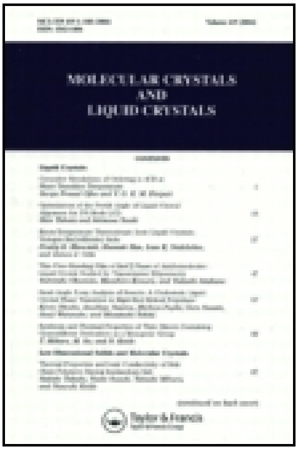

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The Effect of a Long Alkoxyl Group on the Mesomorphic Properties of 4-(4-Alkoxyphenoxycarbonyl)phenyl 3-Alkoxy-4-cyanobenzoates

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The Effect of a Long Alkoxyl Group on the Mesomorphic Properties of 4-(4-Alkoxyphenoxycarbonyl)phenyl 3-Alkoxy-4-cyanobenzoates

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This paper describes syntheses and properties of some members of 4-(4-alkoxyphenoxycarbonyl)phenyl 3-alkoxy-4-cyanobenzoates. The ethoxy and propoxy groups at the adjacent position of the cyano one are unfavorable for the formation of a smectic A phase and the long alkoxy groups such as butoxy, pentyloxy, and hexyloxy ones facilitate the formation of a smectic C phase. The characterization and molecular arrangement of the smectic C phase were made by a differential scanning calorimeter, microscopic observation, and small-angle X-ray diffraction examination, and the roles of the alkoxyl group at the adjacent position of the cyano group on the mesomorphic properties are discussed.

Keywords: Synthesis; thermal properties; lateral alkoxy group; polar liquid crystals; X-ray diffraction

It is well known that the cyano group at the terminal position of liquid crystalline molecules facilitates the antiparallel arrangement of molecules and enhances the formation of some kinds of smectic A phase such as monolayer, bilayer, and partially bilayer arrangements of molecules [1]. For the phenomena, polar interactions such as dipole–dipole and dipole-induced dipole ones are supposed to play important roles. The antiparallel correlation of the dipoles may be unfavorable in point of application since it

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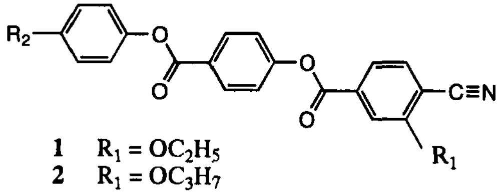
reduces the dielectric anisotropy in the liquid crystalline phases. Therefore, it is very important to clarify the roles of polar interactions upon the mesomorphic and dielectric properties.

In connection with the dielectric properties, it is interesting that the fluorine atom at the adjacent position of the cyano group in the 4-cyanophenyl 4-alkoxybenzoate system increases the dielectric anisotropy in the nematic phase [2]. It has been also reported that a lateral substituent increases the dielectric anisotropy [3]. Thereby, the steric effect of the lateral substituent was supposed to affect the formation of the antiparallel dimers.

Based on these findings, we are interested in the effect of an alkoxyl group at the adjacent position of the cyano one on the mesomorphic properties, as shown below.



1 $R_1 = OC_2H_5$
2 $R_1 = OC_3H_7$
3 $R_1 = OC_4H_9$
4 $R_1 = OC_5H_{11}$
5 $R_1 = OC_6H_{13}$

$R_2 = OC_nH_{2n+1}$(n=4,5,6, and 8)

6 $R_1 = H$ $R_2 = OC_nH_{2n+1}$

4-(4-Alkoxyphenoxycarbonyl)phenyl 4-cyanobenzoates, 6, have been synthesized and are known to show interesting mesomorphism involving smetic A phases having partially bilayer and/or bilayer arrangements of the molecules [4]. In this paper, we describe the syntheses and thermal properties of compounds 1–5 and the liquid crystalline properties are discussed in terms of the molecular structures.

