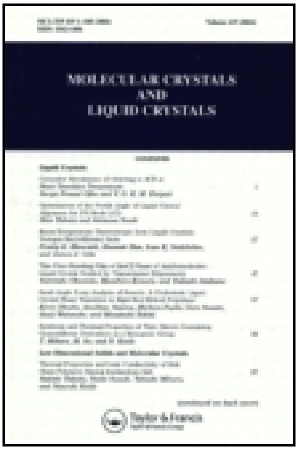

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Influence of the Angular Linkage on the Mesomorphic Properties of Cholesteryl Arylbenzoates

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Influence of the Angular Linkage on the Mesomorphic Properties of Cholesteryl Arylbenzoates

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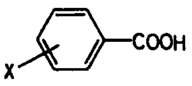
Some cholesteryl esters of arylbenzoic acids incorporating angular linkage such as —CO—, —O—, —S—, and —CH_2—, have been prepared, and the transition temperatures and heats have been determined. The cholesteric–isotropic transition temperatures are likely to correlate with the angular correlation parameters of these carboxylic acid moieties. The mesomorphic phenomena are discussed in terms of the molecular structure and electronic effect of these linkages.

INTRODUCTION

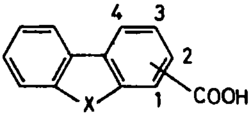
Early studies[1] suggested that compounds tend to form mesophases if their molecules are rod-shaped and possess polar terminal groups. The molecules need not be large or complex, and the requirements are met by simple compounds of general structure in which two para-phenylene rings are linked by a central group which frequently involves an unsaturated linkage, e.g., —CH=N—, —COO—, —N=N—, etc.

On the other hand, mesomorphic compounds incorporating angular linkages such as —CO—, —O—, —S—, and —CH_2—, remain fairly scarce,[2] because these linkages distort the molecular geometry from the required rod-shaped structure. Recently, we reported cholesteryl 4-benzoyl-, 4-phenoxy-, and 4-phenylthiobenzoates exhibited fairly stable cholesteric phase, in spite of the bent structure.[3] In this connection, we are interested in the mesomorphic properties of cholesteryl esters of aryl acids incorporating so-called "non-mesogenic" groups, as shown below. The work reported here was undertaken to provide new information contributing the relative importance of two factors, i.e., geometrical and electronic ones, for the mesophase stability. In the course of this work we have also prepared a number of new liquid crystalline materials that are of interest in their own right.



(A)

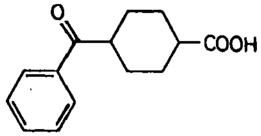
1; X = 4-C_6H_5CO-
2; X = 4-C_6H_5O-
3; X = 4-C_6H_5S-
4; X = 4-$C_6H_5CH_2$-
5; X = 4-C_6H_{11}CO-
7; X = 4-CH_3CO-
8; X = 4-C_6H_5-
9; X = 3-C_6H_5CO-
10; X = 3-$C_6H_5CH_2$-
11; X = 3-C_6H_5O-
12; X = 3-C_6H_5-
18; X = H



(B)

13; X = CO, 2-COOH
14; X = CH_2, 2-COOH
15; X = O, 2-COOH
16; X = O, 3-COOH
17; X = S, 3-COOH

6;



