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L. J. Yu [a] & C. J. Lee [a]

[a] Department of Chemistry, Tamkang University, Tamsui, 25137, Taiwan

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Mesogenic Behaviors of 4-(4-Alkyloxy Benzoyloxy)-Phenyl (3,4-Dialkyloxy)Benzoate Homologues

L. J. YU and C. J. LEE

Department of Chemistry, Tamkang University, Tamsui 25137, Taiwan

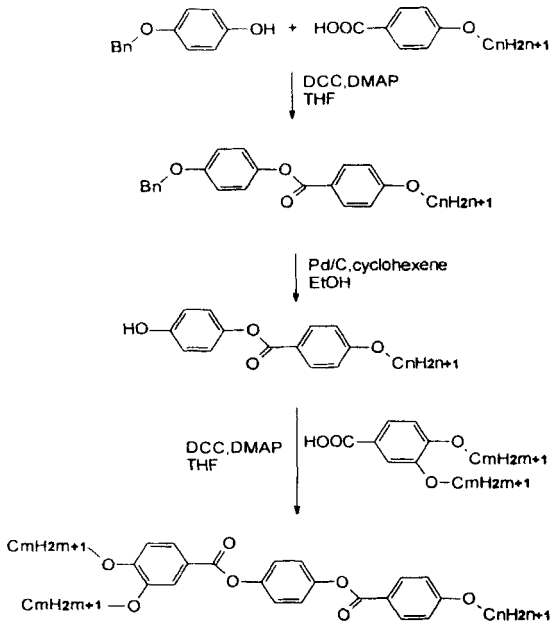
Hydroquinone was esterified with 4-alkyloxybenzoic acid at one end and 3,4-dialkyloxy benzoic acid at the other end. Narrow nematic and smectic C phases were observed for the obtained homologues as compared to those of di(4-alkyloxy)benzoic acid esters. This was attributed to the substitution at the 3-position of the benzoic acid moiety.

INTRODUCTION

Thermotropic rod-like mesogens consisting of more than two flexible chains at the ends have attracted some attentions for the molecular geometry was in between those of the two extremes, i. e., the rod-like and disc-like molecules.[1,2] Interesting properties were reported. [1,2,3] With more than two flexible chains linked to the rigid core, the extra chains would be in the lateral directions and the consequences were the decreasing of mesophase temperature ranges. Extra phenyl rings were then introduced to the rigid core to compensate this effect, and it was pointed out that the number of rings should be equal to the number of chains. [1,2] However, there was no simple rule available for the balance of these two effects since, aside from the geometric factors, the interactions between molecules were complicated by involving more functional groups.

In the present study, homologues were synthesized which consisted of hydroquinone esterified with benzoic acids carried one and two flexible chains. The mesophase behaviour was studied with various flexible chain lengths.

Scheme I



CmHQCn

EXPERIMENTAL

The target molecules were synthesized according to the procedures shown in Scheme I. The 4-alkyloxy benzoic acid was esterified with 4-benzyloxy phenol in the presence of dicyclohexyl carbodiimide (DCC) and 4-dimethylamino pyridine (DMAP) in dry THF. After deprotection by Pd/C in cyclohexene and ethanol, the obtained phenol was esterified with 3,4-dialkyloxy benzoic acid in the presence of DCC/DMAP in dry THF to give the final products, CmHQCn. The proton NMR spectra and the results of

elemental analysis (shown in Table I) of CmHQCn were consistent with those desired stuctures.

The textures of the mesophases were characterized by polarizing optical microscopy (OPTIPHOT-POL, Nikon) in conjunction with a heating stage (FP 82 and FP 800, Mettler). The corresponding enthalpy changes were measured with a scan rate of 10 ℃/min by differential scanning calorimetry (DSC-2, Perkin-Elmer). The proton NMR spectra were recorded by a Bruker AC300 NMR spectrometer.

