Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Hiroko Yamanishi [a] , Ikuyoshi Tomita [a] , Kazuchika Ohta [b] & Takeshi Endo [a c]

[a] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, and Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda, Midoriku, Yokohama, 226-8502, Japan

[b] Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, 386-8567, Japan

[c] Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata, 992-8510, Japan

Version of record first published: 24 Sep 2006

To cite this article: Hiroko Yamanishi, Ikuyoshi Tomita, Kazuchika Ohta & Takeshi Endo (2001): Solid Dimorphism of Tetra-Arylcyclobutadienecobalt Derivatives Bearing Long Aliphatic Lateral Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 369:1, 47-61

To link to this article: http://dx.doi.org/10.1080/10587250108030008

Mol. Cryst. Liq. Cryst., Vol. 369, pp. 47-61
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Solid Dimorphism of Tetra-Arylcyclobutadienecobalt Derivatives Bearing Long Aliphatic Lateral Groups

HIROKO YAMANISHI[a], IKUYOSHI TOMITA[a*], KAZUCHIKA OHTA[b] and TAKESHI ENDO[a*†]

[a]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, and Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda, Midoriku, Yokohama 226–8502, Japan and* [b]*Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, 386–8567, Japan*

(Received November 02, 2000; In final form January 12, 2001)

A new series of disk-like cyclobutadienecobalt derivatives symmetrically substituted by lateral alkoxy groups with different chain lengths (-$O(CH_2)_nCH_3$, n=5, 6, 8, and 12) were prepared and their thermal phase transition behavior was studied in detail by optical measurements using crossed polarizers and differential scanning calorimetry (DSC). These cyclobutadienecobalt derivatives revealed dimorphism: two types of crystals K_1 and K_2 (crystals with lower and higher m.p., respectively) were observed. The thermal transition mechanisms (melt-mediated crystallization) could be clearly observed. The melting points of both K_1 and K_2 became lower as the number of the carbon atoms in the alkoxy chain increased.

Keywords: dimorphism; phase transition; cyclobutadienecobalt; metallocene

1. INTRODUCTION

The disk-like planar transition metal complexes (e.g., β-diketonate complexes[1] and phthalocyanine or porphyrin derivatives[2]) substituted by long alkyl or alkoxy chains have been reported to reveal solid polymorphism and mesomorphism. The metal-containing liquid crystalline materials (e.g., discotic or calam-

* Correspondence author. Tel: 045–924–5413; Fax: 045–924–5489; e-mail: tomita@echem.titech.ac.jp

† Present Address: Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4–3–16 Jonan, Yonezawa, Yamagata, 992–8510, Japan

itic planar liquid crystals) have been paid much attention to because they potentially serve as processable materials with advanced properties such as electronic charge migration and chromism. With an expectation to realize novel redox-active liquid crystals, non-planar sandwich transition metal complexes such as ferrocene derivatives substituted by long alkoxy chains have also been reported to show the mesomorphism.[3] However, none of these examples is based on the disk-like molecular design.

Recently, mesomorphic properties of novel organocobalt polymers having (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt moieties substituted with alkoxy chains have been reported by us and independently by Buntz et al.[4,5] Since the repeating units of the organocobalt polymers, (η^5-cyclopentadienyl)(1,2,3,4-tetra-aryl-η^4-cyclobutadiene)cobalt moieties, have two-dimensional disk-like 1,2,3,4-tetra-aryl-η^4-cyclobutadiene ligands and rather small three-dimensional (η^5-cyclopentadienyl)cobalt moieties, these monomeric units might exhibit unique thermal transition behavior by appropriate design of lateral soft substituents. On realizing discotic metallocenes, it is expected to obtain novel liquid crystalline materials possessing unique properties that originate from metallocene units.

In this paper, we describe the design and synthesis of a new series of disk-like tetra-arylcyclobutadienecobalt derivatives substituted by long alkoxy chains to explore the possibility of a new type of mesomorphic-transition metal complexes. Thermal properties of these derivatives were investigated in detail by microscopic observation and differential scanning calorimetry (DSC).

2. EXPERIMENTAL

2–1 Materials and instruments

Trimethylsilylacetylene,[6] acetylene derivatives (**3a-d**, **4a-d**),[7] and (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**)[8] were prepared according to the literature procedures. Tetrahydrofuran (THF) and toluene were dried over sodium and distilled under nitrogen before use. All the other reagents were used as received. The purification of products was carried out on a JAI LC-908 recycling preparative high-performance liquid chromatography (HPLC) using THF as the eluent (JAIGEL-1H and JAIGEL-2H). ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-EX400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ (tetramethylsilane as an internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer, both in neat samples and KBr

disks. Differential scanning calorimetry (DSC) analyses were carried out on a Shimadzu DSC-60 at scanning rates of 0.5–40 °C/min. Polarizing microscopic observations were performed on an Olympus BX50 microscope equipped with a Mettler FP82 hot stage.

