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MESOMORPHIC PROPERTIES OF SOME CHOLESTERYL ARYLBENZOATES

Mitsuhiro KODEN, Shunsuke TAKENAKA, and Shigekazu KUSABAYASHI

Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

Cholesteryl esters of 4-benzoyl-, 4-phenoxy-,4-thiophenyl,4-benzyl-, 3-benzoyl-,3-benzylbenzoic acids were prepared. The thermal stability of the cholesteric mesophase is largely dependent on the molecular geometry and the electronic nature of the linkage, and decreases by the order of -CO- $>$ -O- $>$ -S- $>$ -CH_2-.

Many materials forming thermotropic liquid crystalline mesophase contain roughly rod-like molecular shape possessing various types of terminal groups, and a polar, usually conjugated, central linkage.[1] The most frequently used central groups for mesomorphic compounds are -C=C-, -COO-, -C=N-, -N=N-, and so on. On the contrary, functional groups such as -CO-, -O-, -S-, and -CH_2- are known to be a "non-mesogenic central group." In fact, mesogens involving these groups as a central group are very rare. This paper will describe the effect of the "non-mesogenic central group" on the thermal stability of the cholesteric mesophase.

Cholesteryl esters of some substituted benzoic acids were prepared by the standard method, and the thermal properties were summarized in Table I. I and II exhibit enantiotropic cholesteric mesophase with a streaked texture on heating and focal conic one on cooling, and a blue phase in the vicinity of the clearing point. III, V, and VI exhibit a monotropic mesophase with a sand-particle schlielen texture similar to that of a twisted smectic C phase.[2] Considering the latent heat for the transition,[3] the mesophase should be assigned to cholesteric one. I, II, and III frequently supercool and exhibit polymorphic phenomena in a crystalline state. Whereas it has been known that a substituent at the para position of benzoate derivative (VIII) results in increasing of the mesophase-isotropic transition temperature by more than 60°C,[4] the substituents at the para position (I to IV), rather, decrease it. Furtheremore, the mesophase of VII, a representative rod-like molecule is more stable than those of I to VI. These facts suggest that the crooked molecular geometry for I to VI is responsible for the rapid reduction of the mesophase thermal stability. In cases of V and VI,the conformational variation must be also taken into consideration. On the other hand, the mesophase thermal stability is also affected by the electronic nature of the

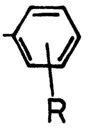
Cholesteryl-OOC-  R		Crystal-Cholesteric			Cholesteric-Isotropic			J^{A}_{22} of
		T °C	ΔH Kcal/mol	ΔS cal/mol/K	T °C	ΔH Kcal/mol	ΔS cal/mol/K	$(C_6H_5)_2X^a$
4-C_6H_5CO-	I	134.2	4.29	10.5	210.3	0.123	0.26	0.34
4-C_6H_5O-	II	154.3	7.48	17.5	176.5	0.071	0.16	0.18
4-C_6H_5S-	III	135.7	7.07	17.3	(91.5	0.044	0.12)^c	0.0
4-$C_6H_5CH_2$-	IV	173.5	8.73	19.6	-			-0.17
3-C_6H_5CO-	V	149.6	9.19	21.8	(71.7	0.035	0.10)^c	
3-$C_6H_5CH_2$-	VI	125.9	9.18	23.0	(51.2	0.081	0.25)^c	
4-C_6H_5-^{b}	VII	182.1	6.32	13.9	291.6	0.326	0.58	0.44
4-H^b	VIII	146.1	5.29	12.6	180.8	0.151	0.33	

Table I Thermodynamic properties of some substituted aromatic esters of cholesterol. The values were obtained by microscopic and DSC (Daini-Seikosha SSC-560) methods on the first or second heating. a; X corresponds to respective linkages. b; The values are slightly different from the reported ones.[4,5] c;Monotropic.

linkage, and decreases by the order of -CO->-O->-S->-CH_2-, where IV exhibits no mesophase. The decrease in the transition temperature is reflected on the decrease of the latent heat. In these crooked systems, therefore, an intermolecular interaction acts a significant role for the molecular alignment in the mesophase, and the molecular polarisability is dominative for the mesophase thermal stability. Recently, benzophenone and diphenyl ether derivatives have been predicted to exhibit the mesomorphic behaviour by Destrade et al.[6,7] from an examination of the angular correlation function, J^{A}_{22}. Certainly, the cholesteric-isotropic transition temperatures for I, II, III, and VII seem to be hyperbolically proportional to the J^{A}_{22} values(Table I).

References

1. G. W. Gray,"Molecular Structure and the Properties of Liquid Crystals",Academic Press, New York, N. Y., 1962, p 149
2. D. Demus and L. Richer, "Texture of Liquid Crystals", Verlag Chemie, New York, N. Y., 1978, p 186
3. R. S. Porter,E. M. Barrall II, and J. F. Johnson, Account Chem. Res.,2,53, 1969
4. E. M. Barrall II, K. E. Bredfeldt, and M. J. Vogel, Mol. Cryst. Liq. Cryst., 18 195, 1972
5. C. Wiegand, Z. Naturforschg., 4b, 249, 1949
6. C. Destrade, H. Gasparoux, and F. Guillon, Mol. Cryst. Liq. Cryst.,40.163, 1977
7. C. Destrade, ibid., 41, 161, 1978

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