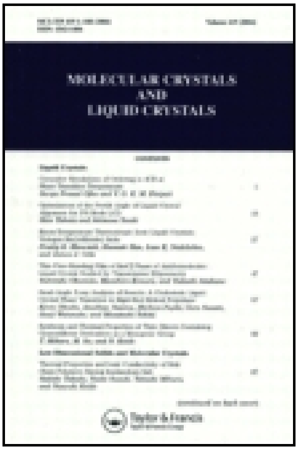

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Liquid Crystals VIII.[1,2] The Mesomorphic Behavior of Some Optically Active Aromatic Schiff's Bases†

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A series of optically active aromatic Schiff's bases containing p-alkoxy and p-acyloxy groups were prepared and their mesomorphic properties were studied. Chirality was achieved by introducing an asymmetric carbon atom into the hydrocarbon chain of either the alkoxy or acyloxy group. Thus, 4-*active*-alkoxybenzylidene-4′-aminophenyl acylates, 4-*active*-alkoxybenzylidene-4′-aminobenzonitriles and bis-(4′-*active*-alkoxybenzylidene)-2-chloro-1,4-phenylenediamines were synthesized. Most of the compounds exhibited both smectic and cholesteric mesomorphism. Several compounds showed only cholesteric behavior. For example, S(+)-4-methoxybenzylidene-4′-aminophenyl p-methylpentanoate was cholesteric between 41 and 78°C. By comparison, the racemic mixture of R and S enantiomers of this compound was nematic between 36 and 78°C.

INTRODUCTION

The previous papers in this series were devoted to the preparation of nematic compounds which exhibit their properties at or below room temperature. In the

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present work, our objective is to prepare nonsteroidal compounds which exhibit cholesteric mesomorphism over a broad temperature range. We accomplished this by incorporating an asymmetric carbon atom (i.e., an atom bonded to four different atoms or groups) into the side chain of alkoxy or acyloxy groups attached to an aromatic Schiff's base nucleus. The resulting compounds were optically active (i.e., chiral) and exhibited the cholesteric mesophase.

Most studies of the properties of cholesteric liquid crystals have been conducted with steroidal-type molecules (e.g., derivatives of cholesterol, stigmasterol, sitosterol, etc.). In many of these studies,[3-5] structure-property relationships were determined. Since so few nonsteroidal, "cholesteric" liquid crystals are known,[6-9] it has not been possible to establish such relationships for this class of compounds. Hence, it seemed desirable to prepare a variety of these compounds in order to obtain structure-property correlations. In this study, we determined the variation of mesomorphic thermal stability as a function of the distance between the asymmetric carbon atom and the dipolar terminal group. In a subsequent paper, we will discuss the electro-optic properties of some of these compounds.