2–2 Synthesis

1-n-Alkoxy-4-iodobenzenes (2a-2d) (Typical Procedure for 1-n-Pentyloxy-4-iodobenzene (2a, n=5)). p-Iodophenol (10.0 g, 45.5)

mmol), 1-bromopentane (6.73 g, 44.6 mmol), K_2CO_3 (18.5 g, 134 mmol), and DMF (100 ml) were placed in a one-neck 300 ml flask equipped with a reflux condenser and a magnetic stir bar. The mixture was kept stirring at 110–120 °C for 12 h, and was poured into aqueous NaOH (1 M, 1200 ml). The resulting suspension was stirred for 30 min and was extracted four times with *n*-hexane (total 400 ml). After drying over Na_2SO_4 and reducing the volume, the organic phase was purified by column chromatography (SiO_2, *n*-hexane, Rf= 0.58). The final product was isolated as a pale-yellow viscous liquid. Yield: 11.3 g (87 %). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, 3H, -CH_3, J = 7.0 Hz), 1.32–1.48 (m, 4H, -CH_2-), 1.77 (m, 2H, -O-$CH_2\underline{CH_2}$-), 3.91 (t, 2H, -OCH_2-, J = 6.6 Hz), 6.66, 6.68, 7.52, 7.55 (4H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.00 (-CH_3), 22.41, 28.10, 28.79 (-CH_2-), 68.06 (-OCH_2-), 82.36, 116.89, 138.10, 158.97 (-C_6H_4-) ppm; IR (neat, cm^{-1}) 2955, 2870 (C-H, aliphatic), 1588, 1487 (C=C), 1244 (C-O), 818 (=C-H, out-of-plane).

1-n-Hexyloxy-4-iodobenzene (2b, n=6)

93 % yield (pale-yellow viscous liquid); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, 3H, -CH_3, J = 7.2 Hz), 1.27–1.49 (m, 6H, -CH_2-), 1.76 (m, 2H, -O-$CH_2\underline{CH_2}$-), 3.91 (t, 2H, -OCH_2-, J = 6.6 Hz), 6.66, 6.68, 7.52, 7.55 (4H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.02 (-CH_3), 22.54, 25.61, 29.07, 31.52 (-CH_2-), 68.04 (-OCH_2-), 82.34, 116.85, 138.08, 158.95 (-C_6H_4-) ppm; IR (neat, cm^{-1}) 2930, 2870 (C-H, aliphatic), 1586, 1485 (C=C), 1244 (C-O), 818 (=C-H, out-of-plane).

1-n-Octyloxy-4-iodobenzene (2c, n=8)

97 % yield (pale-yellow viscous liquid); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 3H,-CH_3, J = 6.8 Hz), 1.22–1.49 (m, 10H, -CH_2-), 1.76 (m, 2H, -O-$CH_2\underline{CH_2}$-), 3.90 (t, 2H, -OCH_2-, J = 6.6 Hz), 6.66, 6.68, 7.52, 7.54 (4H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.11 (-CH_3), 22.63, 25.98, 29.12, 29.20, 29.32, 31.77 (-CH_2-), 68.06 (-OCH_2-), 82.36, 116.89, 138.10, 158.97 (-C_6H_4-) ppm; IR

(neat, cm^{-1}) 2926, 2855 (C-H, aliphatic), 1588, 1487 (C=C), 1244 (C-O), 820 (=C-H, out-of-plane).

1-n-Dodecyloxy-4-iodobenzene (2d, n=12)

98 % yield (white solid); mp 36.3–36.4 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 3H, $-CH_3$, $J = 6.8$ Hz), 1.21–1.48 (m, 18H, $-CH_2-$), 1.76 (m, 2H, $-O-CH_2C\underline{H}_2-$), 3.91 (t, 2H, $-OCH_2-$, $J = 6.6$ Hz), 6.66, 6.68, 7.53, 7.55 (4H, $-C_6H_4-$) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.11 ($-CH_3$), 22.69, 25.96, 29.12, 29.34, 29.54, 29.62, 31.90 ($-CH_2-$), 68.09 ($-OCH_2-$), 82.36, 116.89, 138.12, 158.99 ($-C_6H_4-$) ppm; IR (KBr, cm^{-1}) 2924, 2852 (C-H, aliphatic), 1588, 1487 (C=C), 1244 (C-O), 818 (=C-H, out-of-plane).

(4-n-Alkoxyphenyl)acetylenes (3a-3d) (Typical Procedure for (4-n-Pentyloxyphenyl)acetylene (3a, n=5))

The compound (**3a**) was prepared by modification of the method described by Sonogashira et al.,[7] as follows: **2a** (n=5, 5.00 g, 17.2 mmol), $PdCl_2$ (15.3 mg, 86.2×10^{-3} mmol), CuI (16.4 mg, 86.2×10^{-3} mmol), PPh_3 (45.2 mg, 172×10^{-3} mmol), and diethylamine (50.0 ml) were placed into a two-neck 200 ml flask equipped with a reflux condenser and a magnetic stir bar under nitrogen. The mixture was stirred at 50–55 °C for 1 h, and then cooled to 30 °C. To the resulting mixture, trimethylsilylacetylene (3.65 ml, 25.9 mmol) was added dropwise via a syringe and the reaction mixture was stirred at 50–55 °C for 12 h. After the removal of the solvent under reduced pressure, the residue was treated with 200 ml of diethyl ether, and the insoluble salts were removed by filtration. After reducing the volume of the filtrate, the product was isolated by column chromatography (SiO_2, diethyl ether:n-hexane=10:1, Rf= 0.77) as a pale-yellow viscous liquid. 1-(4-n-Pentyloxyphenyl)-2-trimethylsilylacetylene thus obtained was subjected to desilylation by stirring with KOH (2.00 g, 35.6 mmol) in a mixed solvent of methanol (25.0 ml) and THF (50.0 ml) at room temperature for 12 h. After the removal of the solvent, n-hexane was added and the n-hexane solution was washed with water. After drying over $MgSO_4$ and reducing the volume, the organic phase was purified by column chromatography (SiO_2, n-hexane:toluene=3:1, Rf= 0.56). The product (**3a**) was isolated as a pale-yellow viscous liquid. Yield: 3.07 g (95 %); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.97 (t, 3H, $-CH_3$, $J = 7.2$ Hz), 1.36–1.51 (m, 4H, $-CH_2-$), 1.82 (m, 2H, $-O-CH_2C\underline{H}_2-$), 3.02 (s, 1H, $-C\equiv CH$), 3.98 (t, 2H,$-OCH_2-$, $J = 6.6$ Hz), 6.85, 6.87, 7.44, 7.46 (4H, $-C_6H_4-$) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 13.94 ($-CH_3$), 22.39, 28.08, 28.79 ($-CH_2-$), 67.93 ($-OCH_2-$), 75.63 ($-C\equiv\underline{C}H$), 83.69 ($-\underline{C}\equiv CH$), 113.81, 114.34, 133.46, 159.46 ($-C_6H_4-$) ppm; IR (neat, cm^{-1}) 3316, 3293 (≡CH), 2934, 2872