EXPERIMENTAL

Materials

Ethyl 4-bromo-3-hydroxybenzoate

Bromine (71.7 g, 0.45 mol) was added dropwise to a solution of ethyl 3-hydroxybenzoate (74.45 g, 0.45 mol) in acetic acid (80 ml). After stirring for 5 days at room temperature, residual bromine was decomposed by aqueous solution (5%) of sodium hydrosulfite. The resulting solution was extracted with ether, and the organic layer was washed with sat. sodium bicarbonate and dried over anhydrous sodium sulfate. The extracts were purified by column chromatography on silica gel. The first eluent was recrystallized from a mixed solvent of ether and pet. ether, giving ethyl 4-bromo-3-hydroxybenzoate as colorless needles, 23.5 g (21.4%), mp 97°C. IR: ν_{COO} = 1697 cm^{-1}. ^{1}HNMR: δ = 1.39 (3H, *t*, *J* = 7.3), 4.37 (2H, *q*, *J* = 7.3), 5.79 (1H, *s*), 7.48 (1H, *dd*, *J* = 8.6 and 1.6), 7.54 (1H, *d*, *J* = 8.6), and 7.69 (1H, *d*, *J* = 1.6 Hz) ppm. The residual starting material was recovered by column chromatography.

Ethyl 4-bromo-3-ethoxybenzoate

A solution of ethyl 4-bromo-3-hydroxybenzoate (5.0 g, 0.02 mol), iodoethane (3.7 g, 0.02 mol), and sodium hydroxide (1.3 g, 0.03 mol) in anhydrous DMF (20 ml) was stirred for 10 h at room temperature. After adding ice-cooled water (200 ml), the solution was extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulfate. The crude product was purified with column chromatography on silica gel, where a mixed solvent of ether and pet. ether was used as an elution solvent, giving ethyl 4-bromo-3-ethoxybenzoate as a colorless oil, 3.50 g (64%). IR: ν_{COO} = 1718 cm^{-1}. ^{1}HNMR: δ = 1.39 (3H, *t*, *J* = 7.3), 1.49 (3H, *t*, *J* = 6.9), 4.17 (2H, *q*, *J* = 6.9), 4.37 (2H, *q*, *J* = 7.3), 5.79 (1H, *s*), 7.50 (1H, *dd*, *J* = 8.3 and 1.6), 7.53 (1H, *d*, *J* = 1.6) and 7.60 (1H, *d*, *J* = 8.3 Hz) ppm.

The propoxy and the higher derivatives were prepared by the reaction of the corresponding alkylbromides and ethyl 4-bromo-3-hydroxybenzoate in 3-pentanone.

Ethyl 4-cyano-3-ethoxybenzoate

A solution of ethyl 4-cyano-3-ethoxybenzoate (3.50 g, 0.013 mol) and anhydrous cuprous cyanide (1.7 g, 0.019 mol) in anhydrous DMF (7 ml) was stirred for 20 h at 120°C under a nitrogen atmosphere, and then a solution of ferric chloride (5.2 g) and conc. sulfuric acid (1.3 ml) in water (7.7 ml) was addded to the reaction mixture at 60°C. After stirring for 1 h, the reaction mixture was extracted with toluene (30 ml × 3 times) and the organic layer was washed with sat. sodium chloride solution, and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel, where a mixed solvent of ether and pet. ether was used as an elution solvent, followed by recrystallizations from a mixed solvent of ether and pet. ether, giving ethyl 4-cyano-3-ethoxybenzoate as colorless needles. 1.74 g (62%), mp 77°C. IR: $\nu_{COO} = 1720$, $\nu_{CN} = 2227\,\mathrm{cm}^{-1}$. ^{1}HNMR: $\delta = 1.39$ (3H, *t*, $J = 7.1$), 1.49 (3H, *t*, $J = 6.9$), 4.17 (2H, *q*, $J = 6.9$), 4.37 (2H, *t*, $J = 7.1$), 7.61 (1H, *d*, $J = 1.1$), 7.61 (1H, *d*, $J = 8.3$), and 7.66 (1H, *dd*, $J = 1.1$ and 8.3 Hz) ppm.