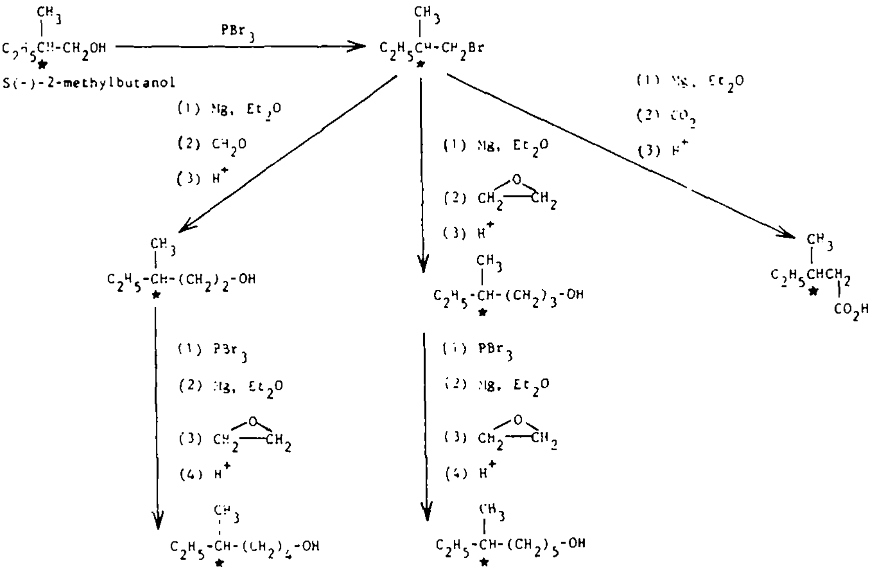
EXPERIMENTAL†

A. Materials

(1) Optically Active Aliphatic Alkyl Bromides S(-)-2-methyl-butanol ($[\alpha]_D^{24} = -5.72°$) was purchased from Eastman Organic Chemicals and treated with phosphorus tribromide to give S(+)-1-bromo-2-methyl-butane.[10] The Grignard reagent was prepared using the bromide, magnesium turnings and anhydrous diethyl ether, and it was treated with formaldehyde, ethylene oxide or carbon dioxide by the standard methods.[11] The higher homologous alcohols obtained in this manner were distilled to a constant boiling point and they were converted to the respective bromides by treatment with phosphorus tribromide. Repeating the above procedure in successive manner yielded the still higher homologous alkyl bromides (Scheme I). The physical constants of these optically active alkanols and the corresponding alkyl bromides were in agreement with those reported in the literature.[12]

2) Optically Active p-Alkoxybenzaldehydes p-Hydroxy-benzaldehyde (Eastman Organic Chemicals) was treated with the respective alkyl bromide and anhydrous potassium carbonate in cyclohexanone by the known method.[13] After evaporation of the solvent, the residue was taken up in diethyl ether and the resulting solution washed with 0.5N sodium hydroxide solution, followed by washings with saturated sodium chloride solution. The ethereal solution was dried (Anhyd. Na_2SO_4), filtered and evaporated to dryness to give a light yellow oil, which was distilled under vacuum. The pure optically active p-alkoxybenzaldehydes (Scheme

SCHEME I

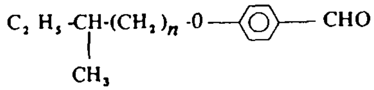


* Asymmetric Carbon Atom

II) were colorless (single spot in TLC, Silica Gel/Chloroform) and had the physical constants shown in Table 1.

TABLE I

Physical Constants of Active *p*-Alkoxybenzaldehydes



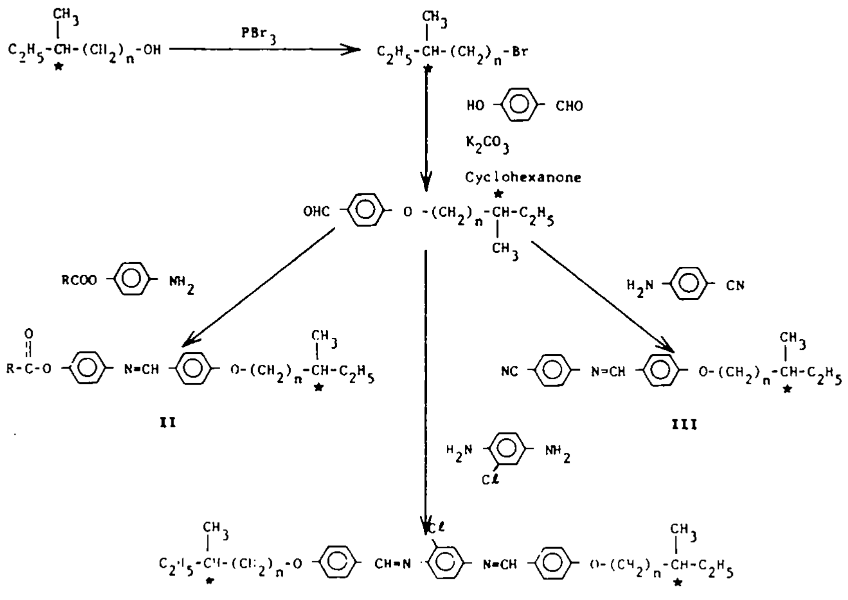
	n				
	1	2	2	4	5
Specific Rotation					
$[\alpha]_D^{25}$	+5.13	+9.86°	+7.40°	+6.16°	+5.71°
b.p., °C	113-15	120	128-9	133-5	139-41
(mm Hg)	(0.09)	(0.10)	(0.08)	(0.08)	(0.06)
d_4^{25}	1.0152	0.9975	0.9866	0.9798	0.9731