(C-H, aliphatic), 2106 (C≡C), 1607, 1507 (C=C), 1248 (C-O), 831 (=C-H, out-of-plane).

(4-n-Hexyloxyphenyl)acetylene (3b, n=6)

83 % yield (pale-yellow viscous liquid); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, 3H, -CH_3, J = 6.6 Hz), 1.25–1.56 (m, 6H, -CH_2-), 1.77 (m, 2H, -O-$CH_2C\underline{H}_2$-), 2.98 (s, 1H, -C≡CH), 3.94 (t, 2H, -OCH_2-, J = 6.6 Hz), 6.81, 6.83, 7.40, 7.42 (4H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 13.98 (-CH_3), 22.56, 25.65, 29.09, 31.52 (-CH_2-), 67.98 (-OCH_2-), 75.63 (-C≡$\underline{C}$H), 83.73 (-$\underline{C}$≡CH), 113.83, 114.38, 133.49, 159.50 (-C_6H_4-) ppm; IR (neat, cm^{-1}) 3315, 3293 (≡CH), 2932, 2870 (C-H, aliphatic), 2108 (C≡C), 1607, 1507 (C=C), 1248 (C-O), 833 (=C-H, out-of-plane).

(4-n-Octyloxyphenyl)acetylene (3c, n=8)

95 % yield (pale-yellow viscous liquid); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 3H, -CH_3, J = 6.6 Hz), 1.22–1.48 (m, 6H, -CH_2-), 1.76 (m, 2H, -O-$CH_2C\underline{H}_2$-), 2.98 (s, 1H, -C≡CH), 3.93 (t, 2H, -OCH_2, J = 6.6 Hz), 6.80, 6.82, 7.39, 7.42 (4H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.03 (-CH_3), 22.61, 25.96, 29.12, 29.20, 29.31, 31.77 (-CH_2-), 67.95 (-OCH_2-), 75.61 (-C≡$\underline{C}$H), 83.69 (-$\underline{C}$≡CH), 113.85, 114.34, 133.46, 159.46 (-C_6H_4-) ppm; IR (neat, cm^{-1}) 3318, 3295 (≡CH), 2928, 2857 (C-H, aliphatic), 2108 (C≡C), 1607, 1507 (C=C), 1248 (C-O), 831 (=C-H, out-of-plane).

(4-n-Dodecyloxyphenyl)acetylene (3d, n=12)

95 % yield (pale-yellow solid); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 3H, -CH_3, J = 6.8 Hz), 1.26–1.44 (m, 18H, -CH_2-), 1.78 (m, 2H, -O-$CH_2C\underline{H}_2$-), 3.00 (s, 1H, -C≡CH), 3.95 (t, 2H, -OCH_2, J = 6.6 Hz), 6.82, 6.84, 7.40, 7.42 (4H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.11 (-CH_3), 22.69, 25.98, 29.14, 29.36, 29.54, 29.58, 29.62, 31.90 (-CH_2-), 68.04 (-OCH_2-), 75.61 (-C≡$\underline{C}$H), 83.75 (-$\underline{C}$≡CH), 113.83, 114.42, 133.53, 159.52 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 3318, 3293 (≡CH), 2922, 2853 (C-H, aliphatic), 2108 (C≡C), 1607, 1508 (C=C), 1250 (C-O), 831 (=C-H, out-of-plane).

1,2-Bis(4-n-alkoxyphenyl)acetylene (4a-4d) (Typical Procedure for 1,2-Bis(4-n-pentyloxyphenyl)acetylene (4a, n=5))

