

NOVEL SMECTIC C MESOGENS. 3-(2-HYDROXY-4-ALKOXYBENZYLIDENE-AMINO)DIBENZOFURANS

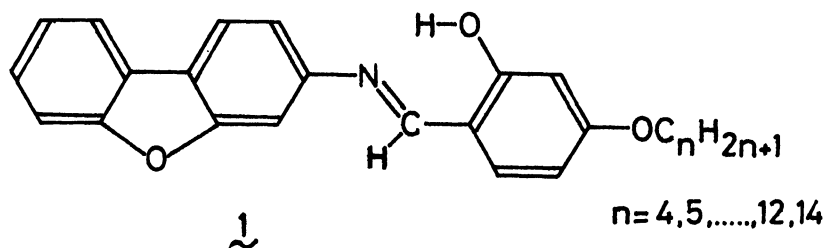
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3-(2-Hydroxy-4-alkoxybenzylideneamino)dibenzofurans(1) were found to be smectic C(S_C) mesogens, which do not contain an "alkyl-core-alkyl" type structure. This implies that the molecular symmetry as seen in the alkyl-core-alkyl structure is a favorable factor but not always required for the appearance of S_C phase and that an appropriate magnitude of the lateral dipole moment is required for the core moiety in the case of an unsymmetrical molecule.

A symmetrical "alkyl-core-alkyl" molecular structure and an appropriate magnitude of the lateral dipole moment are usually considered to be requisites for S_C liquid crystallinity.¹⁾ 2-(4-Alkoxybenzylideneamino)fluorenones(2), however, are known to show S_C phase.²⁾ These molecules have no symmetrical structure (a core-alkyl type), but have large dipole moments ascribable to the fluorenone moiety ($11.21 \times 10^{-30} \text{ C m}$ for fluorenone itself³⁾).

Recently, 3-(4-alkoxybenzylideneamino)dibenzofurans have been found to show no S_C phase, although ethoxy to tetradecyloxy derivatives of them show nematic phase and the longer homologous derivatives than a heptyloxy one show smectic A phase.⁴⁾ These dibenzofuran derivatives are analogous to 2, but their lateral dipole moments are small as compared with 2 because of the smaller dipole moment of dibenzofuran ($2.74 \times 10^{-30} \text{ C m}$ ³⁾). In this study, the title compounds were prepared and whether or not the S_C phase appears was investigated.



The phase transition temperatures are listed in Table 1. These values were determined by observing textures with a Nikon polarizing microscope.

Some homologues of 1 (pentyloxy to dodecyloxy) showed S_C phase. The S_C phase was identified by the miscibility test with terephthalidene-bis(4-butylniline) and the textures were Schlieren and broken-fan in homeotropic and homogeneous areas, respectively. All phase transitions of S_C - S_A and S_C -nematic were monotropic

Table 1. Phase Transition Temperatures (T/°C) of 1

n ^{a)}	T _{C-S_C,S_A, or N}	T _{S_C-S_A or N}	T _{S_A-N}	T _{N-I} ^{b)}
4	154.5			179.6
5	135.0	(113.9) ^{c)}		173.9
6	131.1	(115.7)		175.6
7	125.6	(123.5)	128.0	171.1
8	124.8	125.8	136.2	172.0
9	122.6	(118.4)	144.3	168.3
10	121.8	(117.3)	149.2	167.6
11	120.1	(106.6)	152.5	164.3
12	119.8	(101.6)	154.8	162.7
14	118.6		156.0	158.1

a) carbon number in the terminal alkoxy chain.

b) C:crystal, S_A:smectic A, S_C:smectic C, N:nematic and I:isotropic.

c) ():monotropic transition temperatures.

except for an octyloxy derivative.

The enthalpies of the S_C-S_A phase transition were too small to be detected by a differential scanning calorimeter (Daini Seikosha, model SSC-560S).

The introduction of a hydroxyl group in 2-site of the benzylidene moiety increases the lateral dipole moment, and consequently these compounds 1 come to show S_C phase. This result implies that the molecular symmetry is favorable but not always required for the appearance of S_C phase if the molecule has an appropriate magnitude of the lateral dipole moment.

The length of the terminal alkyl chain significantly affects the S_C-S_A and S_C-nematic phase transition temperatures. The octyloxy derivative has the highest value of the S_C-S_A transition temperature, which decreases with both longer and shorter alkyl lengths. This also implies that there must be a certain relation between the S_C-S_A or S_C-nematic phase transition temperatures and the length of the terminal alkyl chain.

References

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