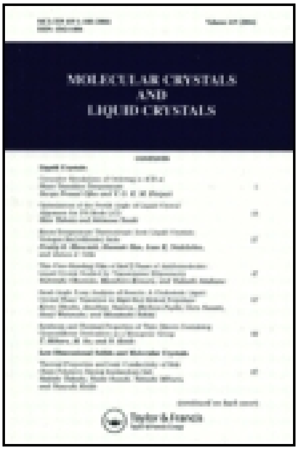

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Discotic Liquid Crystals of Transition Metal Complexes 8[1]: Enantiotropic Nematic Mesomorphism and Helical Formation of Bis[1(p-n-alkoxybiphenyl)-3-alkylpropane- 1,3-dionato]copper(II) Complexes

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To cite this article: K. Ohta , O. Takenaka , H. Hasebe , Y. Morizumi , T. Fajimoto & I. Yamamoto (1991): Discotic Liquid Crystals of Transition Metal Complexes 8[1]: Enantiotropic Nematic Mesomorphism and Helical Formation of Bis[1(p-n-alkoxybiphenyl)-3-alkylpropane- 1,3-dionato]copper(II) Complexes, Molecular Crystals and Liquid Crystals, 195:1, 123-133

To link to this article: http://dx.doi.org/10.1080/00268949108030895

Mol. Cryst. Liq. Cryst., 1991, Vol. 195, pp. 123–133
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Printed in the United States of America

Discotic Liquid Crystals of Transition Metal Complexes 8[1]: Enantiotropic Nematic Mesomorphism and Helical Formation of Bis[1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-dionato]copper(II) Complexes

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(*Received April 16, 1990; in final form July 13, 1990*)

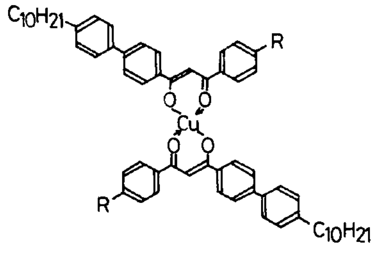
Five new bis(β-diketonato) copper (II) complexes, bis[1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-dionato] copper (II) complexes [abbreviated as C_nO-Comp-C_m: $n = m = 4, 8, 12$; $(n, m) = (8, 4), (12, 4)$] have been synthesized and characterized. It was found that the complexes exhibit nematic mesomorphism. C_4O-Comp-C_4 and C_8O-Comp-C_4 have an enantiotropic nematic mesophase. $C_{12}O$-Comp-C_4, C_8O-Comp-C_8 and $C_{12}O$-Comp-C_{12} have not a discotic columnar mesophase but a monotropic nematic mesophase: moreover, they exhibit helical formation, which can be thought to be extremely close to discotic columnar mesomorphism.

Keywords: discotic liquid crystal, metal complex, nematic, helix, β-diketonato copper(II)

I. INTRODUCTION

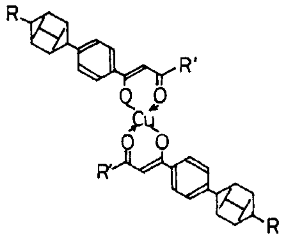
A few of the nematic liquid crystals of organic metal complexes have been reported, to date.[2–13] Among them, two nematic mesogens of bis(β-diketonato) copper (II) complexes have been reported: bis[1-(*p*-*n*-decylbiphenyl)-3-(*p*-substitutedphenyl) propane-1,3-dionato] copper (II) complexes (Formula 1) synthesized by Chandrasekhar *et al.*[7] and bis{1-[4-trans-(4-alkylcyclohexyl)phenyl]-alkylpropane-1,3-dionato} copper (II) complexes (Formula 2) prepared by Mühlberger *et al.*[9] Both give a *monotropic* nematic mesophase.