4-Iodo-1-*n*-pentyloxybenzene (**2a**, *n*=5, 4.28 g, 14.8 mmol), $PdCl_2$ (13.1 mg, 73.8 × 10^{-3} mmol), CuI (14.1 mg, 73.8 × 10^{-3} mmol), PPh_3 (38.7 mg, 0.148 mmol) and diethylamine (25.0 ml) were placed into a two-neck 200 ml flask equipped with a reflux condenser and a magnetic stir bar under nitrogen. The

mixture was stirred at 50–55 °C for 1 h, which was then cooled to 30 °C. To this solution, **3a** (n=5, 2.53 g, 13.4 mmol) in 20.0 ml of diethylamine was added via a syringe and the reaction mixture was stirred at 50–55 °C for 12 h. After removal of the solvent, the residue was treated with 200 ml of chloroform, and the insoluble salts were removed by filtration. After reducing the volume of the filtrate, the final product was isolated by column chromatography (SiO_2, n-hexane:chloroform=4:1, Rf= 0.57). The resulting yellow powder was further purified by recrystallization from diethyl ether to give colorless crystals. Yield: 70 % (3.31 g, 9.45 mmol); $T_{K1\text{-}K2}$ 55.8 °C, T_m 107.2–107.3 °C (lit. T_m 106.5 °C)[9]; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.94 (t, 6H, -CH_3, J = 7.2 Hz), 1.33–1.49 (m, 8H, -CH_2-), 1.79 (m, 4H, -O-$CH_2C\underline{H}_2$-), 3.96 (t, 4H, -OCH_2-, J = 6.6 Hz), 6.84, 6.86, 7.42, 7.44 (8H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.00 (-CH_3), 22.43, 28.15, 28.88 (-CH_2-), 68.00 (-OCH_2-), 87.92 (-C≡C-), 114.45, 115.46, 132.80, 158.93 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 2930, 2857 (C-H, aliphatic), 1604, 1516 (C=C), 1244 (C-O), 831 (=C-H, out-of-plane).

1,2-Bis(4-n-hexyloxyphenyl)acetylene (4b, n=6)

69 % yield (colorless crystals); $T_{K1\text{-}K2}$ 85.7 °C, T_N 97.2–97.6 °C, T_C 104.0–104.4 °C (lit. $T_{K1\text{-}K2}$ 84 °C, T_N 96.5 °C, T_C 105 °C)[9]; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, 6H, -CH_3, J = 7.2 Hz), 1.29–1.51 (m, 12H, -CH_2-), 1.78 (m, 4H, -O-$CH_2C\underline{H}_2$-), 3.96 (t, 4H, -OCH_2-, J= 6.6 Hz), 6.84, 6.86, 7.42, 7.44 (8H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.02 (-CH_3), 22.58, 25.68, 29.16, 31.55 (-CH_2-), 68.04 (-OCH_2-), 87.92 (-C≡C-), 114.45, 115.46, 132.80, 158.93 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 2932, 2859 (C-H, aliphatic), 1609, 1516 (C=C), 1248 (C-O), 831 (=C-H, out-of-plane).

1,2-Bis(4-n-octyloxyphenyl)acetylene (4c, n=8)

76 % yield (colorless crystals); $T_{K1\text{-}K2}$ 71.9–72.1 °C, $T_{K2\text{-}K3}$ 77.8–77.9 °C, T_N 93.1–93.2 °C, T_C 101.6 °C (lit. T_1 72 °C, T_2 77 °C, T_N 92 °C, T_C 101.5 °C)[9]; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, 6H, -CH_3, J = 6.8 Hz), 1.23–1.57 (m, 20H, -CH_2-), 1.78 (m, 4H, -O-$CH_2C\underline{H}_2$-), 3.96 (t, 4H, -OCH_2-, J = 6.4 Hz), 6.84, 6.86, 7.42, 7.43 (8H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.09 (-CH_3), 22.65, 26.01, 29.20, 29.34, 31.79 (-CH_2-), 68.04 (-OCH_2-), 87.94 (-C≡C-), 114.45, 115.48, 132.80, 158.95 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 2922, 2857 (C-H, aliphatic), 1609, 1518 (C=C), 1250 (C-O), 839 (=C-H, out-of-plane).

1,2-Bis(4-n-dodecyloxyphenyl))acetylene (4d, n=12)

61 % yield (colorless crystals); $T_{K1\text{-}K2}$ 92.9–93.0 °C, T_N 93.8 °C, T_C 98.4–98.5°C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 6H, -CH_3, J = 6.8 Hz), 1.22–1.50

(m, 36H, -CH_2-), 1.78 (m, 4H, -O-$CH_2C\underline{H}_2$-), 3.96 (t, 4H, -OCH_2-, J = 6.6 Hz), 6.84, 6.86, 7.42, 7.43 (8H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.38 (-CH_3), 22.69, 26.01, 29.20, 29.34, 29.38, 29.56, 29.65, 31.92 (-CH_2-), 68.06 (-OCH_2-), 87.97 (-C≡C-), 114.47, 115.48, 132.82, 158.95 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 2920, 2851 (C-H, aliphatic), 1611, 1518 (C=C), 1252 (C-O), 839 (=C-H, out-of-plane).