EXPERIMENTAL

Preparation of materials

3- And 4-benzoylbenzoic acids, and 4-cyclohexanoylbenzoic acid were prepared by sodium dichromate oxidation[4] of 3- and 4-methylbenzophenones, and 4-tolylcyclohexylketone, respectively. 4-Phenoxybenzoic acid, 4-phenylthiobenzoic acid, diphenyl-4-carboxylic acid, fluorenone-2-carboxylic acid, and dibenzothiophene-3-carboxylic acid were prepared by the acetylation reaction[5] of diphenyl ether, diphenyl sulfide, diphenyl, fluorene, and dibenzothiophene, followed by hypobromite oxidation[6] of the corresponding acetylated compounds, respectively. Trans-4-benzoylcyclohexane-carboxylic acid was prepared by the Friedel–Crafts reaction of benzene and trans-1,4-cyclohexanedicarboxylic acid chloride, followed by hydrolysis. Dibenzofurane-2-carboxylic acid[7] and 3-derivative[8] were kindly supplied by Dr. T. Keumi. 3- And 4-benzylbenzoic acids, and fluorene-2-carboxylic acid were prepared by hydrazine reduction[9] of 3- and 4-benzoylbenzoic acids, and fluorenone-2-carboxylic acid, respectively. 3-Phenoxybenzoic acid was obtained from Aldrich Chemical Co. 4-Acetylbenzoic acid was obtained from Tokyo Kasei Kogyo Co. Diphenyl-3-carboxylic acid was prepared by Grignard reaction[10] of 3-bromobiphenyl[11] with carbon dioxide. Cholesteryl esters were prepared by esterification between the acid chlorides which were prepared by the reaction of the corresponding acids with phosphorous pentachloride and cholesterol, from benzene and pyridine at room temperature during 10 hours.[12] Esters were purified by column chromatography on silica gel, followed by recrystallization from ethanol. Satisfactory elementary analyses were obtained, as follows.

Analytical data for the cholesteryl esters are given;

		Analytical values (%)			
Compound	Formula	Calculated		Found	
		C	H	C	H
1	$C_{41}H_{54}O_3$	82.78	9.15	82.67	9.14
2	$C_{40}H_{54}O_3$	82.43	9.34	82.22	9.39
3	$C_{40}H_{54}O_2S$	80.22	9.09	80.10	9.10
4	$C_{41}H_{56}O_2$	84.77	9.72	84.95	9.87
5	$C_{41}H_{60}O_3$	81.95	10.07	81.88	9.95
6	$C_{41}H_{60}O_3$	81.95	10.07	81.82	10.09
7	$C_{36}H_{52}O_3$	81.15	9.84	81.03	9.87
8	$C_{40}H_{54}O_2$	84.75	9.60	84.71	9.59
9	$C_{41}H_{54}O_3$	82.78	9.15	82.75	9.13
10	$C_{41}H_{56}O_2$	84.77	9.72	84.83	9.81
11	$C_{40}H_{54}O_3$	82.43	9.34	82.29	9.24
12	$C_{40}H_{54}O_2$	84.75	9.60	84.47	9.75
13	$C_{41}H_{52}O_3$	83.06	8.84	82.96	8.90
14	$C_{41}H_{54}O_2$	85.07	9.40	85.05	9.55
15	$C_{40}H_{52}O_3$	82.71	9.02	82.64	8.84
16	$C_{40}H_{52}O_3$	82.71	9.02	82.56	9.03
17	$C_{40}H_{52}O_2S$	80.49	8.76	80.31	8.77
18	$C_{34}H_{50}O_2$	83.21	10.27	83.02	10.25

Thermodynamic measurements

Identification of the mesophases was carried out using a Nikon polarizing microscope in conjunction with a Mettler FP 52 heated stage and control unit. Transition temperatures and enthalpies were measured using a Daini Seikosha SSC-560 differential scanning calorimeter (DSC). Indium was used as a calibration standard and the accuracy of the enthalpies is estimated as $\pm 10\%$. Entropy values were calculated using the equation, $\Delta S = \Delta H/T$.

Phase diagrams and "virtual" transition temperature

Mixtures of the two components were prepared by fusion and rapid cooling. The transition temperatures of the samples were then obtained with a polarizing microscope. The "virtual" transition temperature of

4 was found by extrapolation[13] from phase diagrams for binary mixtures with 1 or 2.

RESULTS

The transition temperatures along with enthalpy and entropy data for the phase transitions evaluated from DSC measurements are summarized in Tables I and II.

In Figure 1 is shown DSC curve for 1 obtained by heating a sample recrystallized from ethanol at 5 K/min as an example.