Five new bis(β-diketonato) copper (II) complexes, bis[1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropano-1,3-dionato] copper (II), 4a–e (abbreviated as C_nO-Comp-C_m: For-



1

R = C_nH_{2n+1} n=1,2
R = $C_nH_{2n+1}O$ n=1,2,3



2

R = C_nH_{2n+1} n=3,5,7
R' = C_nH_{2n+1} n=1,2,3,5,6,7,8

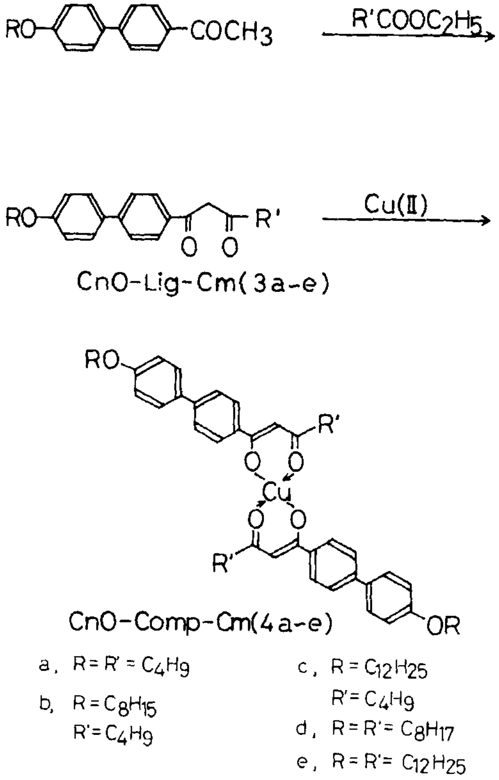
FORMULAS 1 & 2

mula 4 in Scheme 1) have been synthesized in this work. Interestingly, C_4O-Comp-C_4 (4a) and C_8O-Comp-C_4 (4b) have an *enantiotropic* nematic mesophase. The other complexes (4c, d, e) give a monotropic nematic mesophase when the isotropic liquids (I.L.) are rapidly cooled. Moreover, these complexes (4c, d, e) show "helical formation" when the isotropic liquids are cooled very slowly. In this paper, we wish to report on nematic mesomorphism and helical formation in C_nO-Comp-C_m.

II. EXPERIMENTAL

II-1. Synthesis

The synthetic route of 1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-diones (abbreviated as C_nO-Lig-C_m: 3a–e) and the corresponding copper (II) complexes (4a–e) are shown in Scheme 1. The synthesis of the starting material, 4-*n*-alkoxy-4′-acetylbiphenyl was carried out by the same manner described in the previous paper.[14] In Table I and II, are listed elemental analysis data, yields, recrystallization solvents, and the crystalline shapes obtained from recrystallization for 3a–e and 4a–e, respectively. The detailed procedures are described for C_4O-Lig-C_4 (3a) and C_4O-Comp-C_4 (4a) in the following pages.



SCHEME 1 Synthetic route for bis[1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-dionato]copper(II) complexes, C_nO-Comp-C_m (4a–e).

TABLE I

Elemental analysis data, yields, recrystallization solvents, and the crystalline shapes obtained from recrystallization for C_nO-Lig-C_m (3a–e).

Compound R	R'		Elemental analysis Found(calcd.)%		Yield (%)	Recrystallization solvent	Crystalline shape
n	m		C	H			
4	4	(3a)	73.38(73.68)	8.01(7.96)	61	n-hexane	powder
8	4	(3b)	79.37(79.60)	8.88(8.94)	56	n-hexane	powder(K_1)
12	4	(3c)	80.13(80.43)	9.54(9.58)	58	n-hexane	powder
8	8	(3d)	80.13(80.42)	9.54(9.46)	60	a	plate-like
12	12	(3e)	81.20(81.35)	10.48(10.42)	61	CH_2Cl_2	plate-like

a CH_2Cl_2:n-hexane = 3:2 (V/V).