RESULTS and DISCUSSION

The mesophases observed and the corresponding enthalpy changes measured for the CmHQCn homologues were listed in Table II. A phase diagram of C1HQCn series was shown in Figure 1. Only enantiotropic nematic phase was observed for this series. The nematic-isotropic transition temperatures decreased with increasing chain length and exhibited the even-odd effect. Compared to the nematic phase exhibited by 4-(4-alkyloxy benzoyloxy)phenyl 4-methoxybenzoate[4],the clearing temperatures were lowered by about 100 degrees and the thermal ranges of nematic phases were reduced by a factor of 2 to 3. Clearly, the existence of 3-methoxy group reduced the thermal stability of the nematic phase.

The thermal stability of mesophase was reduced further when the dialkyloxy benzoic acid consisted of longer chains as shown in Table II. Three series were studied, i.e., n = 4, 8 and 12. For the series of n = 4, only enantiotropic nematic phases were observed and the temperature ranges (on heating) were 15 degrees (m = 6) or less. The temperature ranges of enantiotropic nematic phases were slightly less for n = 8 series and monotropic smectic C (Sc) phase appeared for m = 6, 7 and 8 homologues. Enantiotropic nematic phases were observed for n = 12 series with even smaller temperature ranges, except that for m = 7 homologue which was monotropic. Monotropic Sc phases were observed for this series except m = 4 homologue.

Table I : The results of elemental analysis of 4-(4-alkyloxy benzoyloxy) phenyl (3,4-dialkyloxy)benzoate homologues, CmHQCn.

m	n	Formular	C %(calcd)	H%(calcd)
1	5	$C_{27}H_{28}O_7$	69.90 (69.83)	6.09 (6.03)
1	6	$C_{28}H_{30}O_7$	70.21 (70.29)	6.28 (6.28)
1	7	$C_{29}H_{32}O_7$	70.73 (70.73)	6.54 (6.50)
1	8	$C_{30}H_{34}O_7$	71.08 (71.15)	6.76 (6.72)
1	9	$C_{31}H_{36}O_7$	71.45 (71.54)	7.00 (6.92)
1	10	$C_{32}H_{38}O_7$	71.86 (71.91)	7.20 (7.12)
1	12	$C_{34}H_{42}O_7$	72.58 (72.60)	7.58 (7.47)
1	14	$C_{36}H_{46}O_7$	73.25 (73.22)	7.92 (7.80)
4	4	$C_{32}H_{38}O_7$	71.82 (71.91)	7.22 (7.12)
5	4	$C_{34}H_{42}O_7$	72.54 (72.60)	7.55 (7.47)
6	4	$C_{36}H_{46}O_7$	73.11 (73.22)	7.88 (7.80)
7	4	$C_{38}H_{50}O_7$	73.59 (73.79)	8.14 (8.09)
8	4	$C_{40}H_{54}O_7$	74.22 (74.30)	8.49 (8.36)
4	8	$C_{36}H_{46}O_7$	73.23 (73.22)	7.87 (7.80)
5	8	$C_{38}H_{50}O_7$	73.82 (73.79)	8.07 (8.09)
6	8	$C_{40}H_{54}O_7$	74.33 (74.30)	8.46 (8.36)
7	8	$C_{42}H_{58}O_7$	74.65 (74.78)	8.64 (8.60)
8	8	$C_{44}H_{62}O_7$	75.16 (75.21)	8.94 (8.83)
4	12	$C_{40}H_{54}O_7$	74.32 (74.30)	8.46(8.36)
5	12	$C_{42}H_{58}O_7$	74.80 (74.78)	8.68(8.60)
6	12	$C_{44}H_{62}O_7$	75.16 (75.21)	8.80(8.83)
7	12	$C_{46}H_{66}O_7$	75.67 (75.62)	9.11(9.04)
8	12	$C_{48}H_{70}O_7$	76.04 (75.99)	9.27(9.23)

Generally speaking, for the series studied here the longer the alkyl chain at the 4-position of benzoic acids the lower the isotropic temperatures. The transition temperatures of crystal to mesophase were also decreased but leveled at about 100℃. Therefore the temperature ranges of mesophase were narrowed with increasing chain length. The extra substitution at 3-position of the benzoic acid reduced further the