3) Schiff's Bases. Equimolar quantities of an optically active p-alkoxybenzaldehyde and a corresponding amine were dissolved in anhydrous ethanol and refluxed for 30-60 min. The reaction mixture was cooled and the crystals which separated were collected and recrystallized several times (either from ethanol or isopropanol) until sharp reproducible transition temperatures were obtained. The infrared and NMR spectra of these Schiff base compounds (Scheme II) confirmed the assigned structures.

B. Determination of transition temperatures

Transition temperatures were determined with both a Thomas-Hoover melting point apparatus and a differential scanning calorimeter (DuPont Model 900 Thermal Analyzer). In the latter case, sample sizes were between 5 and 15 mg while the heating rate was 10°C per min. The materials were contained in hermetically sealed aluminum cups. The transition temperatures were reproducible within 1°C. A Bausch and Lomb polarizing microscope equipped with a hot stage was used to identify the various mesophases.

SCHEME II



* Asymmetric Carbon Atom

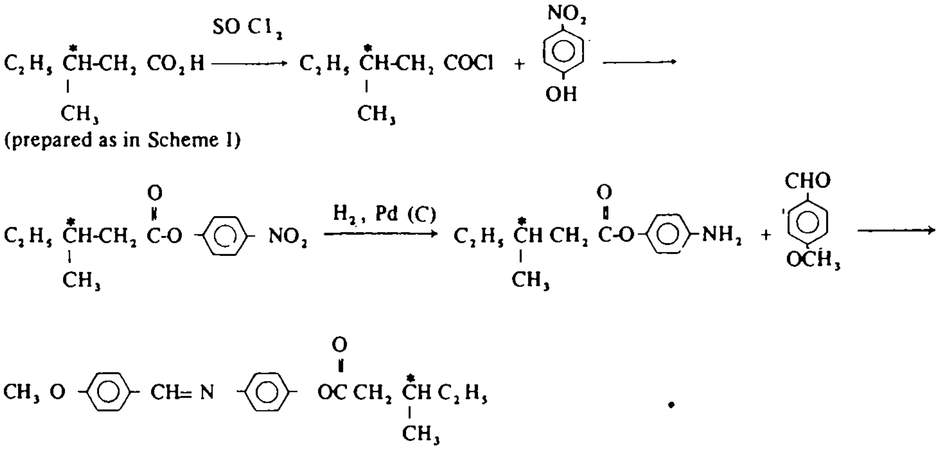
C. Determination of specific rotation

Specific rotation was determined with a Zeiss (.01°) Circle polarimeter using a 4-dm. cell.

RESULTS AND DISCUSSION

An optically active compound may be prepared either by separating the optical enantiomers from a racemic mixture (a mixture of equal proportions of the left and right handed forms), or by synthesizing the compound from an optically active intermediate. We rejected the former method because it is a difficult and tedious one generally requiring a number of time consuming recrystallizations of an adduct of the compound in question with some other optically active material. The latter method is much simpler but it is limited to compounds which can be prepared from the rather scarce number of desirable optically active intermediates. Fortunately, the availability of S-(-)-2-methylbutanol enabled us to prepare a number of useful optically active intermediates and subsequently to synthesize a variety of optically active liquid crystalline compounds.

