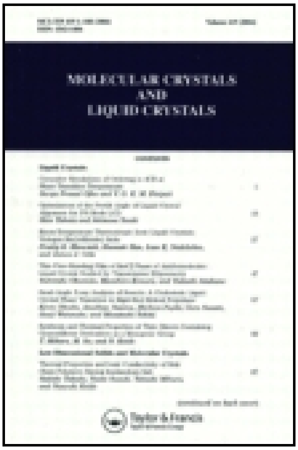

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Liquid Crystalline Formanilides

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Liquid Crystalline Formanilides

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A series of phenyl benzoates and biphenyls having a formylamino terminal have been prepared for a systematic study on their mesomorphic behaviors.

Keywords: Liquid crystal, formanilide

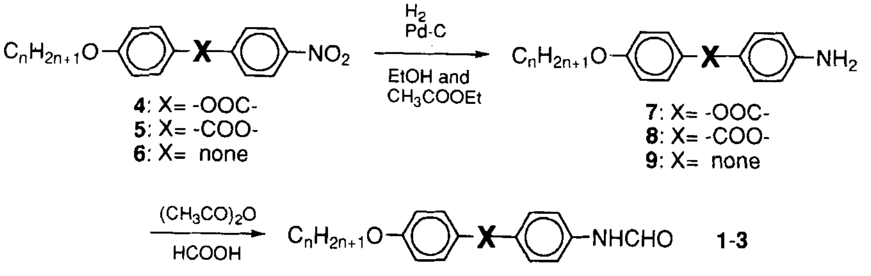
1. INTRODUCTION

Recently we have reported platinum- and palladium-isonitrile complexes as a new family of organometallic liquid crystals.[1] The complexes contain mesogenic isonitriles as a ligand, which have been prepared from corresponding formanilide derivatives. In the course of preparing a variety of formanilides, we have found that a formylamino group (—NHCHO) is well suited for a polar terminal group in mesogens. Though polar groups such as cyano and nitro are well-known as good terminals of liquid crystalline compounds, few examples of formylamino terminals have appeared in the literature.[2] In this paper we wish to report a systematic study on the synthesis and the liquid crystal properties of formanilides having stuructures **1–3** shown in Figure 1.

Synthesis and Characterization

The formanilides were prepared starting from the corresponding nitro derivatives **4** ~ **6**. Thus, reduction of the nitro group with hydrogen using a palladium-on-carbon catalyst gave amines **7** ~ **9**, followed by formylation of the amino group with formic acid and acetic anhydride to give formanilides **1** ~ **3** in good yields (Scheme 1). In the formylation, an *N*-acetylated compound, $CH_3CONHAr$, was also given as a by-product in several percents, but could be removed by recrystallization. Recrystallization from ethanol gave formanilides as white powder. The purity of the final products was checked by HPLC analysis (COSMOSIL 5SL 4.6 × 250 mm). Yields and elemental analysis data for **1–3** are presented in Table 6 in the Experimental section. The identification was made by elemental analysis, IR, ^{1}H NMR and mass spectra.

^{1}H NMR spectra of the formanilides indicated that there exist two conformational isomers (**a** and **b**) in solution, which arise from slow rotation of the —CHO group around the C—N bond at room temperature. The slow rotation is due to the double bond character of the C—N bond (**c** and **d**) illustrated in Figure 2.[3] The complete assignment of an ^{1}H NMR spectrum for **1**($n = 12$) is shown in Figure 3. The broad



SCHEME 1

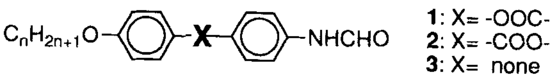


FIGURE 1 Formanilides.