Tetara-arylcyclobutadienecobalt Derivatives (5a-5d) (Typical Procedure for (η^5-Cyclopentadienyl))[η^4-1,2,3,4-tetra(4-n-pentyloxyphenyl)cyclobutadiene]cobalt (5a, n=5))

To a test tube containing **1** (1.13 g, 1.64 mmol) was added a toluene (15.0 ml) solution of **4a** (n=5, 1.00 g, 2.85 mmol) under nitrogen. The mixture was stirred at 53 °C for 12 h and then at 110 °C for 2 h. After filtration and reduction of the volume under vacuum, the product was isolated by column chromatography (SiO_2, n-hexane:diethyl ether=20:1, Rf= 0.63), HPLC, and recrystallization. Recrystallization was performed by the slow addition of THF to the mixture of the cyclobutadienecobalt derivative in boiling MeOH, until the cobalt complex dissolved completely. The solution was cooled rapidly to room temperature and the crystals formed were collected by filtration as yellow crystals. Yield: 0.56 g (48 %). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.94 (t, 12H, -CH_3, J = 6.8 Hz), 1.31–1.51 (m, 16H, -CH_2-), 1.80 (m, 8H, -O-$CH_2C\underline{H}_2$-), 3.95 (t, 8H, -OCH_2-, J = 6.2 Hz), 4.57 (s, 5H, C_5H_5), 6.73, 6.75, 7.34, 7.36 (16H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.03 (-CH_3), 22.48, 28.26, 29.05 (-CH_2-), 67.84 (-OCH_2-), 74.07 (C_4), 82.72 (C_5H_5), 113.87, 128.48, 129.82, 157.39 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 2930, 2868 (C-H, aliphatic), 1607, 1514 (C=C), 1242 (C-O), 833 (=C-H, out-of-plane); Anal. Found (Calcd, for $C_{53}H_{65}CoO_4$): C 77.16 % (77.16), H 7.85 % (7.94).

(η^5-Cyclopentadienyl)[η^4-1,2,3,4-tetra(4-n-hexyloxyphenyl) cyclobutadiene]cobalt (5b, n=6)

67 % yield (yellow crystals); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, 12H, -CH_3, J = 6.8 Hz), 1.23–1.53 (m, 24H, -CH_2-), 1.79 (m, 8H, -O-$CH_2C\underline{H}_2$-), 3.95 (t, 8H, -OCH_2-, J = 6.6 Hz), 4.57 (s, 5H, C_5H_5), 6.73, 6.75, 7.34, 7.36 (16H, -C_6H_4-) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.03 (-CH_3), 22.59, 25.78, 29.31, 31.59 (-CH_2-), 67.86 (-OCH_2-), 74.07 (C_4), 82.71 (C_5H_5), 113.87, 128.48, 129.80, 157.38 (-C_6H_4-) ppm; IR (KBr, cm^{-1}) 2928, 2859 (C-H, aliphatic), 1609, 1514 (C=C), 1242 (C-O), 833 (=C-H, out-of-plane); Anal. Found (Calcd, for $C_{57}H_{73}CoO_4$): C 77.87 % (77.70), H 8.38 % (8.35).

(η^5-Cyclopentadienyl)[η^4-1,2,3,4-tetra(4-n-octyloxyphenyl) cyclobutadiene]cobalt (5c, n=8)

43 % yield (dark yellow crystals); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, 12H, $-CH_3$, J = 6.8 Hz), 1.20–1.52 (m, 40H, $-CH_2-$), 1.79 (m, 8H, $-O-CH_2C\underline{H}_2-$), 3.95 (t, 8H, $-OCH_2-$, J = 6.6 Hz), 4.57 (s, 5H, C_5H_5), 6.73, 6.75, 7.34, 7.36 (16H, $-C_6H_4-$) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.11 ($-CH_3$), 22.67, 26.10, 29.25, 29.38, 31.83 ($-CH_2-$), 67.87 ($-OCH_2-$), 74.09 (C_4), 82.72 (C_5H_5), 113.89, 128.48, 129.82, 157.39 ($-C_6H_4-$) ppm; IR (KBr, cm^{-1}) 2924, 2855 (C-H, aliphatic), 1607, 1514 (C=C), 1244 (C-O), 831 (=C-H, out-of-plane); Anal. Found (Calcd, for $C_{65}H_{89}CoO_4$): C 78.70 % (78.59), H 8.98 % (9.03).

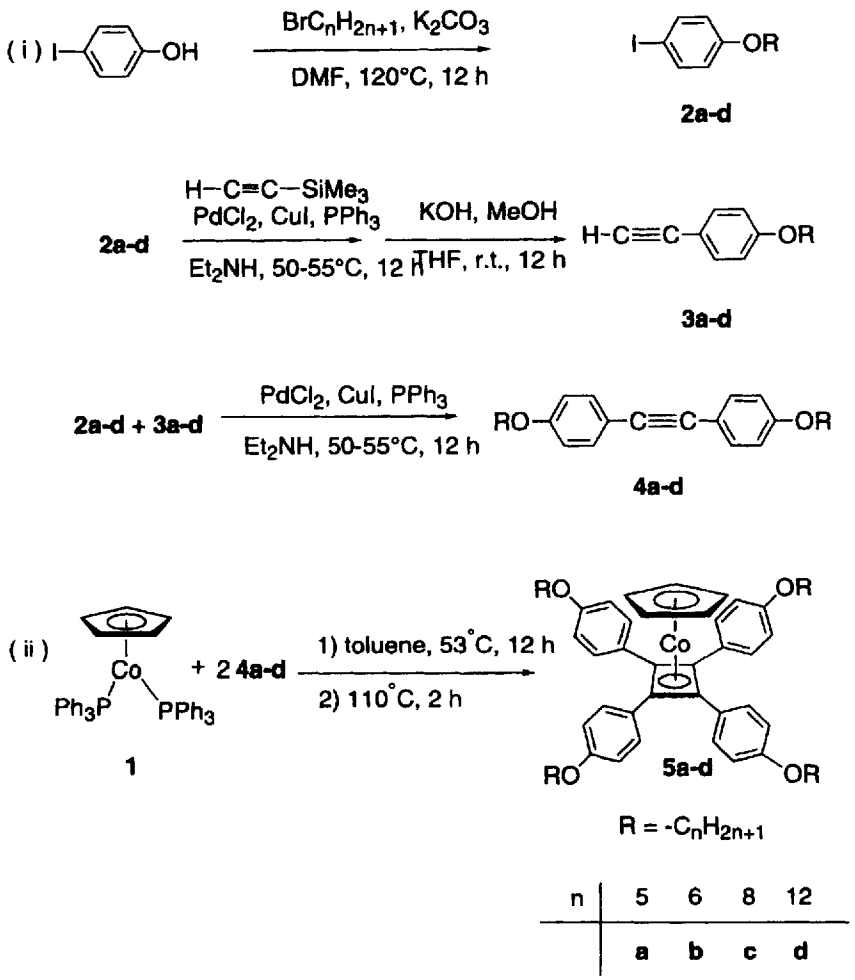
(η^5-Cyclopentadienyl)[η^4-1,2,3,4-tetra(4-n-dodecyloxyphenyl) cyclobutadiene]cobalt (5d, n=12)