Since we had previously prepared the racemic mixture of enantiomers of 4-methoxybenzylidene-4′-aminophenyl β-methylpentanoate[14] which has a nematic range of 36 to 78°C, our first effort involved the independent preparation of one of the enantiomers. This was accomplished by the following sequence of reactions:



I, $[\alpha]_D^{23} = +6.02°$

Since the absolute configuration of (-)2-methyl-1-butanol has been determined chemically [15] (by relating it to S(-)-glyceraldehyde) and since the reactions outlined above and in Scheme I do not involve reactions which would cause inversion of configuration at the asymmetric carbon atom (in fact, less than 10% racemization was found [10] for the sequence alcohol→bromide → Grignard → alcohol), we can safely state that compound I has the S configuration. I was found to be a white solid which melted at 41°C to form a turbid, off-white liquid. A faint iridescence could be seen at certain angles of reflected light. The cholesteric mesophase was found to exist between 41 and 78°C. The higher melting point of the S enantiomer relative to the racemic mixture was not unusual since the latter is a mixture of the R and S antipodes.

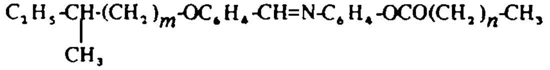
Our success with the preparation of I prompted us to prepare three series of optically active compounds which we expected to exhibit cholesteric mesomorphism: 4-alkoxybenzylidene-4'-aminophenyl acylates (II), 4-alkoxybenzylidene-4'-aminobenzonitriles (III), and bis-(4'-alkoxybenzylidene)-2-chloro-1,4-phenylenediamines (IV) (Scheme II).

1. *4-Active-Alkoxybenzylidene-4'-Aminophenyl Acylates (II).* All 35 compounds in this series (Table 2) exhibited cholesteric mesomorphism, most with only a faint iridescence. As usual, smectic mesomorphism predominated as the length of the hydrocarbon chain increased. However, when the transition temperatures of several of the compounds are plotted against the number of carbon atoms in the side chains, some interesting trends are noted. In one example (Fig. 1), the acyloxy chain is kept short (2 carbon atoms attached to a carbonyl group) while the number of methylene groups separating the asymmetric carbon atom from the ether osygen is increased from one to five. Note that both the smectic and cholesteric mesomorphic thermal stabilities rise as the chain length increases. This phenomenon has been observed in other series of compounds which showed smectic and nematic behavior.[16] In the present case, the terminal interactions are actually *increased* with increasing chain length because the dipolar oxygen atom becomes less shielded by the bulky sec-butyl group. Similar results have been found in a series of racemic mixtures of p-alkoxybenzylidene-p-aminophenyl methyl acylates.[14] As the chain branch in the ester portion of the molecules of these compounds became further separated from the carbonyl group, nematic thermal stability increased.

When the sec-butyl group is kept at a distance from the ether oxygen such that cholesteric thermal stability is high ($m = 4$), an increase in the chain length of the ester portion results in increased smectic thermal stability but little change in cholesteric thermal stability (Fig. 2). This is a common pattern for homologous series of mesomorphic compounds.[6]

TABLE 2

Transition Temperatures of *p*-Active-alkoxybenzylidene-*p*′-phenyl Acylates



$$C_2H_5\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}(CH_2)_m\text{-}OC_6H_4\text{-}CH{=}N\text{-}C_6H_4\text{-}OCO(CH_2)_n\text{-}CH_3$$

Compound	*m*	*n*	m.p°C	S_3S_2	S_2S_1	S_1CH	CHI
1	1	0	70.0				56.0
2	1	1	66.0				66.0
3	1	2	75.0				71.0
4	1	3	70.0				66.0
5	1	4	78.0				71.0
6	1	5	65.0				59.0
7	1	6	68.0				65.0
8	2	0	72.0				55.0
9	2	1	63.0				66.0
10	2	2	65.5				70.5
11	2	3	65.5			64.0	66.5
12	2	4	65.5			61.5	72.0
13	2	5	66.5			59.5	69.0
14	2	6	64.5			61.0	74.0
15	3	0	73.0			67.3	74.1
16	3	1	70.0			72.6	84.2
17	3	2	79.0			81.5	86.8
18	3	3	53.0			85.2[a]	
19	3	4	64.0			85.4	87.3
20	3	5	61.1			83.9	85.5
21	3	6	65.0		81.0	86.5	89.2
22	4	0	67.3			55.5	72.5
23	4	1	40.6			60.9	81.9
24	4	2	49.4			63.7	83.1
25	4	3	36.9			74.2	79.5
26	4	4	46.3		74.5	77.0	83.6
27	4	5	46.5	72.5	73.5	78.6	82.1
28	4	6	57.2	66.6	72.0	81.8	85.1
29	5	0	69.1		69.2	70.7	83.4
30	5	1	53.9	80.2	81.2	82.5	92.0
31	5	2	36.5	$\frac{!}{\mathrm{m}}$	85.4	87.3	94.3
32	5	3	<20[b]	$\frac{!}{\mathrm{m}}$	86.2	89.2	89.7
33	5	4	51.5	84.2	85.4	92.3	93.2
34	5	5	57.6	83.4	86.7	93.4[a]	$\frac{!}{\mathrm{m}}$
35	5	6	52.3	81.8	86.5	97.0[a]	$\frac{!}{\mathrm{m}}$