4-Cyano-3-ethoxybenzoic acid

4-Cyano-3-ethoxybenzoic acid was obtained by hydrolysis of ethyl 4-cyano-3-ethoxybenzoate (1.74 g, 8.0 mmol) as colorless needles. 1.40 g (92%), mp 218°C. IR: $\nu_{COO} = 1720$, $\nu_{CN} = 2227\,\mathrm{cm}^{-1}$. ^{1}HNMR: $\delta = 1.47$ (3H, *t*, $J = 6.9$), 4.35 (2H, *t*, $J = 6.4$), 7.68 (1H, *dd*, $J = 0.7$, and 7.9), 7.70 (1H), and 7.74 (1H, *d*, $J = 7.9$ Hz), and 13.7 (1H, *s*) ppm. 4-Cyano-3-ethoxybenzoic acid is non-mesogenic.

The other members of 3-alkoxy-4-cyanobenzoic acids were obtained similarly, and the melting points for the propoxy, butoxy, pentyloxy, and hexyloxy members are 179, 171, 159, and 156°C, respectively.

4-(4-Butoxyphenoxycarbonyl)phenyl 4-cyano-3-ethoxybenzoate (1a)

4-(4-Butoxyphenoxycarbonyl)phenol and the homologous members were prepared according to the literature [5]. According to the method described in an earlier paper [5], compound **1a** was obtained by the condensation of 4-(4-butoxyphenoxycarbonyl)phenol and 4-cyano-3-ethoxybenzoic acid as colorless needles. IR: $\nu_{COO} = 1720$, $\nu_{CN} = 2227\,\mathrm{cm}^{-1}$. ^{1}HNMR: $\delta = 0.99$ (3H, *t*, $J = 7.4$), 1.44–1.57 (5H, *m*), 1.78 (2H, *q*, $J = 6.5$), 3.98 (2H, *t*, $J = 6.4$), 4.28 (2H, *q*, $J = 6.9$), 6.94 (2H, *d*, $J = 9.2$), 7.12 (2H, *d*, $J = 8.9$), 7.37 (2H, *d*, $J = 8.9$), 7.72 (1H, *d*, $J = 7.9$), 7.75 (1H, *d*, $J = 1.3$), 7.85 (1H, *dd*, $J = 7.9$ and 1.3) and 8.30 (2H, *d*, $J = 8.9$ Hz) ppm.

The purity (98.7%) was checked by a differential scanning calorimeter (DSC) by using a "DSCPURITY" program (Seiko Denshi).

The other compounds were prepared by a similar method to **1a**.

Method

IR spectroscopy was performed on a Horiba FT-200 infrared spectrometer. ^{1}HNMR spectra were taken with a Nihon-Denshi EX-270 spectrometer in chloroform-*d* solution, where TMS was used as an internal standard. Transition temperatures and latent heats were determined using a Seiko

SSC-5200 differential scanning calorimeter (DSC), where indium (99.9%) was used as a calibration standard (mp 156.6°C, 28.4 J/g). The DSC thermogram was operated at a heating rate of 5°C/min. Mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system FP-900. The homogeneous alignment between glass surfaces was achieved by treatment of glass plates with polyimide (Tore SP-810). The homeotropic alignment was achieved by treatment of glass surfaces with cetyltrimethylammonium bromide.

X-ray diffraction experiments were performed with a Rigaku-denki RINT 2200 diffractometer. The reflection angle (2θ) was calibrated by examination of both left and right angles. The temperature was controlled by a Rigaku PTC-20A thermocontroller. The powdered sample crammed into a quartz capillary (1.5 mm ϕ) was heated up to the isotropic solution, and the measurement was carried out on the cooling process.