38 % yield (dark yellow crystals); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, 12H,$-CH_3$, J = 6.8 Hz), 1.21–1.54 (m, 72H, $-CH_2-$), 1.79 (m, 8H, $-O-CH_2C\underline{H}_2-$), 3.94 (t, 8H, $-OCH_2-$, J = 6.6 Hz), 4.57 (s, 5H, C_5H_5), 6.72, 6.75, 7.34, 7.36 (16H, $-C_6H_4-$) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.11 ($-CH_3$), 22.69, 26.12, 29.34, 29.43, 29.60, 29.63, 29.67, 31.92 ($-CH_2-$), 67.86 ($-OCH_2-$), 74.07 (C_4), 82.72 (C_5H_5), 113.87, 128.48, 129.80, 157.39 ($-C_6H_4-$) ppm; IR (KBr, cm^{-1}) 2924, 2855 (C-H, aliphatic), 1607, 1514 (C=C), 1244 (C-O), 833 (=C-H, out-of-plane); Anal. Found (Calcd, for $C_{81}H_{121}CoO_4$): C 79.98 % (79.89), H 10.09 % (10.02).

3 RESULTS AND DISCUSSION

3–1 Synthesis

Starting from tolanes bearing alkoxy substituents ($RO-C_6H_4-C\equiv C-C_6H_4-OR$, **4a-4d**), symmetrically-substituted cyclobutadienecobalt derivatives (**5a-5d**) were prepared by cyclometallation followed by a rearrangement, as shown in Scheme 1. The purification of the cyclobutadienecobalt derivatives was carried out by column chromatography and HPLC. The products thus obtained are viscous liquids which hardly crystallize without solvents. On standing the viscous liquid at ambient temperature, crystallization takes place very slowly. However, the process was not reproducible. Thus, the recrystallization was performed from boiling THF/MeOH to obtain yellow or dark yellow colored crystals and the samples after recrystallization were used for the study of thermal transition behavior.



SCHEME 1 Synthetic procedure for cyclobutadienecobalt derivatives (**5a-d**)

3–2 Photomicrographs

The phase transition behavior of the cyclobutadienecobalt derivatives (**5a-5d**) was examined in detail by optical measurements using crossed polarizers. For example, the cyclobutadienecobalt derivative (**5a**) proves not to have mesomorphic properties but to show a solid dimorphism: K_1 and K_2 (m.p.= 127.0°C and 139.2°C, respectively). The K_1 crystals of **5a** with lower m.p. melt to the isotropic liquid at 129.0°C which turns to another more stable K_2 crystals with

higher m.p. from the isotopic liquid at that temperature. That is, melt-mediated crystallization could be clearly observed as follows. The crystals K_1 melted on standing above the m.p. of K_1 (Figure 1a-1b). Just after K_1 melted, plate-like crystals (K_2) started to form from the isotropic liquid phase (Figure 1c-1d). By raising the temperature to 139.2°C (above the m.p. of K_2), the formed K_2 crystals melted again to form an isotropic liquid.

Likewise, the crystals of **5b** and **5c** exhibit solid dimorphism. That is, these two complexes revealed melt-mediated crystallization, as confirmed by similar experiments. In the case of crystals of **5d** bearing longer aliphatic substituents, only one m.p. at 42.4–44.1°C (probably the K_2-I.L. phase transition) was observed when the sample was heated from room temperature to 45.0 °C.

3–3 DSC Thermograms

The dimorphic transition process of the cyclobutadienecobalt derivatives was confirmed further by DSC measurements. Figure 2 shows six DSC thermograms of **5a** taken under different heating rates (1.25, 2.50, 5.00, 10.0, 20.0, and 40.0°C/min), in part of which two endothermic peaks and one exothermic peak could be observed. At a heating rate of 2.5°C/min., for example, the endothermic peak (I), the exothermic peak (II), and the endothermic peak (III), attributable to the melting of K_1, recrystallization to K_2, and the melting of K_2, respectively, were clearly observed. The intensity of each peak is dependent upon the heating rate, where the slower rate decreased the intensity of the peak (I) and increased that of the peak (III). The decrease of the intensity of the peak (I) at the slow heating rate (1.25°C/min) might be due to the cancellation of the endothermic melting process of K_1 by the exothermic recrystallization to K_2. The relaxation process from K_1 to K_2 might also be a possible reason to decrease the intensity of the peak (I) at the slow heating rate, although this relaxation can not be observed in DSC. The melt-crystallization process requires time and, consequently, the intensities of the peaks (II) and (III) are also dependent upon the heating rate. All the cyclobutadienecobalt derivatives are apt to from a supercooled liquid (*vide supra*). Because the rates of recrystallization from I.L. is very slow, the cooling process did not exhibit any exothermic peaks attributable to recrystallization from I.L. even a slow at cooling rate (e.g., 2.5°C/min). On standing the isotropic liquid of **5a** obtained after DSC measurement at ambient temperature for rather long time (e.g., 2days), the sample often perfectly turns again to the crystalline form which is, however, not reproducible. Accordingly, the DSC study was performed only with the virgin samples.