TABLE II

Elemental analysis data, yields, recrystallization solvents, and the crystalline shapes obtained from recrystallization for C_nO-Comp-C_m (4a–e).

Compound R n	R' m	Elemental analysis Found(calcd.)% C	H	Yield (%)	Recrystallization solvents	Crystalline shapes
4	4 (4a)	72.08(72.29)	7.10(7.18)	51	benzene	powder
8	4 (4b)	73.81(73.87)	8.03(8.07)	81	ethyl acetate	powder
12	4 (4c)	75.15(75.29)	8.75(8.99)	93	ethyl acetate	powder(K_1)
8	8 (4d)	75.15(75.16)	8.75(8.70)	55	benzene	powder
12	12 (4e)	77.08(76.93)	9.79(9.73)	74	benzene	powder(K_1)

1-(p-n-butyloxybiphenyl)-3-butylpropane-1,3-dione (*C_4O-Lig-C_4: 3a*). 4-*n*-butyloxy-4'-acetylbiphenyl (2.0 g, 7.5 mmol) was dissolved in freshly distilled dry tetrahydrofuran (ca. 50 ml). The solution was refluxed for 2 hr. in the presence of 60% sodium hydride (0.57 g, 15 mmol). Ethyl *n*-pentanate (4.9 g, 37 mmol) was then added to the solution at room temperature and refluxed again for 12 hr. After cooling in an ice-water bath, an aqueous solution of hydrochloric acid (1N ca. 30 ml) was added to the mixture. The yellow precipitate was collected, washed with water, and air dried. The product was recrystallized from *n*-hexane to give yellow powder (1.6 g, 61%).
MS (m/e) = 352 (M^+), I.R. (KBr, disk, cm^{-1}) 1600 (C = C), ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm) 1.0 (t, 6H, CH_3), 1.7 (m, 8H, $(CH_2)_2$), 2.4 (t, 2H, $COCH_2$), 4.0 (t, 2H, OCH_2), 6.2 (s, 1 H, enol CH), 6.9 ~ 7.9 (m, 8H, biphenyl), 16.1 (s, 1H, enol OH), keto:enol = 0:100.

Bis[1-(p-n-butyloxybiphenyl)-3-butylpropane-1,3-dionato]copper(II) complex (*C_4O-Comp-C_4: 4a*). To an ethanolic solution of 0.40 g (1.1 mmol) of C_4O-Lig-C_4 (3a) at 80°C, ca. 2 ml of an aqueous solution (28%) of ammonium hydroxide and then an aqueous solution of 0.10 g (0.57 mmol) of cupric chloride dihydrate were added. The resulting green-gray precipitate was collected, washed with water and a small portion of ethanol several times, and air dried. Recrystallization of the product from benzene gave green powder of the complex (0.22 g, 51%).

For these C_nO-Comp-C_m complexes, C and H elemental analysis were satisfactory (Table II).

II-2. Measurements

Phase transition behaviors of these compounds synthesized here were observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, FP80 and FP82, and measured with a differential scanning calorimeter, Rigaku Thermoflex TG-DSC. The X-ray diffraction powder patterns were employed to characterize the mesophases in the present compounds. The patterns were measured with Cu-Kα radiation, using a Rigaku Geigerflex equipped with a hand-made heating plate controlled by a thermoregulator.[15]

III. RESULTS AND DISCUSSION

III-1. Mesomorphism of 1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-dione (C_nO-Lig-C_m: 3a–e)

All of the β-diketones (3a–e) have a smectic A (S_A) mesophase. In Table III are summarized the phase transition temperatures and their enthalpy changes of 3a–e. The S_A mesophase of 3a–e was established by microscopic observations and X-

TABLE III

Phase transition temperatures (T) and enthalpy changes (ΔH) of C_nO-Lig-C_m (3a–e).