(a) Smectic I --- Isotropic transition

(b) Smectic at room temperature

S_3S_2 ; S_2S_1 ; are inter-smectic transitions

S_1CH; Smectic I ←→ cholesteric transition

CHI; Cholesteric ←→ Isotropic transition

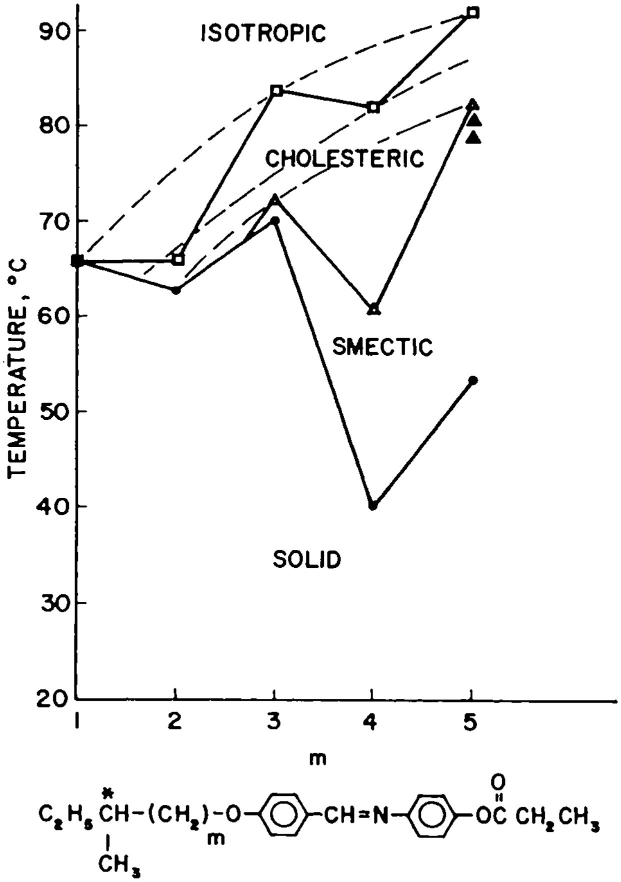


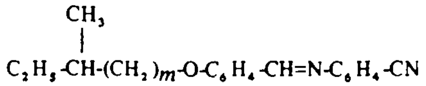
FIGURE 1 Phase transition plot for 4-active-alkoxy-benzylidene-4′-aminophenylpropionates; –●– melting points, ▲ smectic–smectic, –△– smectic–cholesteric, –□– cholesteric–isotropic transitions.

2. *4-Active-Alkoxybenzylidene-4′-Aminobenzonitriles (III)*. Four out of the five compounds in this series exhibited cholesteric mesomorphism (Table 3). As with series II, both the smectic and cholesteric thermal stabilities rose as the distance between the asymmetric center and the ether oxygen atom increased (Fig. 5). This was further evidence for increased terminal interactions as a result of deshielding of the ether oxygen by the sec-butyl group.

