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THE EFFECT OF THE ALKYL CHAIN LENGTH ON THE LIQUID CRYSTALLINE PROPERTIES OF P-SUBSTITUTED CHOLESTERYL 4-BENZOYLBENZOATES

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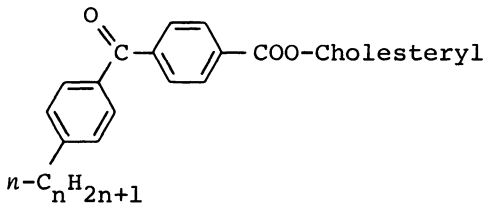
A homologous series of cholesteryl 4-(4'-*n*-C_nH_{2n+1}-benzoyl)benzoates (n=0-15) was prepared. Whereas these molecules have a large bent shape around the carbonyl group, all homologues show a cholesteric phase. In addition, the homologues with n=7-15 show two kinds of smectic phases. The effect on these mesophases of increasing the alkyl chain length is quite striking. Cholesteryl and benzophenone portions are indispensable for the mesomorphism.

Recently, we examined the mesomorphic properties of cholesteryl esters of arylbenzoic acids including such angular linkages as -CO-, -O-, -S-, and $-CH_2-$, indicating that benzophenone had a remarkable mesogenic power in spite of the bent structure.[1] In this connection, we are interested in the mesomorphic properties of cholesteryl 4-(4'-*n*-alkylbenzoyl)benzoates. The angular carbonyl group will move stepwise to the geometrical center of the molecule with increasing n, the number of carbon atoms of the 4'-*n*-alkyl group. Then one can expect that a chain elongation gives some informations about the angular effect on the mesomorphic phenomena. This paper describes the mesomorphic properties of a homologous series of cholesteryl 4-(4'-*n*-alkylbenzoyl)benzoates.



The thermal properties of cholesteryl 4-(4'-*n*-C_nH_{2n+1}-benzoyl)benzoates are summarized in Table 1 and Figure 1. With increasing n, the cholesteric-isotropic transition temperatures for the first four homologues go down rapidly without showing so-called 'odd-even' effect, and there is a tendency for the cholesteric-isotropic transition temperatures to give gradual decrease for the remaining homologues. The homologues with n=7-15 show two kinds of mesophases,

Table 1. Thermodynamic Data for Cholesteryl 4-(4'-*n*-C_nH_{2n+1}-benzoyl)benzoates.

n	T_{MP}	ΔH_{MP}	ΔS_{MP}	$T_{M_3-M_2}$ *3	T_{M_2-Ch} *4	T_{Ch-I} *5
0 *1	407.4	17.9	44.0	-	-	483.5
1 *2	431.5	17.9	41.4	-	-	479.1
2	452.2	29.9	66.0	-	-	466.3
3	447.5	28.5	63.6	-	-	(442.4)
4	440.5	26.0	58.9	-	-	442.7
5	435.7	39.3	90.2	-	-	435.7
6	424.5	24.6	57.6	-	-	426.3
7	402.6	2.4	6.0	421.3 *6	(415.8)	426.0
8	394.1	2.2	5.6	417.3 *6	(415.8)	423.0
9	362.3	5.9	16.4	413.1	413.1	420.2
10	279.8	5.0	17.9	403.2	408.2	415.2
11	314.0	5.1	16.2	406.0	409.1	414.6
13	351.1	7.7	21.9	401.1 *6	-	407.0
15	355.5	10.8	30.3	396.9	397.3	400.5

T, ΔH, and ΔS represent the transition temperature (K), enthalpy ($KJmol^{-1}$), and entropy ($JK^{-1}mol^{-1}$), respectively. Parentheses indicate monotropic metastable transitions. *1) This compound underwent a change in crystal form at 392.7 K. *2) This compound also underwent a change in crystal form at 423.3 K. *3) $\Delta S_{M_3-M_2}$ is ca. 67 $JK^{-1}mol^{-1}$. *4) ΔS_{M_2-Ch} is ca. 3.5 $JK^{-1}mol^{-1}$. *5) ΔS_{Ch-I} is ca. 1.5 $JK^{-1}mol^{-1}$. *6) T_{M_3-Ch}

namely, M_2 and M_3, which show isotropic and mosaic textures on cooling, respectively. The thermal stabilities of these mesophases also decrease with increasing n. As is evident from the plots of the transition temperatures against n (Figure 1), the feature is fairly different from those of cholesteryl alkanoates[5] and 4-alkoxybenzoates.[6] The thermal stabilities of crystalline phase go down with increasing n, producing a minimum at the homologue with n=10. Then there is a tendency for the thermal stabilities of crystalline phase to give an increase for the remaining homologues. The entropies for the M_2-Ch and Ch-I transitions are very small (ca. 3.5 and 1.5 $JK^{-1}mol^{-1}$, respectively), and are almost independent of n. Although the entropies for the M_3-M_2 transition (ca. 67 $JK^{-1}mol^{-1}$) acquire more than 70% of the total, they are also independent of n. As shown in Table 1, the entropies for the crystal-Ch or crystal-M_3 transition increase as a function of n. Thus, the effect on these mesophases of increasing the alkyl chain length is quite striking, and the roles of the long chain in these mesophases are assumed to be different from the ordinary ones.[7]

The M_2 phase is miscible with the smectic A phase of cholesteryl myristate.