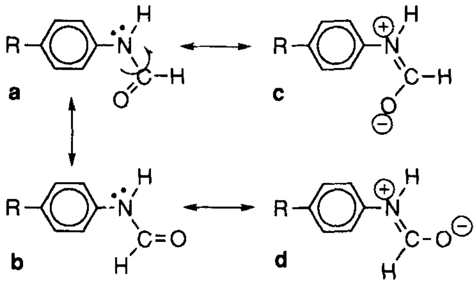


FIGURE 2 Conformational isomers of formanilides.

signals at 7.38 and 7.66 ppm (shoulder signal) were assigned to the proton of —N*H*CHO, and the two doublet signals at 8.46 ($J = 1.4$ Hz) and 8.88 ($J = 11.2$ Hz) ppm to the proton of —NHC*H*O. Decoupling the broad singlet at 7.38 ppm collapsed the doublet at 8.46 ppm to a singlet peak, and decoupling the broad signal at 7.66 ppm also collapsed the doublet at 8.88 ppm to a singlet. Two aromatic protons on the ortho position to the —NHCHO group was represented by two apparent sets of doublets centered at 7.17 and 7.69 ppm. The difference in the chemical shifts seems to be also attributed to the different conformation, **a** and **b**, of the —NHCHO group. Two aromatic protons meta to the —NHCHO group similarly appeared as two sets of doublets in the range of $\delta = 8.17$–8.21 ppm due to the same reason.

Phase Behavior

Several compounds thus synthesized here exhibited thermotropic liquid-crystalline behavior. We used a polarizing microscope for the observation of phase behaviours, and transition temperatures were determined using differential scanning calorimetry. The thermal data are collected in Tables 1–3.

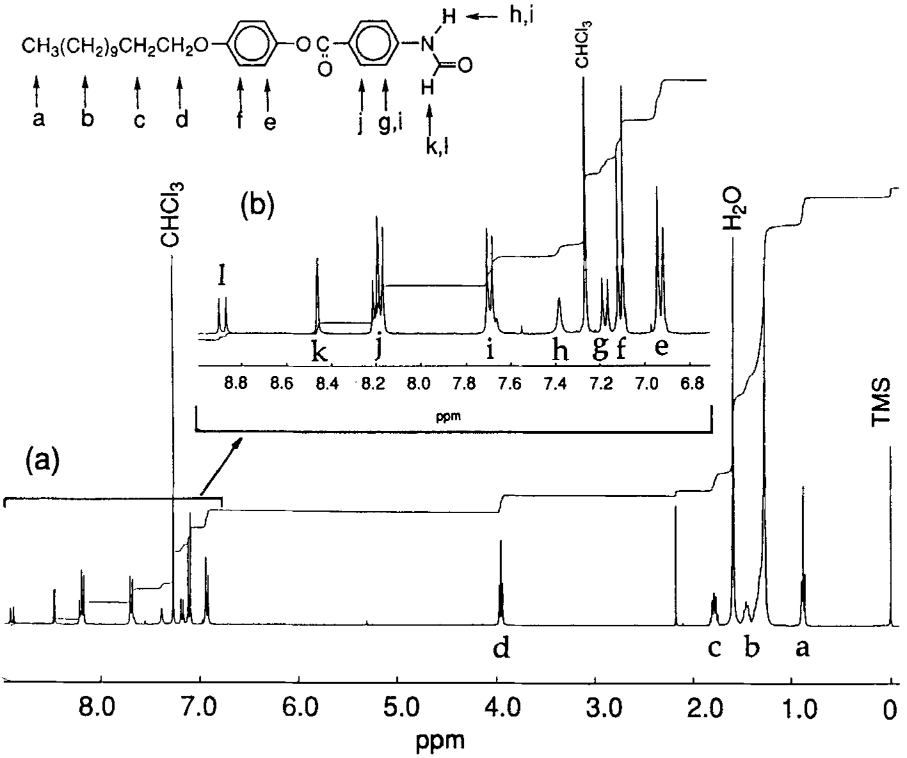


FIGURE 3 ^{1}H NMR spectra of (a) 1 ($n = 12$) and (b) the aromatic region in cholroform at room temperature.