Table II : Transition temperature (℃) and enthalpies of transition (kJ/mol, in parentheses) for 4-(4-alkyloxybenzoyloxy)phenyl (3,4-dialkyloxy)benzoate homologues, CmHQCn.

m	n	I	N	Sc	recryst.	mp
1	6	· 160.0(0.39)	· 70.2(8.91)	-	·	119.4(10.34)
1	7	· 152.2(0.40)	· 76.0(9.92)	-	·	121.9(11.69)
1	8	· 149.0(0.38)	· 82.6(9.44)	-	·	129.8(12.36)
1	9	· 142.2(0.27)	· 84.0(10.49)	-	·	115.8(12.36)
1	10	· 138.8(0.39)	· 88.5(9.39)	-	·	118.8 (9.57)
1	12	· 133.0(0.51)	· 94.6(11.44)	-	·	122.8 (11.8)
1	14	· 127.8(0.60)	· 95.7(10.49)	-	·	119.1 (13.6)
4	4	· 123.8(0.34)	· 103.5(9.53)	-	·	120.2(12.49)
5	4	· 117.0(0.37)	· 95.7(12.09)	-	·	112.9(13.95)
6	4	· 115.4(0.31)	· 87.5(7.08)	-	·	100.0(10.35)
7	4	· 110.2(0.33)	· 87.3(9.59)	-	·	100.9(12.29)
8	4	· 108.5(0.25)	· 93.5(9.97)	-	·	106.0 (9.74)
4	8	· 117.0(0.41)	· 98.4(9.50)	-	·	107.7(11.73)
5	8	· 111.0(0.45)	· 92.2(9.94)	-	·	101.9(12.05)
6	8	· 111.3(0.41)	· 93.5(1.78)	· 84.2(6.43)	·	100.7 (9.87)
7	8	· 108.3(0.40)	· 97.0(1.87)	· 91.4(7.47)	·	103.4(10.24)
8	8	· 107.2(0.51)	· 97.6(1.72)	· 95.5(10.5)	·	106.1(12.92)
4	12	· 107.0(0.30)	· 92.5(8.63)	-	·	103.2 (9.53)
5	12	· 103.7(0.47)	· 91.2(2.07)	· 80.4(8.03)	·	95.0 (10.08)
6	12	· 105.2(0.31)	· 96.5(1.82)	· 82.5(6.34)	·	101.6(10.24)
7	12	· 103.5(0.32)	· 100.2(1.91)	· 86.3(7.79)	·	105.0(10.94)
8	12	· 103.6(0.38)	· 101.6(1.92)	· 84.5(9.16)	·	101.5 (9.14)

thermal stability of the mesophase and the effect was more pronounced with longer chain length. The homologues present here behaved more like rod-like mesogen, unlike the tetra-, penta- and hexa-catenar mesogens which

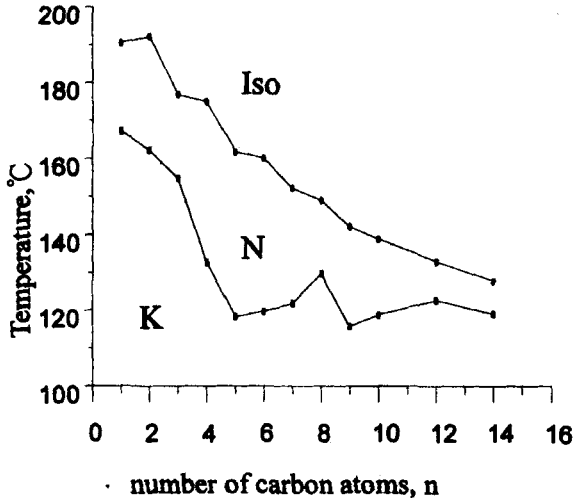


Figure 1. The phase diagram of 4-(4-alkyloxy benzoyloxy)phenyl(3,4-dimethoxy)benzoate

exhibited calamitic and columar phases. [1,2]

Acknowledgments

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