RESULTS AND DISCUSSION

Transition temperatures and the latent heats obtained from the DSC *thermogams are summarized for* **1**–**5** in Table I.

The latent heats for the nematic-isotropic transition (N-I) are small almost independent of the length of the alkoxyl group at the adjacent position of the cyano one. The transition temperatures are plotted against the carbon number of the alkoxyl group attached at the adjacent position of the cyano group in Figure 1.

Usually, the liquid crystals having a polar group such as cyano or nitro group at the terminal position of the liquid crystalline core tend to show orthogonal phases when the terminal alkoxyl group is suitably long [1]. The formation of tilt phases such as smectic C phases (S_C) are rare cases, where the molecules involve at least one azomethine linkage [6, 7]. For 4-(4-alkoxyphenoxycarbonyl)phenyl 4-cyanobenzoates (6), the smectic A phase (S_A) having a bilayer arrangement appears to be formed from the earlier homolog, and shows complex polymesomorphism involving the S_A phase having a partially bilayer structure [4]. This polymesomorphism has been also found for both alkyl [8] and nitro derivatives [9]. Therefore, we assume that 4-(4-alkoxyphenoxycarbonyl)phenyl 4-cyano- and 4-nitrobenzoate systems essentially favor the formation of the S_A phases having the bilayer or partially bilayer arrangements.

Introduction of the alkoxyl group at the adjacent position of the cyano group tends to reduce the nematic-isotropic (N-I) transition temperatures,

TABLE I Transition temperatures and latent heats for **1**–**5**

		Transition temperatures ($T/^{\circ}C$)							Latent heats (kJ/mol)			
Compounds	*n*	*C*		S_C		*N*		*I*	$\Delta H_{C\text{-}S_C}$	$\Delta H_{S_{C\text{-}N(I)}}$		$\Delta H_{N\text{-}I}$
1a	4	•	150	–	(	•	147)	•	39.3			0.5
1b	5	•	137	–		•	143	•	39.2			0.6
1c	6	•	138	–		•	143	•	33.9			0.7
1d	8	•	138	–		•	143	•	40.5			0.6
2a	4	•	142	–	(	•	123)	•	45.7			0.4
2b	5	•	128	–	(	•	120)	•	32.5			0.4
2c	6	•	126	–	(	•	124)	•	33.6			0.7
2d	8	•	125	–	(	•	123)	•	37.1			0.9
3a	4	•	125	–	(	•	120)	•	29.1			0.5
3b	5	•	113	–		•	117	•	29.1			0.6
3c	6	•	118(	•	102)	•	121	•	46.2	2.0		0.6
3d	8	•	105	•	110	•	122	•	22.7	1.5		0.5
4a	4	•	116	–	(	•	115)	•	• 29.8			0.8
4b	5	•	112(	•	104)	•	114	•	40.6	3.9		0.7
4c	6	•	105	•	109	•	118	•	26.3	3.6	•	0.8
4d	8	•	105	•	116	•	120	•	23.9		6.0* 1	
5a	4	•	112	•	112	•	117	•	22.2	2.6		0.8
5b	5	•	108	•	109	•	116	•	24.8	3.8		0.9
5c	6	•	106	•	116	•	120	•	23.5		6.4* 1	
5d	8	•	100	•	119	•	120	•	24.4		7.1* 1	

* 1 The values are the sum of the latent heats for the S_C–N and N-I transitions. Parentheses indicate a monotropic transition.