Compound	Phase[a] $\xrightarrow[\Delta H(\text{kcal/mol})]{T\ ^{\circ}C}$ Phase
3a	$K \xrightarrow[3.0]{126.1} S_A \xrightarrow[1.4]{155.4}$ I.L.
3b	$K_1 \xrightarrow[0.5]{98.7} K_2 \xrightarrow[3.6]{110.2} S_A \xrightarrow[2.1]{152.5}$ I.L.
3c	$K \xrightarrow[6.0]{105.2} S_A \xrightarrow[1.4]{133.8}$ I.L.
3d	$K \xrightarrow[6.5]{125.3} S_A \xrightarrow[2.1]{137.0}$ I.L.
3e	$K \xrightarrow[6.6]{124.4} S_A \xrightarrow[4.0]{125.8}$ I.L.

[a] Phase nomenclature: K = crystal, S_A = smectic A mesophase, and I.L. = isotropic liquid.

ray diffraction studies. These mesophases exhibit a focal-conic texture. In an X-ray diffraction powder pattern of these mesophases, three narrow peaks were observed in the low-angle region. The ratio of the spacings is exactly 1:1/2:1/4. Therefore, these mesophases have a lamellar structure. Moreover, these mesophases gave also a diffuse band around $2\theta = 20°$ in the X-ray wide-angle region, corresponding to the melt of the alkoxy chains. From these results, the mesophases could be assigned as a S_A mesophase. The temperature range of the mesophase of 3e is only 1.4°C. Interestingly, *p*-*n*-alkoxybiphenylbutane-1,3-diones in the previous paper[14] have a smectic E (S_E) and a S_A mesophase, whereas the present β-diketones, 3a–e, have only a S_A mesophase.

III-2. Nematic mesomorphism and helical formation of bis[1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-dionato] copper (II) complexes (4a–e)

In Table IV, are summarized the phase transition temperatures and their enthalpy changes of 4a–e. The shorter chain-substituted complexes, 4a, b have an *enantiotropic* nematic mesophase. On the other hand, the longer chain-substituted complexes, 4c, d, e, have a *monotropic* nematic mesophase, which could be observed only on a *rapid* cooling stage from the isotropic liquid (I.L.). Furthermore, they show helical formation on a *very slow* cooling stage from the I. L., as described below (Part C).

A. Enantiotropic nematic mesophase of C_4O-Comp-C_4 (4a) and C_8O-Comp-C_4 (4b). Figure 1 shows a photomicrograph of the enantiotropic nematic mesophase of 4a at 202°C. A typical schlieren texture with two and four brushes of nematic mesophase can be observed in this picture. 4b also gave the same texture. For 4a → 4b (R = R′ = *n*-butyl → R = *n*-octyl, R′ = *n*-butyl), the clearing point and melting point become lower but the temperature range of the nematic mesophase spreads a little (Table IV). For 4b → 4c (R = *n*-octyl, R′ = *n*-butyl → R = *n*-dodecyl, R′ = *n*-butyl), the enantiotropic mesophase disappears and a monotropic nematic mesophase appears instead.

B. Monotropic nematic mesophase of C_8O-Comp-C_8 (4d) and $C_{12}O$-Comp-C_{12} (4e). In the previous papers, it has been reported that the homologous bis(β-diketonato)copper(II) complexes with *four peripheral long chains*, bis[1,3-di(*p*-*n*-alkylphenyl)-propane-1,3-dionato]copper(II), have a discophase with a columnar and layered structure[16] or a discotic lamellar mesophase.[17] Therefore, we expected that 4d and 4e in the present complexes substituted by *four long alkyl chains* might exhibit discotic mesomorphism. Contrary to our expectation, these four-long-chain-substituted complexes, 4d and 4e, gave only a monotropic nematic mesophase, the same case as 4c.