The endothermic peak at 392.7 K is due to crystal–crystal transition. Dewar *et al.* reported similar thermograms for cholesteryl 4-chloro- and 4-bromobenzoates.[14]

These compounds except for 4 exhibit mesomorphic properties. The cholesteric phase appeared in 1–8 except for 3 and 4, and 13–18 showed ordinary streaked and/or focal conic textures. On the other hand, 3 and 9–12 showed a texture similar to that for the smectic C phase of 4-(terephthaldiylidene-diamino)-bis-(L-2-methylbutyl α-methyl-cinnamate).[15] Then, we examined the miscibility relation of the mesophases between 9 and 1. As shown in Figure 2, the mesophase of 9 is completely miscible with the cholesteric phase of 1.

The direct measurement of the cholesteric–isotropic transition temperature for 4 was unable because of solidification even in rapid cooling. Then the "virtual" transition temperature[13] was evaluated from the miscibility diagram of state for binary mixture of 4 and 1 or 2. In both experiments the "virtual" transition temperature was close to 373 K (Figure 3).

These compounds exhibit somewhat complicating melting behavior, especially in 9–12. For example, cholesteryl 3-benzoylbenzoate, 9, exhibits three crystal forms. The recrystallized sample called here C_1 melts at 422.8 K, showing no crystal–crystal transition. Three crystal forms, C_1, C_2, and C_3 can be obtained by cooling the isotropic phase. C_1, C_2, and C_3 melt at 422.8, 401.3, and 385.7 K, respectively. The $C_3 \rightarrow C_2$, $C_3 \rightarrow C_1$, and $C_2 \rightarrow C_1$ transitions were not observed microscopically. In some cases, the transition such as $C_3 \rightarrow I \rightarrow C_2 \rightarrow I \rightarrow C_1 \rightarrow I$, i.e., triple melting behavior, was observed. These polymorphism in solid state are also recognized in 4-substituted compounds. The polymorphism is represented by the idealized free energy-temperature diagrams, as shown in Figure 4.

In this connection, we examined the melting behavior for the carboxylic acids of 9–11. The melting points for 3-benzoyl, 3-benzyl, and

TABLE I

Thermodynamic properties of some cholesteryl esters of (A) series

Compound	$T_{\text{C—I}}$ K	$\Delta H_{\text{C—I}}$ kJ mol^{-1}	$\Delta S_{\text{C—I}}$ JK^{-1} mol^{-1}	$T_{\text{C—Ch}}$ K	$\Delta H_{\text{C—Ch}}$ kJ mol^{-1}	$\Delta S_{\text{C—Ch}}$ JK^{-1} mol^{-1}	$T_{\text{Ch—I}}$ K	$\Delta H_{\text{Ch—I}}$ kJ mol^{-1}	$\Delta S_{\text{Ch—I}}$ JK^{-1} mol^{-1}
1*[1]				407.4	17.95	44.06	483.5	0.50	1.03
2*[2]				427.5	30.75	71.93	449.7	0.29	0.62
3	408.9	29.58	72.34				(364.7	0.17	0.47)
4	446.7	36.78	82.28				[373	—	—]
5	482.1	36.82	76.37				(478.0	0.72	1.51)
6*[3]				450.7	37.09	82.29	490.8	0.67	1.37
7				454.9*[4]	25.56	56.19	529.5	1.13	2.13
8*[5]				455.3	26.44	58.07	564.8	1.38	2.44
9	422.8	38.45	90.94				(344.9	0.17	0.49)
10	397.4	36.69	92.33				(324.4	0.34	1.05)
11	407.0	40.84	100.30				(326.9	0.46	1.41)
12	412.9	29.16	70.62				(348.2	—	—)
18*[6]				418.8	22.13	52.84	457.8	0.63	1.38

All transition temperatures were evaluated from the onset of the DSC peak. C—I = crystal–isotropic transition, C—Ch = crystal–cholesteric one. Ch—I = cholesteric–isotropic one.