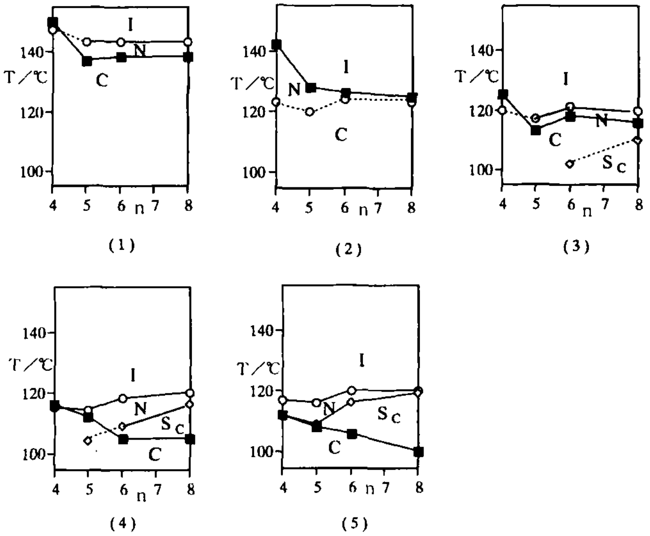


FIGURE 1 Plots of transition temperatures (T/°C) *vs.* carbon number, *n* for: (1) **1**, (2) **2**, (3) **3**, (4) **4**, and (5) **5**. C, S_C, N, and I indicate crystal, smectic C, nematic, and isotropic phases, respectively. Dashed lines indicate a monotropic transition.

and disappearance of the orthogonal phase such as the S_A one having a bilayer arrangement.

For the ethoxy compounds **1** the formation of the N phase is enantiotropic except for **1a**, and the N-I transition temperatures are almost independent of the terminal alkoxy chain length (R_2), and averages 143°C. The N-I transition temperatures are lower (*ca.* 80°C) than that for the unsubstituted compounds (**6**). The formation of the S_A phase was not observed even in the monotropic process, where the recrystallization occurred at *ca.* 95°C.

For the propoxy compounds **2** a similar trend is observed and the average N-I transition temperature is 122°C, which is lower by 21°C than **1**. The formation of the S_A phase was not observed even in the monotropic process.

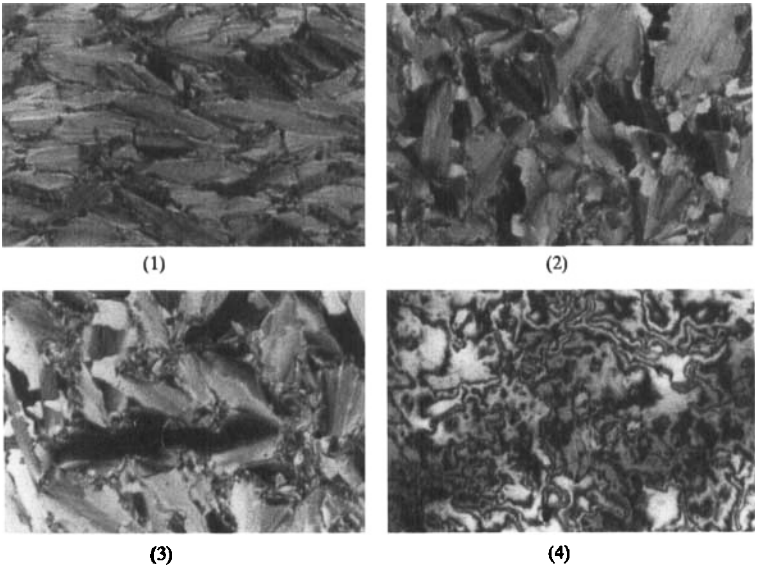
For **3**, **4**, and **5**, a similar trend was observed where the average N-I transition temperatures are almost same as the **2**. These facts indicate that the N-I transition temperatures are strongly dependent on the chain length of R_1, and are almost independent of the alkoxy chain lengths of both R_1 and R_2, when the alkoxy chain of R_1 is longer than the ethoxy group.

As we can see from Figure 1, the melting points also show a similar trend and are almost independent of the alkoxy chain length (R_2), when the alkoxy chain (R_1) is longer than the ethoxy group. These facts indicate that the alkoxyl group of R_1 plays very important roles in determining the thermal properties not only of the nematic phase but also the crystalline phase.

