform (7:3) as an eluent, followed by recrystallization from chloroform–hexane to give $\mathbf{1_{C10}}$ as colorless needle crystals (119.5 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.88 (6H, t, $J = 6.0$ Hz), 1.27–1.48 (28H, m), 1.77 (4H, quint, $J = 6.8$ Hz), 1.93 (18H, br s), 3.94 (4H, t, $J = 6.5$ Hz), 6.87 (4H, d(AA′BB′), $J = 9.0$ Hz), 7.31 (4H, d(AA′BB′), $J = 9.0$ Hz). IR (ATR, neat): ν/cm^{-1} 3057 (w), 2953 (m), 2919 (s), 2885 (s), 2870 (s), 2850 (s), 1611 (m), 1578 (w), 1510 (s), 1469 (m), 1439 (w), 1390 (w), 1301 (m), 1254 (s), 1236 (s), 1180 (s), 1114 (w), 1031 (m), 985 (w), 835 (m), 796 (m), 723 (w), 621 (w), 542 (m). LRMS (EI, 70 eV): m/z, 655 ((M + 2)$^+$, 46), 654 ((M + 1)$^+$, 62), 653 (M$^+$, 100), 513 (19), 372 (40). Found: m/z 652.52186. Calcd for $C_{46}H_{68}O_2$: M, 652.52193.

Synthesis of 4,9-Bis(4-hydroxyphenyl)diamantane (5). To a solution of 4,9-bis(4-pentyloxyphenyl)diamantane ($\mathbf{1_{C5}}$) (60.2 mg, 0.117 mmol) in dry dichloromethane (5 mL) under nitrogen atmosphere at 0 °C was added 1.0 mol dm^{-3} boron tribromide dichloromethane solution (0.25 mL, 0.25 mmol), and the resulting mixture was warmed up to rt. After stirring for 13.5 h, water was added and the resulting mixture was extracted with ethyl acetate three times. The combined organic layer was washed with sat. brine, and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using hexane–ethyl acetate (4:1) and then (3:2) as the eluent, to give a colorless powder. The powder was purified by reprecipitation from hexane–ethyl acetate to give **5** as a colorless powder (36.4 mg, 84%). Mp 355.0–356.0 °C, ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.93 (12H, br s), 1.95 (6H, br s), 6.78 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.25 (4H, d(AA′BB′), $J = 8.9$ Hz), 8.10 (2H, s). IR (ATR, neat): ν/cm^{-1} 3595 (s), 3380 (br s), 3251 (br s), 3023 (m), 2910 (s), 2883 (s), 2847 (m), 1613 (m), 1596 (m), 1513 (s), 1452 (m), 1378 (m), 1247 (s), 1181 (m), 1048 (w), 1013 (w), 986 (w), 826 (m), 797 (m), 581 (m), 537 (m). LRMS (EI, 70 eV): m/z, 373 ((M + 1)$^+$, 31), 372 (M$^+$, 100), 186 (8). Found: m/z 372.20766. Calcd for $C_{26}H_{28}O_2$: M, 372.20893.

Synthesis of 4,9-Bis(4-hexanoyloxyphenyl)diamantane ($\mathbf{2_{C6}}$). To a suspension of 4,9-bis(4-hydroxyphenyl)diamantane (**5**) (27.8 mg, 0.746 mmol) in dry THF (3 mL) and dry pyridine (0.5 mL) under nitrogen atmosphere was added hexanoyl chloride (0.05 mL, 0.36 mmol) at 0 °C. The resulting suspension was warmed up to rt and stirred for 3 h. To it was added dry THF (8 mL) and dry pyridine (3.5 mL) and the resulting mixture was refluxed for 5 h. After cooling to rt, water was added and the solvent evaporated. To the residue was added chloroform and the organic layer was separated. The organic layer was washed with water and sat. brine, and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using hexane–chloroform (19:1) as an eluent, to give a colorless powder. The powder was recrystallized from chloroform–methanol to give $\mathbf{2_{C6}}$ as colorless needle crystals (17.7 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.93 (6H, t, $J = 7.0$ Hz), 1.37–1.42 (8H, m), 1.73–1.81 (4H, m), 1.95 (18H, br s), 2.55 (4H, t,

$J = 7.3$ Hz), 7.03 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.40 (4H, d(AA′BB′), $J = 8.7$ Hz). IR (ATR, neat): ν/cm^{-1} 3036 (w), 2954 (m), 2910 (s), 2880 (s), 2870 (s), 2849 (s), 1753 (s), 1505 (m), 1460 (w), 1439 (w), 1415 (w), 1376 (w), 1317 (w), 1247 (w), 1205 (m), 1169 (m), 1141 (m), 1109 (m), 1074 (w), 1014 (w), 984 (w), 837 (m), 796 (w), 540 (w). LRMS (EI, 70 eV): m/z, 568 (M$^+$, 3), 470 (18), 372 (100). Found: m/z 568.35230. Calcd for $C_{38}H_{48}O_4$: M, 568.35526.

Synthesis of 1,3-Bis(4-hexyloxyphenyl)adamantane ($\mathbf{6_{C6}}$). To a suspension of sodium hydride (abt. 60% in oil, 29.6 mg, 0.722 mmol) and dry DMF (2.5 mL) was added dry DMF solution (1 mL) of 1,3-bis(4-hydroxyphenyl)adamantane (88.4 mg, 0.276 mmol) under nitrogen atmosphere at 0 °C, and the resulting solution was stirred for 30 min at this temperature. To this suspension was added 1-bromohexane (0.11 mL, 0.786 mmol) and the resulting mixture was warmed up to rt. After stirring for 12 h, the reaction temperature was raised to 50 °C and stirred for 3 h then to 70 °C and stirred for 2 h. After cooling to rt, water was added and the resulting mixture was extracted with chloroform for three times. The combined organic layer was washed with water and sat. brine, and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using hexane–ethyl acetate (19:1) as an eluent, to give $\mathbf{6_{C6}}$ as a colorless powder (98.3 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.89 (6H, t, $J = 7.0$ Hz), 1.33 (8H, m), 1.44 (4H, m), 1.76 (6H, m), 1.90 (4H, br s), 1.91 (4H, br s), 1.98 (2H, br s), 2.28 (2H, br s), 3.93 (4H, t, $J = 6.6$ Hz), 6.85 (4H, d(AA′BB′), $J = 8.9$ Hz), 7.29 (4H, d(AA′BB′), $J = 8.9$ Hz). IR (ATR, neat): ν/cm^{-1} 3051 (w), 3038 (w), 2934 (s), 2925 (s), 2917 (s), 2850 (s), 1607 (m), 1577 (w), 1510 (s), 1473 (m), 1451 (w), 1392 (w), 1292 (w), 1245 (s), 1182 (s), 1127 (w), 1111 (w), 1058 (w), 1026 (m), 1007 (w), 995 (w), 825 (m), 802 (m), 730 (w), 612 (w), 551 (m). LRMS (EI, 70 eV): m/z, 489 ((M + 1)$^+$, 54), 488 (M$^+$, 100), 404 (14), 320 (3.3). Found: m/z 488.36898. Calcd for $C_{34}H_{48}O_2$: M, 488.36543.

Supporting Information

DSC charts and polarized microscopic textures of $\mathbf{1_{C1}}$, $\mathbf{1_{C3}}$, $\mathbf{1_{C5}}$, $\mathbf{1_{C7}}$, $\mathbf{1_{C9}}$, and $\mathbf{6_{C6}}$. This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

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