*[1] This compound underwent a change in crystal form at 392.7 K (ΔH = 15.00 kJ mol^{-1}, ΔS = 38.20 JK^{-1} mol^{-1}).

*[2] This compound also underwent a change in crystal form at 416.3 K (ΔH = 2.77 kJ mol^{-1}, ΔS = 6.53 JK^{-1} mol^{-1}).

*[3] This compound showed a monotropic smectic phase ($T_{\text{S—Ch}}$ = 379.0 K).

*[4] This peak involved a shoulder at ca. 452 K.

*[5] C. Wiegand (*Z. Naturforsch.*, **4B**, 249 (1949)) gives $T_{\text{C—Ch}}$ = 454 K and $T_{\text{Ch—I}}$ = 563 K.

*[6] This compound underwent a change in crystal form at 409.9 K (ΔH = 5.94 kJ mol^{-1}, ΔS = 14.49 JK^{-1} mol^{-1}). The thermodynamic data are slightly different from the reported values (M. J. S. Dewar and A. C. Griffin, *J. Chem. Soc.*, Perkin II, 713 (1976)). (); monotropic transition. []; "virtual" monotropic transition.

TABLE II

Thermodynamic properties of some cholesteryl esters of (B) series

Compound	T_{C-Ch} or C—S K	ΔH_{C-Ch} or C—S kJ mol^{-1}	ΔS_{C-Ch} or C—S JK^{-1} mol^{-1}	T_{S-Ch} K	ΔH_{S-Ch} kJ mol^{-1}	ΔS_{S-Ch} JK^{-1} mol^{-1}	T_{Ch-I} K	ΔH_{Ch-I} kJ mol^{-1}	ΔS_{Ch-I} JK^{-1} mol^{-1}
13	454.0	7.20	15.86	468.5*[1]	15.23	32.44	537.9*[2]	—	—
14	439.7	14.14	32.16	458.0	27.20	59.39	577.8	1.05	1.82
15	464.5	9.58	20.62	471.4	13.22	28.04	571.8	0.96	1.68
16	464.2	32.47	69.95				492.2	0.67	1.36
17	422.3	26.86	63.60				478.2	0.50	1.05

See footnote in Table I.

*[1] This transition involved one more transition at ca. 466 K.

*[2] This compound gradually decomposed above 520 K.

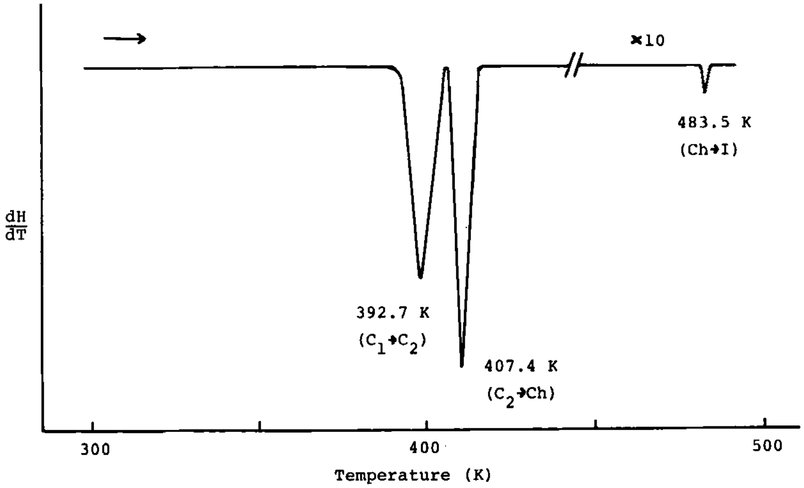


FIGURE 1 Thermogram of cholesteryl 4-benzoylbenzoate, 1, recrystallized from ethanol. Scan speed 5 K/min.