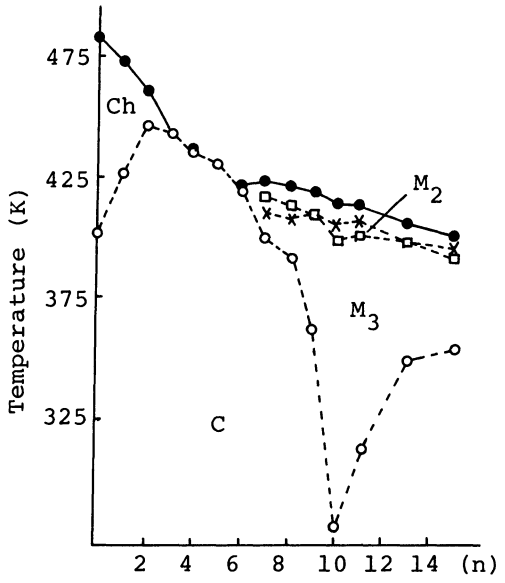
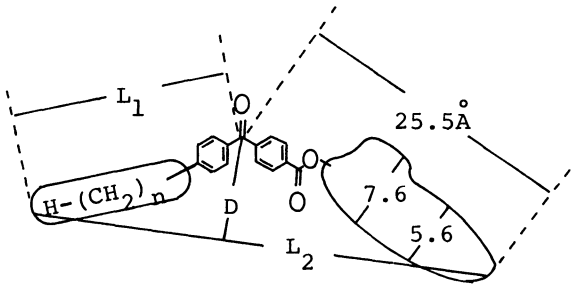


Figure 1. Plots of Transition Temperatures against n. Key; ●,Ch-I; ×,M_2-Ch; □,M_3-M_2 or Ch; ○,C-Ch, M_3, or I.



n	L_1 (Å)	L_2 (Å)	D (Å)
0	7	29	4
4	11	34	5
7	15	38	7
11	20	43	8
15	25	47	9

Figure2. Molecular Geometries.

To elucidate fluidlike molecular properties of the M_3 phase, the infrared absorption spectra and the X-ray diffractions of the undecyl derivative were studied. The infrared absorption bands between 1300 and 1250 cm^{-1} due to asymmetric stretching of C-(CO)-C and ester groups, and between 1180 and 1100 cm^{-1} due to symmetric stretching of these groups[8,9] become broad and their intensities become weak by rising temperature from 300 to 340 K, though many other bands were almost independent of temperature. These results clearly indicate that at the crystal-M_3 transition a restriction for a mobility around the carbonyl and ester groups is released and these portions of the molecules become disorganized.

The X-ray diagrams for the M_3 and M_2 phases of the undecyl derivative exhibit a characteristic pattern of the smectic phase, where the layer spacing calculated as 42.0-43.7 Å (±1.0 Å) throughout these phases.

The notable thermal properties should be concerned with the molecular shapes. A chain elongation brings about an increase in both molecular breadth (D) and length (L_2), as shown in Figure 2, where geometries are approximated by X-ray data[10,11] and measurements of the extended length of the molecular model, and values of the angle between the C-C bonds linking the carbonyl group for benzophenone is 122°.[11] The molecular length of the undecyl derivative is consistent with the layer spacing obtained from the X-ray diffraction studies. Therefore, we assume that molecules in the smectic phases arrange perpendicularly to the

smectic layer, and that they are considerably apart from each other due to wide molecular breadth. Under such circumstances, the short-range interactions between the alkyl chains recognized in ordinary mesogenic compounds[7] may be weak or negligible, and the alkyl chains have a flexibility. These assumptions are consistent with the fact that enthalpies and entropies for mesophase-mesophase and mesophase-isotropic phase transitions are almost independent of the chain length.

Considering the fact that benzophenones involving long alkyl and alkoxy groups exhibit no liquid crystalline property,[12] the steroid portion in this series must play significant roles in stabilization of the liquid crystalline phases. Indeed, replacement of a cholesteryl group of the tridecyl derivative with a β-sitosteryl results in a disappearance of the mesophases (T_{C-I}=389.6 K, ΔH=27.0 KJmol^{-1}). On the other hand, the undecyl derivative in which the carbonyl group has been replaced by the methylene group also show no mesophase (T_{C-I}=364.7 K, ΔH=30.5 KJmol^{-1}). Therefore, the mesogenic power of the benzophenone portion[13] is also indispensable for the mesomorphic phenomena.

As far as we know, the mesomorphism in bent molecules is very rare,[14] and further work on the interesting phenomena is underway.

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