One difference in the plots in Figure 1 is seen on the formation of the smectic phase. **1** and **2** show neither S_A nor S_C phases, while the unsubstituted compounds (**6**) show the S_A phase with orthogonal properties. On the other hand, **3** and the higher compounds show a smectic C phase, and its temperature range becomes wider with increasing the alkoxy chain of R_2. These facts indicate that the ethoxy and propoxy groups at the adjacent position of the cyano group do not favor any layer arrangement, and so the compounds are the boundary for the formation of the orthogonal and tilt phases.

The microscopic textures for the smectic phase are shown in Figure 2.

The monotropic smectic phase formed by **3c** (Fig. 2-1) shows a partially broken focal conic fan texture under a homogeneous alignment. The smectic phase for **4d** shows a broken focal conic fan texture while the texture may be fine. On the other hand, the smectic phase for **5b** shows a fully grown broken focal conic fan texture, and shows a schlieren texture under a homeotropic alignment. These facts indicate that the texture in the smectic phase is also



(1) (2) (3) (4)

FIGURE 2 Micrographs (100 X) of the S_C phases for: (1) **3c** (at 98°C, homogeneous), (2) **4d** (at 111°C, homogeneous), (3) **5d** (at 99°C, homogeneous), (4) **5d** (at 99°C, homeotropic). The textures were obtained from the nematic phase by cooling (cooling rate of 1°C/min). The homogeneous and homeotropic alignments were achieved by treating the glass surfaces with polyimide (Tore SP-810) and cetyltrimethylammonium bromide, respectively. (See Color Plate IV).

fairly effected by the alkoxy chain at the adjacent position of the cyano group. The optical characteristics suggest that the smectic phase has a tilt nature. Considering that the latent heats for the smectic-nematic transition are not so high, the tilt smectic phase is assigned to the C modification.

The smectic phase was further characterized by the small-angle X-ray diffraction experiment. A typical example is shown in Figure 3.

The profile for **3c** at 103°C ($T_{S\text{-}N}$-7°C) shows broad reflection maxima at 2.94° (30.0 Å) arising from the layer arrangement of molecules and 20° (4.4 Å) arising from the lateral order of molecules within the layer. The broad feature for the latter supports the above assignment of the S_C phase. The broad feature for the former indicates that the smectic layer is

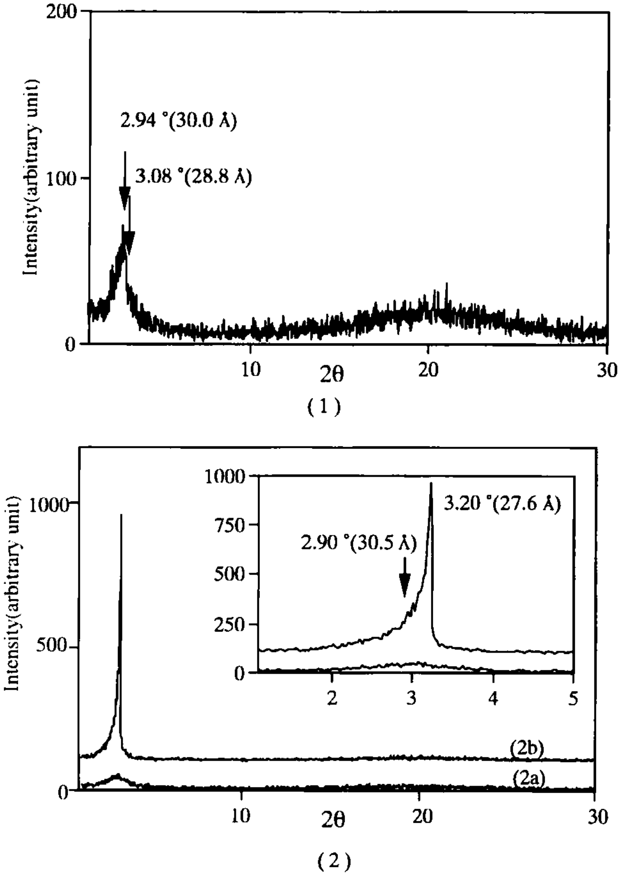


FIGURE 3 X-ray profiles for: (1) **3d** at 103°C (S_C), and (2) **5c** at 105°C (2a, (S_C)) and 114°C (2b, (S_C)).