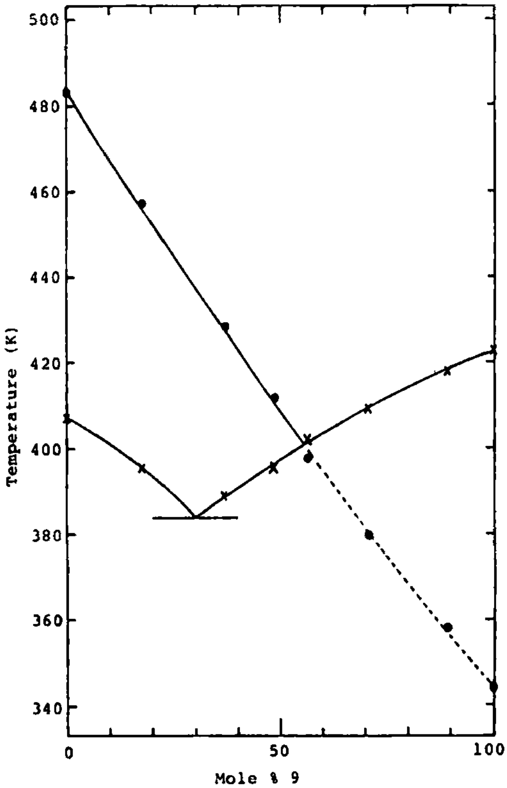


FIGURE 2 The binary phase diagram for 1 and 9.

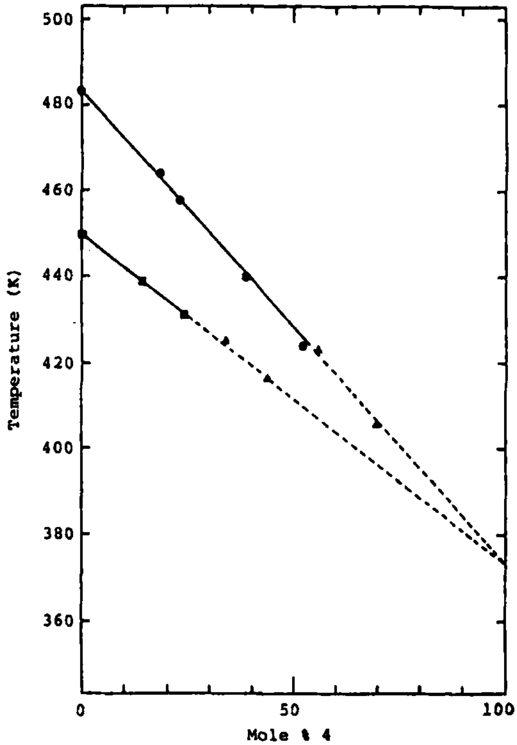
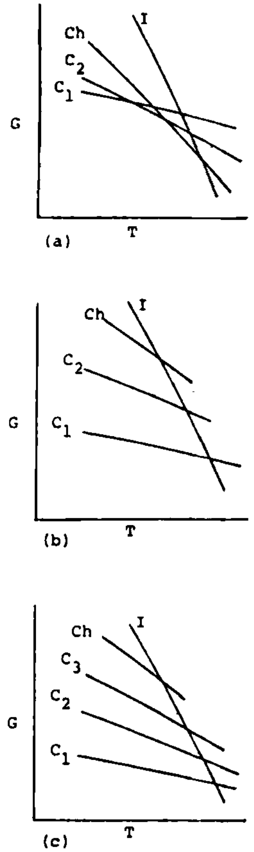


FIGURE 3 Cholesteric–isotropic transition lines in the binary phase diagrams for (a) 4 and 1 (●, ▲) and (b) 4 and 2 (■, ▲). In each case the points ●, and ■ denote reversible transitions and the others (▲) monotropic ones.

3-phenoxybenzoic acids are 438, 379, and 418 K (peak tops of the DSC curves), respectively, and the similar plural melting phenomena were not recognized. However, 3-(4′-toluoyl)benzoic acid exhibits complicating phase change, where at least three melting points at 427, 435, and 437 K are observed in addition to the change in crystalline form at ca. 413 K. Similarly, 3-(3′-toluoyl)benzoic acid also exhibits three melting points at 417, 430, and 449 K.