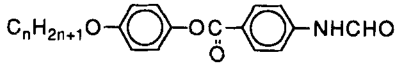
Compound **1** has the same structure as **2** except the direction of the ester group. Compounds **1** with $n = 8$ and 9 showed only a monotropic S_A phase, whereas those with $n = 10$, 11 and 12 showed an enantiotropic S_A phase. On the contrary, we found that compounds **2** where $n = 9$, 10, 12 and 14 exhibited an enantiotropic S_C phase in a lower temperature range compared with **1**. Shortening the chain length ($n = 7$ and 8) of terminal alkyls in **2** resulted in the appearance of an N phase; for $n = 7$ a monotropic N phase and for $n = 8$ an enantiotropic N in addition to a monotropic Sc phase were observed. The different phase behavior between **1** and **2** indicates that the direction of the ester group remarkably influences the properties of liquid crystals.

The phase behavior of related compounds, which have some kinds of terminal groups including —NHCHO and —NH_2, is shown in Table 5. The amino compounds in Table 5 as well as those in Table 4 showed no mesomorphic behavior at all. Compounds **10c** and **11c**, having an acetylamino group, also showed no mesophase. Replacement of one hydrogen atom in an amino group by a formyl group results in the appearance of a mesophase. This is because the introduction of a formyl group produces an appropriate intermolecular force for forming a mesomorphic phase. But in the case of the introduction of an acetyl group, the same effect was not observed.

Compounds **10d** and **10e** showed N and S_A phases, respectively. The introduction of an imino group, —NH—, to **10e** results in considerable increase of the melting point

TABLE 1

Transition Temperature (°C) and Enthalpies (kJ/mol)^{a} for Compound **1**

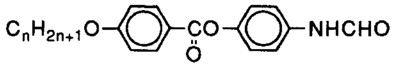


n	Phase behaviors						Recrystallized temperature
	C		*S$_A$*		*I*		
8	·	186 [44]	(·	181)^{c} [6.0]	·		154
9	·	188 [51]	(·	182)^{d} [6.7]	·		160
10	·	185 [50]^{b}	·	186^{d}	·		157
11	·	179 [40]	·	186 [5.1]	·		152
12	·	170 [40]	·	185 [5.1]	·		145

^{a}Values in parentheses. ^{b}Combined enthalpy. ^{c}Monotropic transition. ^{d}From optical observation.

TABLE 2

Transition Temperature (°C) and Enthalpies (kJ/mol)^{a} for Compound **2**



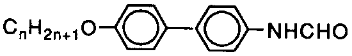
n	Phase behaviors							Recrystallized temperature
	C		*S$_C$*		*N*		*I*	
5	·	136 [26]					·	126
6	·	134 [27]					·	124
7	·	133 [30]			(·	126)^{d} [1.8]	·	123
8	·	130 [27]^{b}	(·	126)^{c}	·	133	·	118
9	·	127 [22]	·	135 [5.3]			·	113
10	·	125 [21]	·	141 [6.5]			·	110
12	·	121 [15]	·	145 [6.1]			·	106
14	·	119 [18]	·	149 [8.1]			·	104

^{a}Values in parentheses. ^{b}Combined enthalpy. ^{c}Monotropic trensition.

and preventing the formation of a mesophase as seen for **10c**. The increase in melting point may be due to a strong intermolecular interaction by a hydrogen bonding and an ionic character of the amido group. The same tendency was observed in the comparison of **10a** with **10d**, though the liquid crystal properties are retained. Consequently a formylamino terminal seems to be more favorable than an acetylamimo group which is known to promote the formation of nematic phases.[4]

TABLE 3

Transition Temperature (°C) and Enthalpies (kJ/mol)[a] for Compound 3

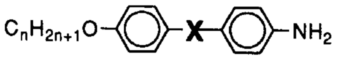


n	C		S_C		S_A		I	Recrystallized temperature
		Phase behaviors						
5	•	184 [28]					•	180
6	•	176 [27][b]			•	179	•	170
7	•	173 [19]			•	180 [8.5]	•	167
8	•	168 [21]			•	181 [9.1]	•	163
9	•	166 [22]			•	180 [9.3]	•	161
10	•	165 [22]			•	180 [8.8]	•	160
11	•	165 [20]	(•	162)[c]	•	179 [8.1]	•	160
12	•	164 [18]	(•	166)[c]	•	177 [7.9]	•	159

[a] Values in parentheses. [b] Combined enthalpy. [c] Monotropic transition.