3. *Bis-(4′-Active-Alkoxybenzylidene)-2-Chloro-1,4-Phenylenediamines (IV)*. The compounds of this series (Table 4) had very broad cholesteric temperature

TABLE 3

Transition Temperatures of *p*-Active-alkoxybenzylidene-*p*'-aminobenzonitriles



$$C_2H_5\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}(CH_2)_m\text{-}O\text{-}C_6H_4\text{-}CH{=}N\text{-}C_6H_4\text{-}CN$$

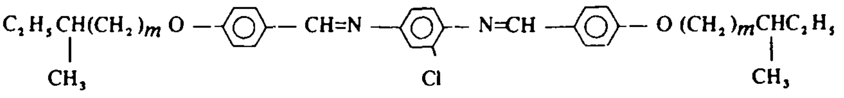
m	m.p°C	S–Ch	Ch–I
1	57.0	-----	39.0[a]
2	63.0	-----	50.0[a]
3	40.0	48.0	66.0
4	55.0	59.0	66.5
5	34.0	77.0[b]	-----

S–Ch: Smectic-Cholesteric Transition
Ch–I: Cholesteric-Isotropic Transition
[a] Monotropic with respect to its melting point
[b] The transition was smectic to isotropic

ranges. Again, both the smectic and cholesteric thermal stabilities rose as the asymmetric center became further separated from the ether oxygen atom.

TABLE 4

Transition Temperatures of Bis-(4'-active-akloxybenzylidene)-
2-chloro-1,4-phenylene-diamines



Compound	*m*	*mp*	S–Ch	Ch–I
–	1	70	–	113
–	2	55	–	141.5
36	3	50	43.5[a]	146
37	5	29	94.4	146.5

(a) Monotropic transition

Compound 36 had a cholesteric range of nearly 100°C. It was a yellow material with a viscous cholesteric mesophase which exhibited bright iridescence. The smectic mesophase had an optical rotation of -25,000 degrees/mm at room temperature (450 nm).[17]

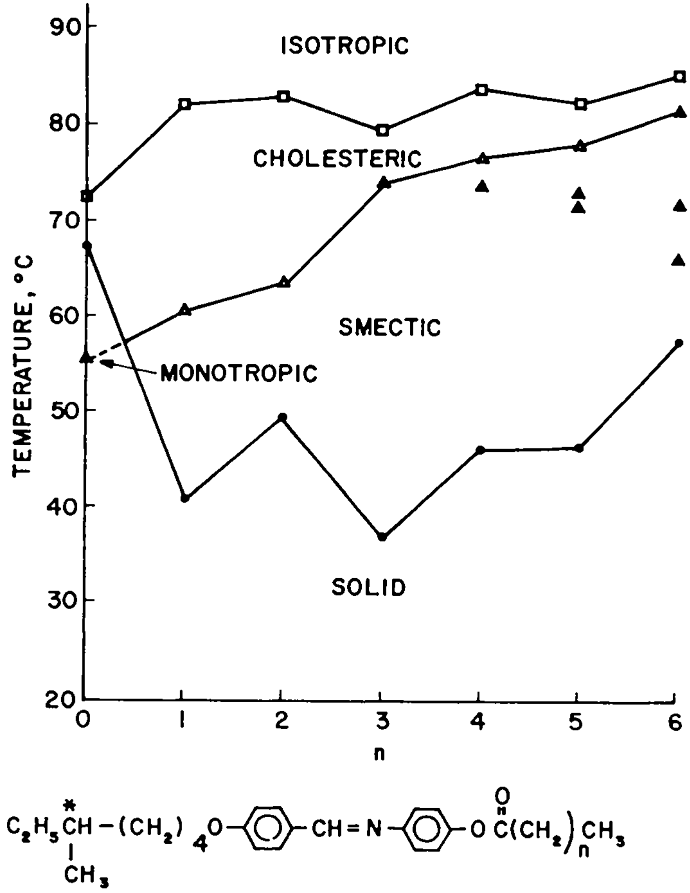
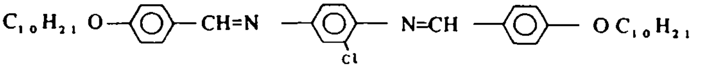