DISCUSSION

An important subject in this paper is to try to relate the change in the thermal stability of the cholesteric phase to changes in molecular structure and electronic nature. For the convenience, the geometries and electronic natures for diphenyl compounds linked by a single atom are summarized in Table III.



	$T_{C_1-C_2}$ (K)
1	392.7
2	416.3
18	409.9

	T_{C_2-I} (K)
3	388.2
12	-

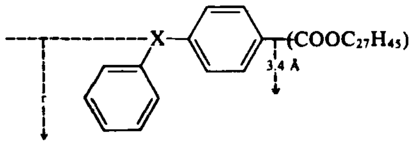
	T_{C_3-I} (K)	T_{C_2-I} (K)
9	385.7	401.3
10	344.2	389.3
11	332.8	404.4

FIGURE 4 Idealized free energy-temperature diagrams, along with transition temperature data which are not indicated in Tables I and II. Slope differences are in some instances exaggerated for clarity: (a) 1, 2, and 18; (b) 3 and 12; (c) 9, 10, and 11.

They intrinsically possess the angular shape and considerable thickness due to non-bonded repulsive interactions between the ortho hydrogens, though the resonance interactions between the aromatic rings and the linkage will tend to make CO, O, and S molecules more coplanar than the CH_2 molecule. Furthermore, rotation of the terminal aryl rings produces a formation of many conformational isomers. In the case of cholesteryl 3-benzoylbenzoate, for example, four extreme isomers are illustrated as shown in Figure 5.

These isomers will be energetically equivalent in the isotropic medium because the benzoyl group is far apart from the cholesteryl moiety. The parallel arrangement of molecules in the cholesteric phase, on the other hand, will favor energetically A and B isomers. If this effect

TABLE III



X	r[*1] (Å)	Molecular polarizability (CC)	Dipole moment (D)	J_{22}^{A}[*6]
CO	5.8	243.6[*2]	3.02[*2]	0.30
O	5.8	80.3[*3]	1.10[*3]	0.18
S	6.6	107.2[*4]	1.46[*4]	0
CH_2	6.2	59.3[*5]	0.2[*5]	−0.17

[*1] The radius involving the van der Waals one were evaluated from the reported values (E. B. Fleischer, N. Sung and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968). N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, **70**, 1564 (1948). F. K. Fong, *J. Chem. Phys.*, **40**, 132 (1964).).

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[*6] See Ref. 18 in the text.

were large enough for 9 to exist exclusively as A and B isomers under these conditions, there would be a decrease in entropy of Rln2, i.e., 5.77 JK^{-1} mol^{-1}, on passing from the isotropic liquid to the cholesteric phase. Since the observed values of ΔS_{Ch-I} for 9–12 are far smaller than the expected value, tendency for particular isomers to be favored in the cholesteric phase must be quite small. A similar explanation (also using ΔS_{N-I}) was proposed by Dewar *et al.* for conformational equilibrium of bis-p-methoxyphenyl terephthlate.[16] Then the isomers C and D are assumed to disturb the parallel arrangement of molecules and decrease the mesophase stability. In solid state, on the other hand, these isomers will be distinguishable each other, and the conformational equilibrium produces different kinds of crystalline forms, similar to the melting behavior of glycerides.[17] Then the polymorphism in solid state or plural melting behavior for 9–11 and 3-(4′-toluoyl)- and 3-(3′-toluoyl)benzoic acids should be concerned with the conformational isomerism.