ambiguous while the state is the S_C phase from the microscopic and thermal points of view. These trends were also observed in **4b**. The profile for **5c** at 114°C($T_{SC\text{-}N}$-2°C) shows two broad reflections at *ca.* 3.0 and *ca.* 20°, indicating that the smectic layer is ambiguous. At 105°C($T_{SC\text{-}N}$-11°C), the profile shows a sharp and intense reflection at 3.20°(26.8 Å) at 102°C ($T_{SC\text{-}N}$-14°C). As we can see from the figure, interestingly, the intense peak is dissymmetric and is accompanied by a broad shoulder in the range between 2.7 and 3.2°.

These trends were also observed in **4c**, **4d**, **5b**, and **5d**.

For compound **3c** X-ray diffraction study was unsuccessful due to recrystallization. The layer spacings for the compounds are summarized in Table II.

In order to correlate the layer spacings with the molecular properties, the molecular geometries were estimated by a semi-empirical molecular orbital calculation by the AM1 method (MOPAC, Ver. 6.0).

As we can see, the molecular geometries for the compounds are strongly dependent on the conformation of the alkoxyl group at the adjacent position of the cyano one. Two extreme conformers, **A** and **B**, are indicated in Figure 4.

In the calculations, of course, a zigzag conformation is the most stable for two alkoxyl groups. Although the calculation indicates that the terminal alkoxyl group(R_2) extends to the side of the aromatic ring, the rotational barrier around the ether oxygen is only 0.5 kcal/mol, so that the alkoxyl group is assumed to keep rotational freedom at the liquid crystalline temperature. On the other hand, the situation of the alkoxyl group(R_1) at the adjacent position of the cyano one is different. As we can see from Figure 4, conformer **A** is the most stable in point of energy, so that we

TABLE II Comparison of layer spacings of the S_C phase (upper column) and calculated molecular lengths (lower column) in Å unit. The values in parentheses are the maximum of the broad reflection, as shown in Figure 3

Compounds	**a**	**b**	**c**	**d**
3			S_C *1 26.6	S_C (30.0) 28.8
4		S_C (27.0) 26.0	S_C 26.8 26.9	S_C 28.6 28.8
5	S_C *1 26.0	S_C 26.9 26.9	S_C 27.6 27.8	S_C 29.2 29.8

*1 X-ray data were not obtained due to recrystallization.