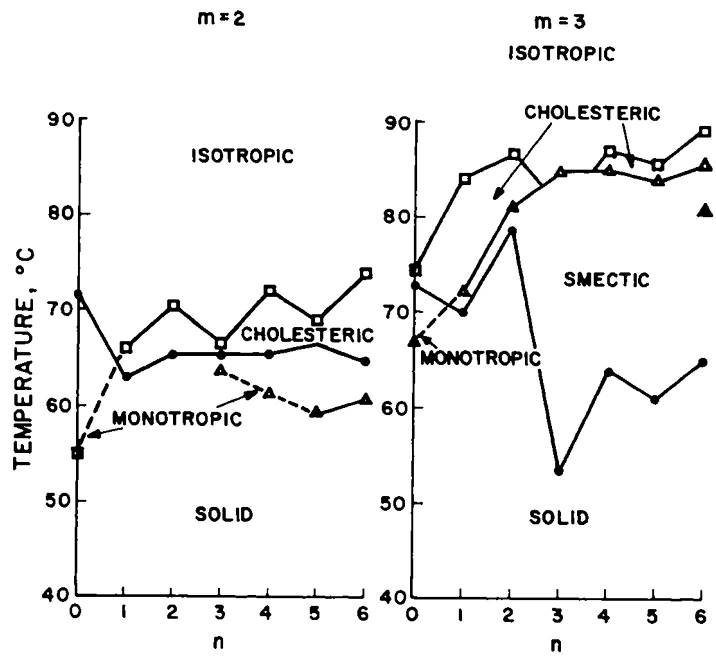
FIGURE 2 Phase transition plot for p-active-5-methylheptyloxybenzylidene-p'-aminophenylacylates; –●– melting points, ▲ smectic–smectic, –△– smectic–cholesteric, –□– cholesteric–isotropic transitions.

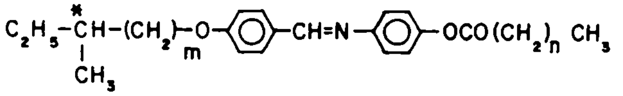
In order to further establish the nature of the smectic mesophase in these compounds, mixtures of compound 37 and the bis-(4-*n*-decyloxy) derivative (38) were prepared. The latter compound has been reported[18] to have a



(38)

biaxial smectic structure with the smectic layers tilted by about 45°. Since the resulting mixtures showed continuous uninterrupted mesophases, it was concluded that the smectic mesophase of 37 also had a tilted structure. One can





$C_2H_5-\overset{*}{C}H(CH_3)-(CH_2)_m-O-C_6H_4-CH=N-C_6H_4-OCO(CH_2)_nCH_3$

FIGURE 3 Phase transition plot for 4-active-alkoxybenzylidene-4'-aminophenylacylates; –●– melting points, ▲ smectic–smectic, –△– smectic-cholesteric, –□– cholesteric-isotropic transitions.

visualize that the biaxial smectic strata are twisted layer after layer as one moves his observation point normal to the layers.

Finally, it was found that the rotatory power of the conical (twisted) smectic mesophase was insensitive to temperature changes. In contrast to the cholesteric mesophase, where thermal fluctuations need only disrupt individual molecules to produce changes in optical rotation, greater amounts of energy are required to disrupt an entire smectic layer.