On the other hand, the DSC measurements of **5b** and **5c** did not give clear information on the dimorphism, where only one broad endothermic peak was

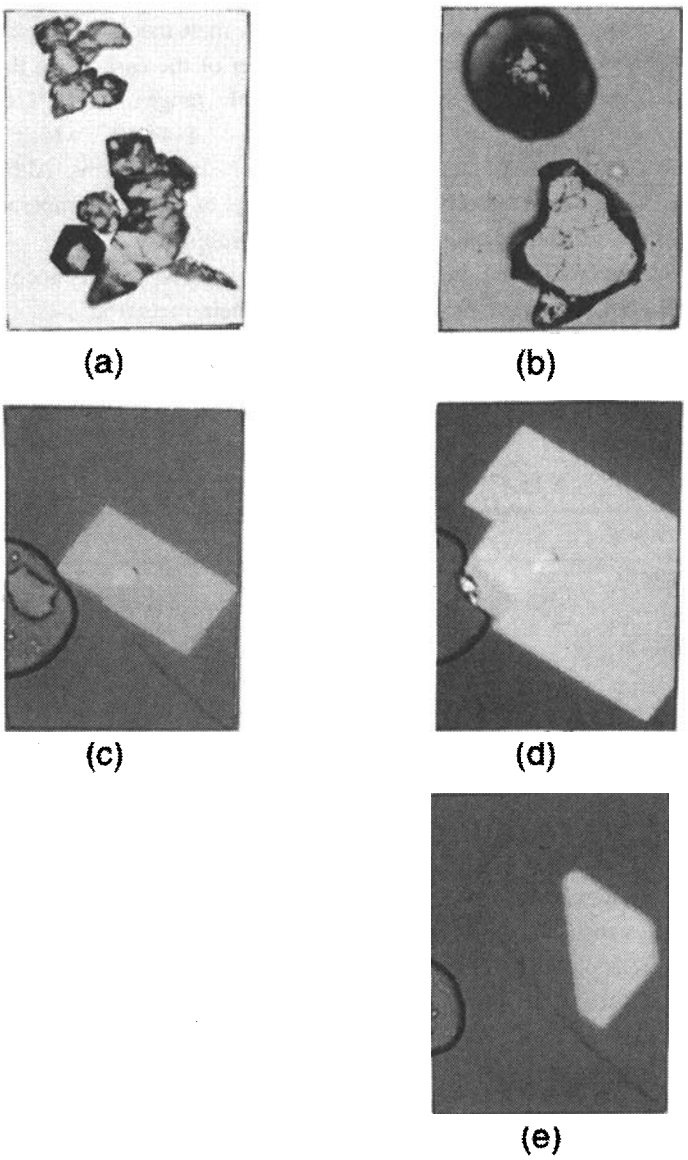
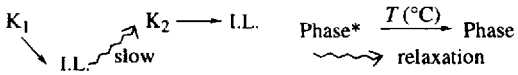


FIGURE 1 Photomicrographs of melt-mediated crystallization of **5a**. (a) Crystals (K_1) obtained by recrystallization were set on a plate at room temperature. (b) The sample was heated to 127.0°C from room temperature at a heating rate of 10°C /min and the crystals K_1 started to melt at 127.0°C (m.p. of K_1). (c) Plate-like crystals (K_2) were formed from the isotropic liquid after annealing at 129.0°C for 5 min. (d) By holding the temperature of the sample at 129.0°C for an additional 15 min., the plate-like crystals (K_2) in (c) grew bigger. (e) The sample in (d) was heated to 139.2°C (the K_2 crystals were melting) (See Color Plate I at the back of this issue)

observed even at a slow heating rate (1.25°C/min), probably because the m.p. of K_1 is very close to that of K_2 and because the melt-mediated crystallization requires a longer period by increasing the number of the carbons in the alkoxy chain. In the case of **5d**, the DSC measurement in the range of −50.0°C to 70.0°C showed two endothermic peaks at 7.5–8.0°C and 42.4–44.1°C, which might be attributed to the melting points of two different crystalline forms. Although the optical measurement of **5d** did not reveal the m.p. at a lower temperature, this result may indicate that **5d** also reveals solid dimorphism.

As summarized in Table I, the melting points of both K_1 and K_2 become lower as the number of the carbon atoms in the alkoxy chain increased.

TABLE I Phase transition temperatures (T) of cyclobutadienecobalt derivatives



Compound	$K_1 \rightarrow I.L.$	$K_2 \rightarrow I.L.$
5a (n=5)	126.8 – 127.0	139.2 – 139.4
5b (n=6)	109.0 – 110.0	127.3 – 128.6
5c (n=8)	70.3 – 73.7	79.7 – 79.8
5d (n=12)	*ca.* 7.5–8.0	42.4 – 44.1

* Phase nomenclature: K= crystal, I.L.= isotropic liquid.