TABLE 4

Yields and Melting Temperatures[a] of Compounds 7–9



7:X = —OOC—
8:X = —COO—
9:X = none

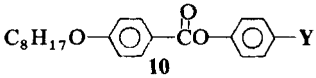
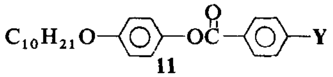
(n)	Yield(%)[b]	m.p. (°C)	(n)	Yield(%)[b]	m.p. (°C)
7(8)	95	161.0–162.1	**8**(5)	89	94.6–95.8
7(9)	88	160.3–161.1	**8**(6)	95	84.0–85.2
7(10)	82	157.0–157.8	**8**(7)	91	88.6–90.5
7(11)	97	155.6–156.2	**8**(8)	93	92.2–93.4
7(12)	65	151.0–152.2	**8**(9)	87	91.6–93.0
9(5)	85	88.6–90.1	**8**(10)	84	92.8–93.5
9(6)	89	87.5–88.5	**8**(12)	95	90.8–91.6
9(7)	91	93.8–94.6	**8**(14)	95	92.8–93.3
9(8)	91	91.8–93.3			
9(9)	94	96.7–98.5			
9(10)	94	98.0–99.0			
9(11)	83	100.9–101.8			
9(12)	92	100.0–100.9			

[a] From optical observation.
[b] Based on the nitro derivatives.

On the other hand, all of the isocyano derivatives, which are synthesized from the liquid-crystalline formamides by dehydration, showed liquid-crystal properties (N and/or S_A) at the temperature range 50–90°C. Unfortunately, the isocyano compounds thus prepared are somewhat thermally unstable, though they are stabilized on coordination to metals.[1,5]

TABLE 5

Phase Behavior of the Related Compounds

	Y	Phase behavior	
		 10	 11
a	NHCHO	$C \xrightarrow{130} N \underset{131}{\overset{133}{\rightleftharpoons}} I$; $C \xleftarrow[118]{} S_c \xleftarrow[126]{} N$	$C \underset{157}{\overset{185}{\rightleftharpoons}} S_A \underset{183}{\overset{186}{\rightleftharpoons}} I$
b	NH_2	$C \underset{85}{\overset{93}{\rightleftharpoons}} I$	$C \underset{147}{\overset{158}{\rightleftharpoons}} I$
c	$NHCOCH_3$	$C \underset{159}{\overset{168}{\rightleftharpoons}} I$	$C \underset{151}{\overset{167}{\rightleftharpoons}} I$
d	CHO	$C \underset{37}{\overset{59}{\rightleftharpoons}} N \underset{65}{\overset{67}{\rightleftharpoons}} I$	
e	$COCH_3$	$C \underset{67}{\overset{84}{\rightleftharpoons}} S_A \underset{89}{\overset{93}{\rightleftharpoons}} I$	

Temperatures determined by DSC.

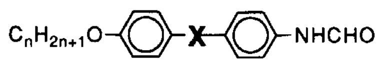
Experiment

Elemental microanalyses were performed by the Material Analysis Center, ISIR, Osaka University. IR spectra were obtained with a Hitachi 295 infrared spectrophotometer. ^1H NMR spectra were recorded with a Brucker WM-360 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Textures of liquid crystals were observed using an Olympus BH-2 polarising microscope in conjunction with a Mettler FP52 heating stage and an FP5 control unit, and phase transition temperatures and enthalpies were determined using a Shimazu DSC-50 differential scanning calorimeter. The apparatus was calibrated with standard samples of indium (156.6°C, 28.44 J/g) and tin (232.1°C, 60.5 J/g). The rate of heating or cooling was fixed to 5°C/min. under an argon atmosphere.