In contrast to the bis(*p*-*n*-alkoxybiphenylbutane-1,3-dionato)copper(II) complexes (C_nO-Cu) exhibiting discotic rectangular ordered columnar (D_{ro}) mesomorphism as described in the previous paper,[1] the present C_nO-Comp-C_m (4a–e) show not discotic columnar mesomorphism but nematic mesomorphism. The possible reasons can be thought of as illustrated in Figure 2. When the R′ (C_m) groups of the C_nO-Comp-C_m complex 4 in Scheme 1 are small methyl groups (small circles

TABLE IV

Phase transition temperatures (T) and enthalpy changes (ΔH) of C_nO-Comp-C_m (4a–e).

Compound	Phase[a] $\xrightarrow{T^{o}C[\Delta H(kcal/mol)]}$ Phase
	$\rightsquigarrow$ relaxation
4a	$K \xrightleftharpoons{201.0[10.4]} N \xrightleftharpoons{205.3[0.1]} I.L.$
4b	$K \xrightleftharpoons{170.0[6.9]} N \xrightleftharpoons{176.3[0.1]} I.L.$
4c	$\begin{tikzcd} K_1 \arrow[r, "111.5[0.3]"] & K_2 \arrow[rr, shift left, "153.3[12.3]"] & & I.L. \arrow[ll, shift left, "very slow"] \arrow[dl, "rapid cooling"] \\ & & N \arrow[ul, squiggly, "fast"] & \end{tikzcd}$
4d	$\begin{tikzcd} K \arrow[rr, shift left, "166.9[15.9]"] & & I.L. \arrow[ll, shift left, "very slow"] \arrow[dl, "155 rapid cooling"] \\ & N \arrow[ul, squiggly, "fast"] & \end{tikzcd}$
4e	$\begin{tikzcd} & & & I.L. \arrow[dr, squiggly] & & \\ K_1 \arrow[r, "108.5"] & K_2 \arrow[r, "128.5"] & K_3 \arrow[ur, "139.5"] & & K_4 \arrow[r, shift left, "147.5"] & I.L \arrow[l, shift left, "very slow"] \arrow[dll, "137 rapid cooling"] \\ & & & N \arrow[ul, squiggly, "fast"] & & \end{tikzcd}$

[a]Phase nomenclature: K = crystal, N = nematic, and I.L. = isotropic liquid.

in Figure 2-A), the complexes become the C_nO-Cu complexes exhibiting D_{ro} mesomorphism (Figure 2-A). When the R′ (C_m) groups are bulky *n*-butyl groups (big circles in Figure 2-B), the complexes become the C_nO-Comp-C_4 derivatives exhibiting *enantiotropic nematic* mesomorphism for *n* = 4 (4a) and *n* = 8 (4b) (Figure 2-B). When the R′ (C_m) groups are the longer *n*-octyl or *n*-dodecyl groups, the complexes become C_8O-Comp-C_8 (4d) or $C_{12}O$-Comp-C_{12} (4e) exhibiting *mono-*