Plausible free energy (F) vs. temperature (T) diagrams for the cyclobutadienecobalt complexes (**5a-5d**) that show melt-mediated crystallization are shown in Figure 3. That is, two cases of F-T diagrams can be taken into consideration: one is a monotropic relation between K_1 and K_2 where the free energy of K_1 is constantly higher than that of K_2 below their melting points (Figure 3a) and the other is an enantiotropic relation between K_1 and K_2 which involves the inversion of the free energies of K_1 and K_2 below their melting points (Figure 3b). In both cases, the melt-mediated transition may occur by the melting of K_1 followed by the crystallization to K_2. We believe that the plausible mechanism of Figure 3a works for the cyclobutadienecobalt derivatives (**5a-d**), because of the heating rate dependency,[10] as shown in Figure 2.

4 CONCLUSION

As a first attempt to prepare sandwich cyclobutadienecobalt derivatives exhibiting discotic mesomorphism, a new series of disk-like cyclobutadienecobalt

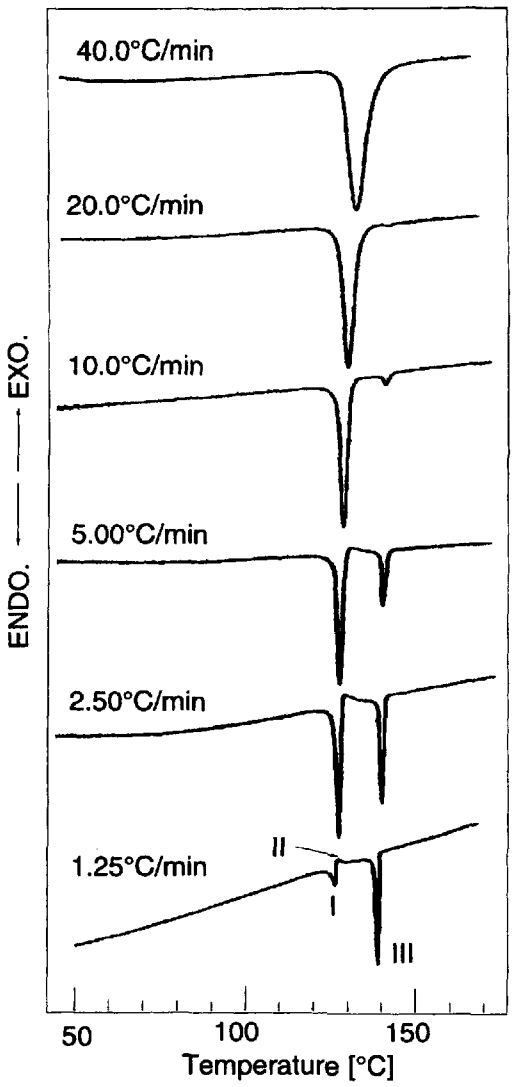


FIGURE 2 DSC thermograms of **5a** taken under various heating rates

derivatives symmetrically substituted by alkoxy groups ($-OC_nH_{2n+1}$) having different chain lengths (n=5, 6, 8, and 12) were prepared and their thermal transition behavior was investigated by means of microscopic observations and DSC measurements. It is unfortunate that all the cyclobutadienecobalt derivatives did not

show the mesophase but solid dimorphism: two kinds of crystalline forms K_1 and K_2 appeared depending upon the thermal history.

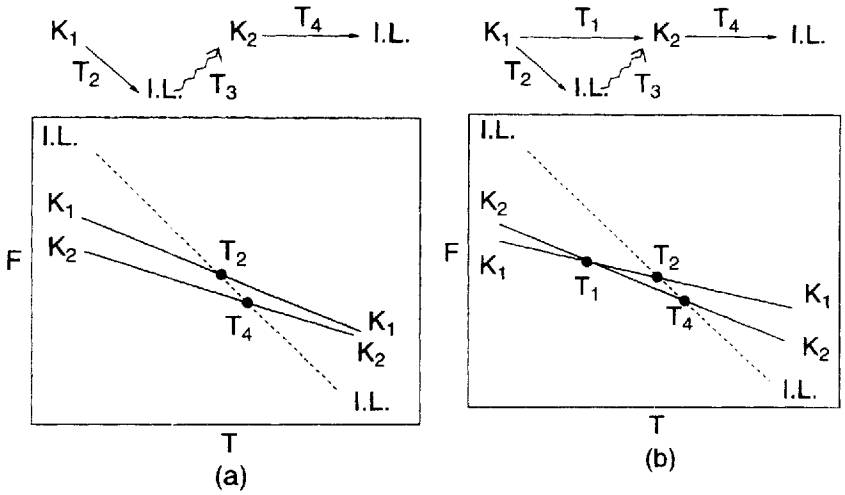


FIGURE 3 Schematic Free energy (F) vs. temperature (T) diagrams of the present system

Judging from preceding examples of thermal transition behavior of planar organometallic complexes[1], the appearance of dimorphism might mean that the appropriate design of the structure of the derivatives of cyclobutadienecobalt also potentially realizes novel liquid crystalline organometallic complexes. Further attempts by structural variations are now on-going to realize a new class of thermotropic mesogens.

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