Synthesis of 4′-*n*-octyloxyphenyl 4-aminobenzoate 7($n = 8$) 4′-*n*-Octyloxyphenyl 4-nitrobenzoate, which was prepared from 4-nitrobenzoic acid and 4-*n*-octyloxyphenol, (9.86 g, 26.5 mmol) was stirred in the presence of 5% palladium-on-carbon catalyst (0.7 g) in ethanol/ethyl acetate (300 ml/50 ml) under a positive pressure of hydrogen at room temperature until diminution of hydrogen finished (about 5 hours). The mixture was then filterd and the solvent was removed. The residue was purified by recrystallization from ethanol to 7($n = 8$), giving white crystals. Yield 8.61 g (95%); MS (70 eV) M/z 341 (M^+,2), 120 (100%); IR (nujol) 3430, 3350, 3240, 1715, 1650, 1600, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.89$ (3H, t, J = 7 Hz, CH_3), 1.29–1.45 (10H, m, alkyl), 1.78 (2H, tt, J = 7 Hz, 7 Hz, OCH_2CH_2), 3.95 (2H, t, J = 7 Hz, OCH_2), 4.13 (2H, broad, NH_2), 6.68

TABLE 6

Yields and Elemantal Analyses of Complexes 1–3



1:X = —OOC—
2:X = —COO—
3:X = none

(*n*)	Yield(%)[a]	Microanalysis found (calculated) *C*	*H*	*N*
1(8)	95	71.38 (71.52)	7.25 (7.37)	3.81 (3.79)
1(9)	92	72.01 (72.04)	7.52 (7.62)	3.41 (3.65)
1(10)	94	72.69 (72.52)	7.79 (7.86)	3.46 (3.52)
1(11)	94	72.98 (72.96)	8.13 (8.08)	3.60 (3.40)
1(12)	93	73.33 (73.38)	8.32 (8.29)	3.44 (3.29)
2(5)	86	69.66 (69.71)	6.26 (6.47)	4.19 (4.28)
2(6)	82	70.26 (70.36)	6.59 (6.79)	4.25 (4.10)
2(7)	90	70.88 (70.96)	6.91 (7.09)	3.75 (3.94)
2(8)	89	71.32 (71.52)	7.17 (7.37)	3.66 (3.79)
2(9)	86	71.88 (72.04)	7.36 (7.62)	3.68 (3.65)
2(10)	88	72.24 (72.52)	7.79 (7.86)	3.62 (3.52)
2(12)	74	73.62 (73.38)	8.04 (8.29)	3.18 (3.29)
2(14)	59	73.97 (74.13)	8.55 (8.66)	2.99 (3.08)
3(5)	81	76.11 (76.30)	7.60 (7.47)	4.79 (4.94)
3(6)	86	76.53 (76.74)	7.86 (7.80)	4.81 (4.71)
3(7)	89	76.95 (77.14)	7.96 (8.09)	4.21 (4.50)
3(8)	91	77.22 (77.50)	8.11 (8.36)	4.20 (4.30)
3(9)	89	77.62 (77.84)	8.32 (8.61)	4.11 (4.13)
3(10)	85	77.99 (78.14)	8.79 (8.83)	3.90 (3.96)
3(11)	92	78.55 (78.43)	8.98 (9.05)	3.64 (3.81)
3(12)	86	78.56 (78.70)	8.99 (9.25)	3.53 (3.67)

[a] Based on the amino derivatives.

(2H, d, J = 9 Hz, Ar), 6.90 (2H, d, J = 9 Hz, Ar), 7.08 (2H, d, J = 9 Hz, Ar), 7.99 (2H, d, J = 9 Hz, Ar).

Physical data of **8** (*n* = 8): MS (70 eV) m/z 341 (M^+, 7), 233 (78), 121 (100%); IR (nujol) 2380, 3380, 1720, 1605, 1520 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.89$ (3H, t, J = 7 Hz, CH_3), 1.29–1.47 (10 H, m, alkyl), 1.82 (2H, tt, J = 7 Hz, 7 Hz, OCH_2CH_2), 3.60 (2H, broad, NH_2), 4.03 (2H, t, J = 7 Hz, OCH_2), 6.71 (2H, d, J = 9 Hz, Ar), 6.95 (2H, d, J = 9 Hz, Ar), 8.12 (2 H, d, J = 9 Hz, Ar).