The cholesteric–isotropic transition temperatures decrease by the order of 13–15 > 7–8 > 16–17 > 1–6 > 9–12, indicating that the structural factors such as rigidity and linearity are of the primary importance for the mesophase stability. Indeed, the bent shape in the termi-

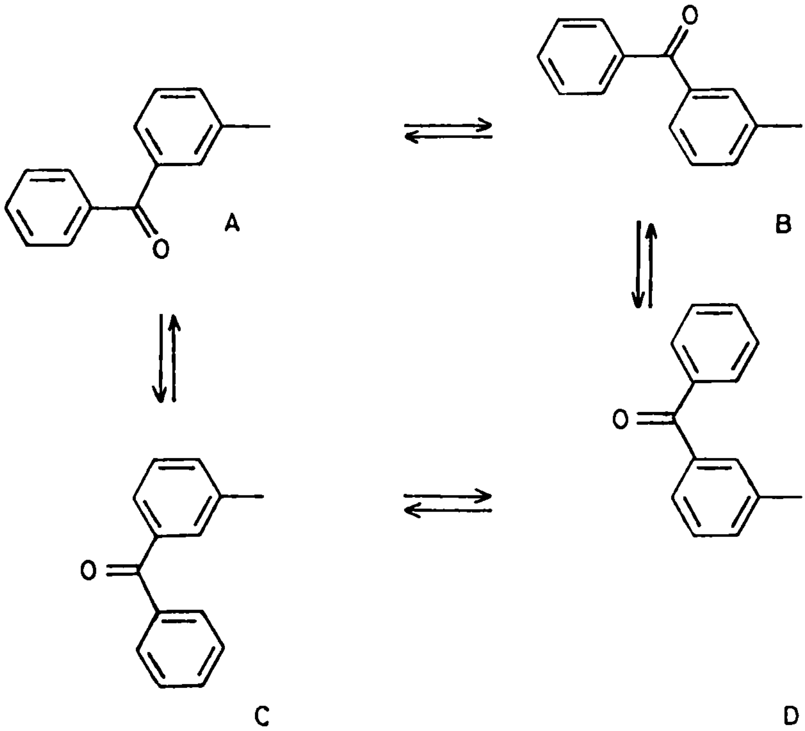

FIGURE 5 Diagrammatic representation of four extreme isomers in the case of cholesteryl 3-benzoylbenzoate.

nal portion of molecule appears to be of the primary cause of decreased mesophase stability for 1–6 and 9–12. The cholesteric–isotropic transition enthalpies for 1–6, 9–12, and 16–17, possessing bent shape are relatively smaller than those for the other compounds. This indicates that the bent shape gives rise to intermolecular separation and decreases intermolecular attraction in the cholesteric phase. As is evident from the comparison of 5 with 7, however, replacement of the methyl group at 4 position of the aromatic ring by cyclohexyl one results in decrease in the cholesteric–isotropic transition temperatures by only 50 K. Whereas the molecular geometries of 1–4, on the other hand, are quite similar each other (see Table III), the cholesteric–isotropic transition temperatures for 1–4 vary from ca. 360 to 480 K. This variation is far larger than the difference between the cholesteric–isotropic transition temperatures for 5 and 7. These facts suggest that the mesophase stability is strongly dependent on the electronic effect of the carboxylic acid moiety rather than the steric effect. Our trouble is that 1, 5, and 6 have the similar cholesteric–isotropic transition temperature. It may be noted that the replacement of phenyl ring with cyclohexyl ring results in increases in ΔH_{Ch-I} and ΔS_{Ch-I}, though this replacement would decrease the polarizability of molecule. This may imply that the cyclohexyl ring is favorable for the molecular packing in mesophase compared with the phenyl ring.

Recently, Destrade *et al.* provided a close relation between the angular correlation parameter, J_{22}^{A}, measured by means of depolarized Rayleigh scattering and the mesogenic power of several central rigid cores.[18] The J_{22}^{A} values for several diphenyl compounds are listed in Table III. The angular correlation parameter is formulated by

$$J_{22}^{A} = \frac{1}{2} Z < 3\cos^2\theta - 1 >$$

where θ is the angle between the symmetric axes of the molecules with its Z neighbors. This formalism is quite analogous to the order parameter in the nematic liquid crystal. The plot of the cholesteric–isotropic transition temperatures versus the J_{22}^{A} values[18] is shown in Figure 6.