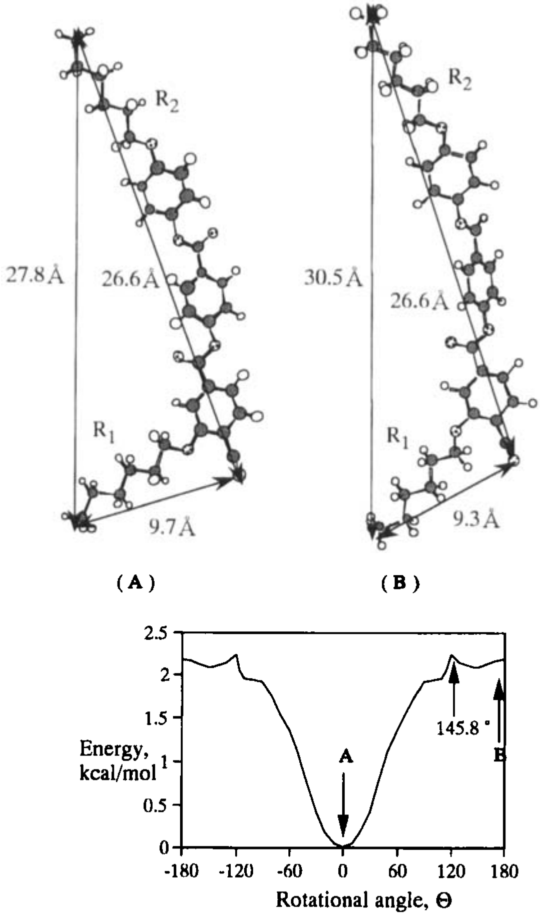


FIGURE 4 Molecular geometries and the conformational energy calculated by an AM1 method (MOPAC, Ver. 6.0) for 5c.

assume that the conformer is preferentially present in the gas phase. However, the long alkoxyl group will promote the bent shape of the entire molecular structure, and conformer **A** might be unfavorable in the liquid and liquid crystalline phases. In the model, the longest molecular length for 5c is calculated to be 27.8 Å.

On the other hand, conformer **B** keeps the best linearity of the entire molecule, and might be preferable for the formation of the liquid crystalline phases. However, the calculation indicates that conformer **B** is less stable than conformer **A**, where the energy difference is *ca.* 2.2 kcal/mol, as shown in the figure. Although the energy difference is not enough to freeze the rotation of the alkoxyl group around the ether oxygen, it is enough to reduce the population of conformer **B**. Thereby, the longest molecular length for 5c is 30.5 Å which is longer (2.7 Å) than conformer **A**.

The molecular lengths calculated from conformer **A** are summarized in the lower columns of Table II, and compared with the layer spacings obtained from the X-ray experiments.

Interestingly, the layer spacings obtained from the reflection maxima completely agree with the molecular lengths calculated from conformer **A**, except for 3d and 4b.

Furthermore, we have to note that the sharp reflection at 3.20° for 5c (Fig. 3) is accompanied by a shoulder in the range between 2.7 and 3.2°. In the figure, we indicated an arrow at 2.90° corresponding to the molecular length calculated from conformer **B** in Figure 4. Apparently, the broad shoulder suggests 5c is also present as the conformational mixtures between two extreme conformers **A** and **B**, where the bent shape is preferential.

On the other hand, the X-ray profile for 3d shows the intense reflection maximum at 2.94° (30.0 Å) with a broad shoulder in the range between 2.5 and 2.9° (30–35 Å). The maximum length (30.0 Å) is apparently longer than the molecular length for conformer **A** (3.08° (28.8 Å), indicated by arrow in Fig. 3). Therefore, we assume that the molecular arrangement of the S_C phases of 3d and 4b is a mixture of tilt and orthogonal arrangements like the S_A phase of 6 in addition to the tilt one like the other compounds, though the phase is optically biaxial.

Dubois *et al.*, reported that 4-(4-pentylphenoxycarbonyl)phenyl 3-cyano-4-alkyl- and 3-cyano-4-alkoxybenzoates show N and S_A phases even in the lower members [10, 11]. In these systems the lateral polar interactions are assumed to enhance the layer arrangement of the molecules. Apparently, the role of the alkoxyl group at the adjacent position of the cyano one is opposite to the present compounds.

CONCLUSION

For 4-(4-alkoxyphenoxycarbonyl)phenyl 4-cyano-3-R-benzoate systems the homologous members with R$=$H tend to show orthogonal phases such as smectic A phases, where the polar interactions around the cyano group may play some important roles. The alkoxyl group at the adjacent position to the cyano one strongly prohibits the formation of the orthogonal arrangement, and the extension of the alkoxy chain recovers the layer arrangement of the molecules, where the molecules form the tilt smectic phase. The long alkoxyl group is assumed to weaken the polar interactions around the cyano group.

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