Physical data of **9** (*n* = 8): MS (70 eV) m/z 297 (M^+, 43), 185 (100%); IR (nujol) 3150, 1605, 1500, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.94$ (3H, t, J = 7 Hz, CH_3), 1.25–1.43 (10 H, m, alkyl), 1.80 (2H, tt, J = 7 Hz, 7 Hz, OCH_2CH_2), 3.60 (2H, broad NH_2), 3.98 (2H, t, J = 7 Hz, OCH_2), 6.74 (2H, d, J = 9 Hz, Ar), 6.93 (2H, d, J = 9 Hz, Ar), 7.36 (2H, d, J = 9 Hz, Ar), 7.44 (2H, d, J = 9 Hz, Ar).

The other amino derivatives were synthesized in the same manner and their yields and melting point data are collected in Table 4.

Synthesis of [4-(4′-*n*-octyloxyphenyloxycarbonyl)phenyl]formamide **1** (*n* = 8)

Acetic anhydride (8.3 ml) was added dropwise to a solution of 4′-*n*-octyloxyphenyl 4-aminobenzoate (3.41 g, 10 mmol) in formic acid (50 ml). After stirring for 1 hour, ice-water (10 ml) was introduced, and the mixture was concentrated to half at reduced pressure. The precipitate was collected and washed with water. After drying in vacuum, the crude product was purified by recrystallization from ethanol to give **1** (*n* = 8) as white powder. Yield 3.50 g (95%); MS (70 eV) m/z 369 (M^+, 4), 148 (100%); IR (nujol) 3340, 1720, 1700, 1595, 1530, 1410, 1280 cm^{-1}; ^{1}H NMR $\delta = 0.88$ (3H, t, J = 7 Hz, CH3), 1.27–1.48 (10H, m, alkyl), 1.79 (2H, tt, J = 7 Hz, 7 Hz, $OCH_2C\mathit{H}_2$), 3.96 (2H, t, J = 7 Hz, OCH_2), 6.92 (2H, d, J = 9 Hz, Ar), 7.11 (2H, d, J = 9 Hz, Ar), 7.17 (0.8H, d, J = 9 Hz, Ar), 7.38 (0.6H, broad, N*H*CHNO), 7.69 (1.6H, m, Ar, N*H*CHO), 8.19 (2H, m, Ar), 8.46 (0.6H, d, J = 1 Hz, NHC*H*O), 8.88 (0.4H, d, J = 11 Hz, NHC*H*O).

Physical data of **2** (*n* = 8): MS (70 eV) m/z 369 (M^+, 1), 233 (87), 121 (100%); IR (nujol) 3320, 3220, 3070, 1755, 1700, 1620, 1460, 1260 cm^{-1}; ^{1}H NMR $\delta = 0.90$ (3H, t, J = 7 Hz, CH_3), 1.30–1.50 (10H, m, alkyl), 1.82 (2H, tt, J = 7 Hz, 7 Hz, $OCH_2C\mathit{H}_2$), 4.04 (2H, t, J = 7 Hz, OCH_2) 6.97 (2H, dd, J = 9 Hz, 2 Hz, Ar), 7.23–7.12 (3.5H, m, Ar, N*H*CHO), 7.59 (1.5H, m, Ar, N*H*CHO), 8.13 (2H, d, J = 9Hz, Ar), 8.38 (0.5H, d, J = 2 Hz, NHC*H*O), 8.66 (0.5H, d, J = 11 Hz, NHC*H*O).

Physical data of **3** (*n* = 8): MS (70 eV) m/z 325 (M^+, 49), 213 (100%); IR (nujol) 1765, 1680, 1290 cm^{-1}; ^{1}H NMR $\delta = 0.89$ (3H, t, J = 7 Hz, CH_3), 1.25–1.47 (10 Hz, m, alkyl), 1.81 (2H, tt J = 7 Hz, 7 Hz, $OCH_2C\mathit{H}_2$), 3.99 (2H, t, J = 7 Hz, OCH_2), 6.97 (2H, dd, J = 9 Hz, 4 Hz, Ar), 7.12 (1H, d, 9 Hz, Ar), 7.18 (0.5H, broad, N*H*CHO), 7.47–7.60 (5.5H, m, Ar, N*H*CHO), 8.41 (0.5H, d, J = 2Hz, NHC*H*O), 8.71 (0.5H, d, J = 11 Hz, NHC*H*O).

The other formamide derivatives were similarly prepared.

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