The cholesteric–isotropic transition temperatures for the 4-substituted series, 1–4 and 8, are likely to correlate with the J_{22}^{A} values. In addition, ΔH_{Ch-I} for 1–3 and 8 are related to the J_{22}^{A} values. These facts indicate that the electronic effect of the carboxylic acid moiety is responsible for the intermolecular attraction in the cholesteric phase and for the mesophase stability.

The thermal stability of the mesophase for the 3-substituted series, 9–12, is comparatively low perhaps due to their geometrical disadvantage and/or conformational variation as shown in Figure 5. The cholesteric–isotropic transition temperatures are slightly dependent on the J_{22}^{A} values. This fact indicates that the electronic effect of the carboxylic acid moiety is of the secondary importance for the enhancement of the mesophase stability.

Although biphenyl compounds, 8 and 13–15, exhibit relatively stable mesophase due to their rigid and linear structures, the transition temperatures lack correlation with the J_{22}^{A} values. Since two phenyl rings are directly combined and X locates at the 3 position with respect to the carbonyl group, the electronic effect of X would scarcely increase the polarizability anisotropy of the molecules. Rather the steric effect of X decreases the mesophase stability as mentioned by Gray *et al.*[19] Although 16 and 17 have the similar structural characteristics, the cholesteric–isotropic transition temperatures are expected to depend on the J_{22}^{A} values (Figure 6). This would be attributed to the fact that X locates at the 4-position with respect to the carbonyl group.

Considering the large mesogenic power for benzophenone and di-

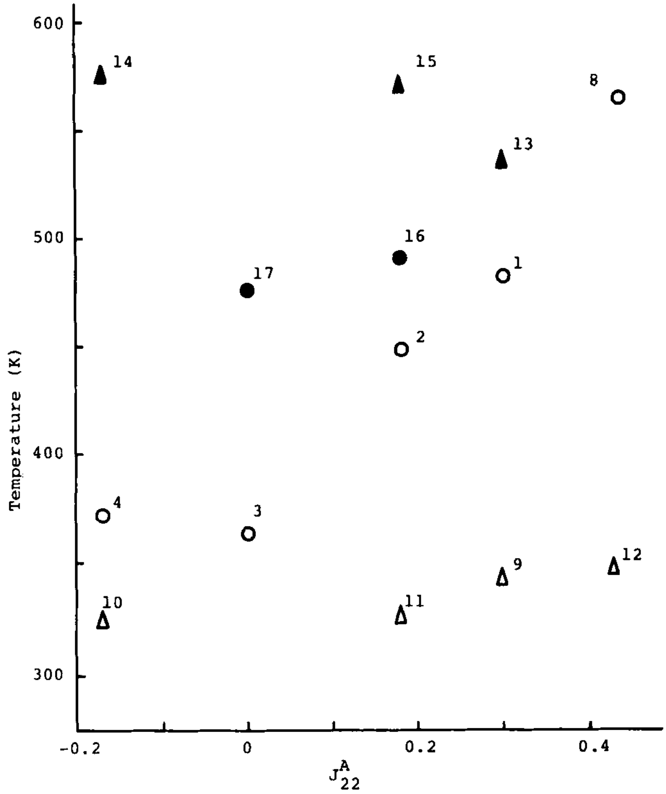

FIGURE 6 Relation between the cholesteric–isotropic transition temperatures and the J^A_{22} value of the core $C_6H_5—X—C_6H_5$. ○, 4-substituted series (1–4 and 8); △, 3-substituted series (9–12); ●, biphenyl series with X at 4-position with respect to the ester group (16 and 17); ▲, biphenyl series with X at 3-position with respect to the ester group (13–15).

phenylether, it may be rather strange that mesogenic compounds incorporating these skeletons are very rare. Further examinations of the validity of the J^A_{22} is underway.

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