Acknowledgements

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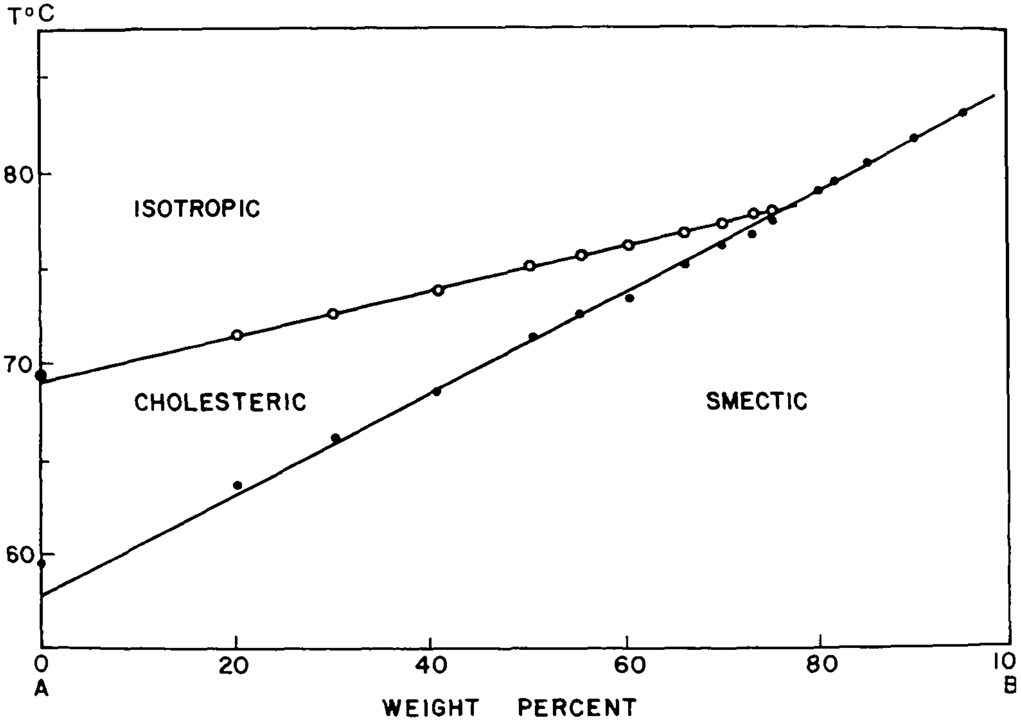

FIGURE 4 Phase diagram of mixtures containing C_2H_5-$CH(CH_3)(CH_2)_2OC_6H_4CHNC_6H_4$-$OCO(CH_2)_5CH_3$(A) and $C_2H_5CH(CH_3)(CH_2)_3OC_6H_4CHNC_6H_4CHNC_6H_4OCO(CH_2)_3CH_3$(B).

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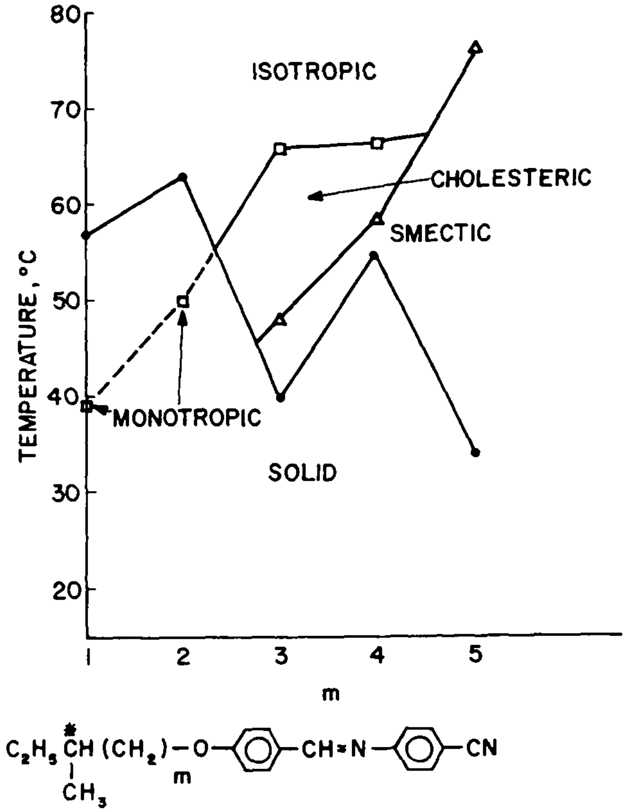

FIGURE 5 Phase transition plot for 4-active-alkoxybenzylidene-4'-aminobenzonitriles; –●– melting points, –Δ– smectic-cholesteric, –□– cholesteric-isotropic transitions.

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