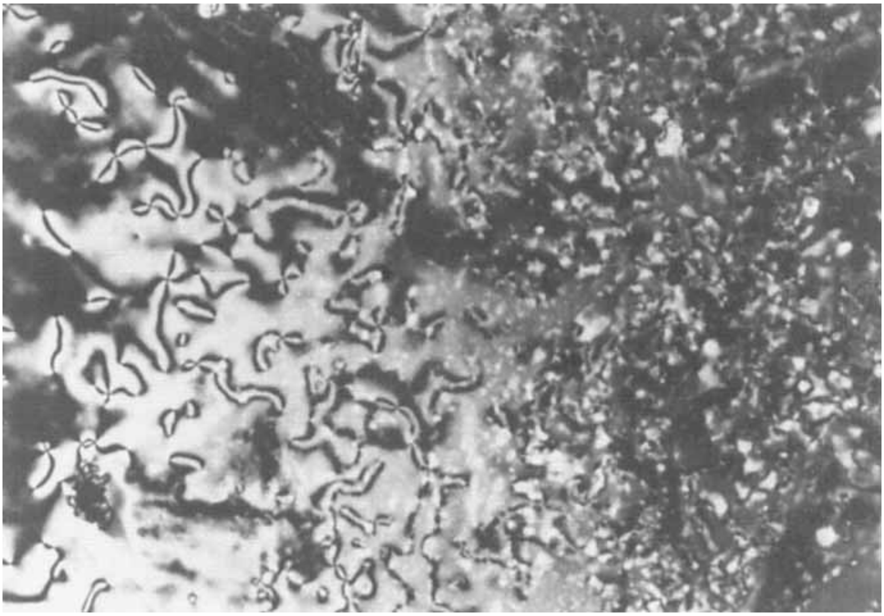


FIGURE 1 Photomicrograph of the nematic (N) mesophase in C_4O-Comp-C_4 (4a) at 202°C. See Color Plate III.

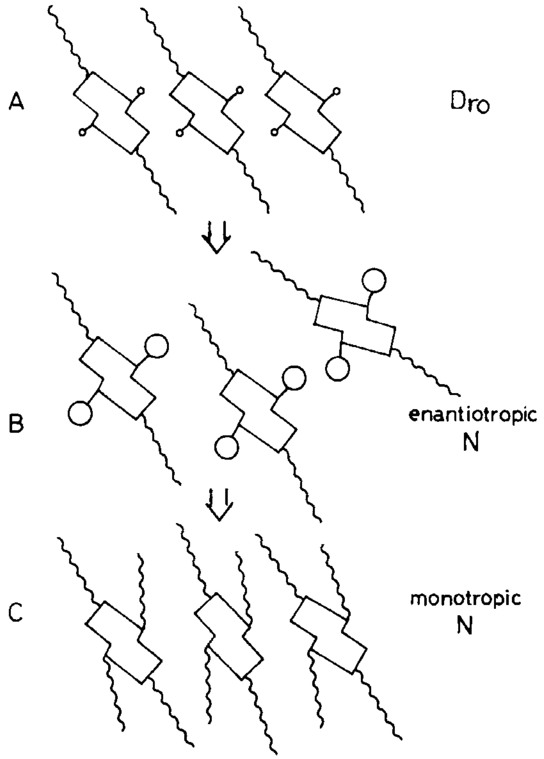


FIGURE 2 Possible reasons of the appearance of nematic mesophases in C_nO-Comp-C_m.

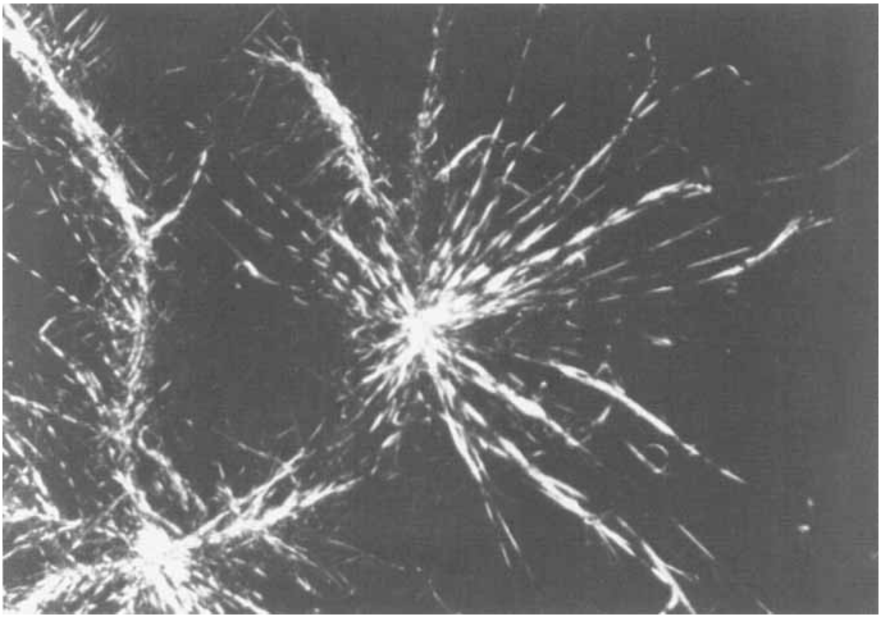
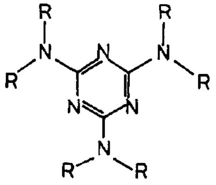


FIGURE 3 Photomicrograph of the helices of $C_{12}O$-Comp-C_{12} (4e) obtained by holding the isotropic liquid at 144°C over night. See Color Plate IV.

tropic nematic mesomorphism (Figure 2-C). Therefore, changing from small methyl groups to bulky *n*-butyl groups (A → B in Figure 2), the steric hindrance of the both sides of the molecule toward the neighbouring molecules may cause disturbance of the arrangements of molecules to change the mesomorphism from D_{ro} to enantiotropic nematic. On the other hand, changing from *n*-butyl groups to the longer *n*-octyl or *n*-dodecyl groups (B → C in Figure 2), these longer flexible chains may cause conquest of the disturbance to recover the order of the molecular arrangement and prevent the mesomorphism from showing enatiotropic nematic to monotropic nematic.

C. Helical formation of $C_{12}O$-Comp-C_4 (4c), C_8O-Comp-C_8 (4d), and $C_{12}O$-Comp-C_{12} (4e). The complexes, 4c–e, give a monotropic nematic mesophase only on rapid cooling the I.L. at ≤ -20°C. On the other hand, when the I.L. was holding at 1 ~ 3°C below the m.p. for more than 3 h the helices appeared. The helices in Figure 3 could be obtained when the I.L. of 4e had been holding at 144°C over night. A similar helical formation was reported for 2,4,6-tris(didecylamino)-*s*-triasines (Formula 5) by Lattermann *et al.*[18] They synthesized these compounds 5 in an attempt to obtain a new discotic liquid crystal. Although they do not exhibit mesomorphism, they show helical formation in a supercooled melt. Moreover, they reported the assumption that the helical formation was caused by stacking of the center discs. Yanagawa *et al.* reported that dimyristoyl-5′-phosphatidyldeoxytidine having two long alkyl chains (Formula 6) forms double helices like DNA by self-assembling, and that the formation of double helices for this compound was attributable to the columnar formation of the disc-like cytosin part and to the effect



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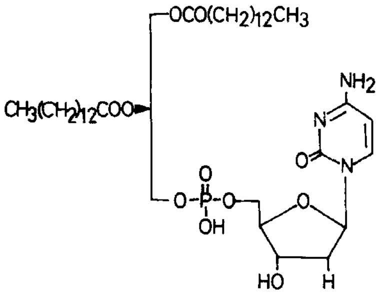

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FORMULAS 5 & 6

of the two long chains.[19] Recently, it has been reported that highly concentrated DNA is a discotic columnar liquid crystal.[20]

From these facts, we considered that helical formation of long chain-substituted compounds is a property of molecular aggregation extremely close to discotic columnar mesomorphism. Long chain-substituted organic metal complexes exhibiting helical formation may play an important biological role in the future. Therefore, the study on these types of organic metal complexes would make a new field in science.

IV. CONCLUSION

C_4O-Comp-C_4 (4a) and C_8O-Comp-C_4 (4b) have an enantiotropic nematic mesophase. $C_{12}O$-Comp-C_4 (4c), C_8O-Comp-C_8 (4d), and $C_{12}O$-Comp-C_{12} (4e) gave not a discotic mesophase but a monotropic nematic mesophase. Moreover, it is noteworthy that 4c, d, and e exhibit helical formation extremely close to discotic columnar mesomorphism.

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