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Liquid-Crystalline Properties of Dissymmetric Molecules Part 8: The Effect of Conformation on the Mesomorphic Properties for Liquid–Crystal Compounds Having a Lateral Long Alkoxy Group

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This paper describes the liquid–crystal properties of 4-(4-alkoxyphenoxycarbonyl)phenyl 3-alkoxy- (**1**), 3-alkoxy-4-methyl- (**2**), and 3-alkoxy-2-methyl-benzoates (**3**). Most of the homologs of **1** are non-mesogenic, due to the long alkoxy group at the 3 position restraining the appearance of liquid–crystal properties. The substitution of a methyl group at the 2 or 4 position effectively facilitates the appearance of a nematic phase. The average effective order for the nematic-isotropic transition temperatures is **3** > **2** > **1**. The liquid–crystal properties of these compounds are discussed in terms of the change in the conformation of the alkoxy group at the 3 position.

Generally, rod-like or calamitic liquid–crystal (LC) materials have flexible hydrocarbon chains at the terminal position of the LC core in order to enhance the LC properties. The hydrocarbon chains are attached directly at the LC core or through a linkage, such as –O–, –S–, and –COO– bonds. In such systems two critical conformers are possible, and the relative conformation of the terminal chains determines the entire molecular shape, as shown in Fig. 1.

When the terminal hydrocarbon chains are short, because the entire molecular shapes of both conformers resemble each other, the conformational difference would not affect the LC properties. When the hydrocarbon chains are sufficiently long, however, the entire molecular shapes of two conformers (**L** and **B** denote linear and bent shapes, respectively) are dependent on the relative conformation of both terminal hydrocarbon chains, and both conformers might have different LC properties. Of course, because two conformers are equivalent regarding the energy in the gas and liquid phases, and fast exchange of each other at the usual LC temperature, they are not readily distinguishable under the usual conditions. In such cases, the long (or rotational) molecular axis has been regarded as an average of two critical conformers, for example, the dotted line in Fig. 1.[1]

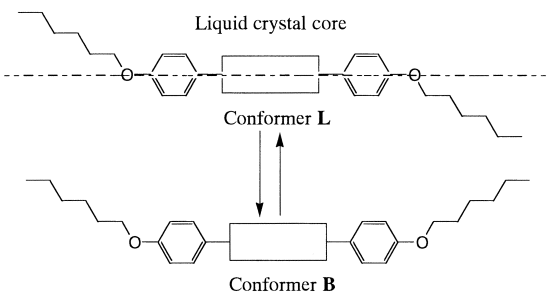


Fig. 1. Conformational isomerism of liquid crystals having terminal alkoxy groups.

The bent shape of the entire molecules becomes notable with increasing the carbon number of the terminal hydrocarbon chains, due to the bent angle of the hydrocarbon–O–phenyl bond, as shown in Fig. 1. Of course, the zigzag conformation of the hydrocarbon chains would be more or less reformed by the intra-flexibility of the hydrocarbon chains, so as to enhance the linearity of the entire molecular shape in the LC states.

The conformational effect is more serious in compounds having a lateral long hydrocarbon chain, as shown in Fig. 2.

In such systems the entire molecular shape is strongly dependent on the conformation of the lateral hydrocarbon chain. Conformer **L** results in linearity in the entire molecular shape, and would be preferable for the appearance of LC properties, according to the general concept for LC properties. On the other hand, conformer **B** gives a notable bent shape in the entire molecular shape, and would not be preferable for LC properties. Regarding energy, in practice, because there is no fundamental difference between two conformers, two extreme conformers should distribute equally in the liquid and gas phases, with their physical properties being the mathematical average of both conformers. If the rotation of the hydrocarbon chain around ether bond can be restricted and conformer **L** is preferential, the molecules are expected to have high LC prop-

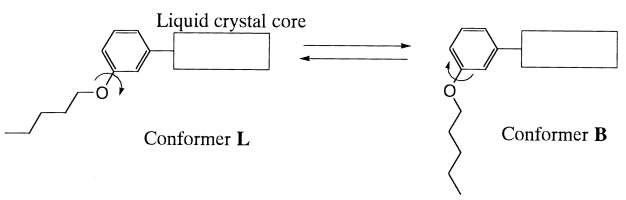


Fig. 2. Conformational isomerism of liquid crystals having a lateral alkoxy group.

erties, just like 4-substituted compounds. On the other hand, conformer **B** may not be suitable for the appearance of the usual calamitic LC phases. In practice, it has been well known that materials having a lateral long hydrocarbon chain have low LC properties,[2–10] and sometimes the physical properties are fairly different from those of the usual calamitic LCs.[11–20]

Recently, some molecules with a bent shape in the LC core have been known to exhibit different mesomorphic properties from those of the usual calamitic LC materials. The mesomorphic properties of these kinds are one of the current interests in connection with the ferroelectric properties of achiral molecules.[21,22]

According to this concept, we designed some compounds having a long lateral alkoxy group and examined their mesomorphic properties (Fig. 3).

For compounds **1**, two extreme conformers (**L** and **B** in Fig. 2) would distribute in the liquid phase, due to rotation around the ether bond. Compounds **2**, having a methyl group at the R_2 position, would have a bent molecular shape preferentially, due to a steric hindrance between the methyl and the alkoxy groups. In compounds **3**, having a methyl group at the R_3 position, on the other hand, the linear shape would be preferential for the same reason. The substituent effect, therefore, would give some important information concerning the conformational effect on the LC properties.

In this work, the LC properties of **2** and **3** were examined and compared with those of compounds **1**. The results are discussed here in terms of the conformational effect of the alkoxy group at the R_1 position.

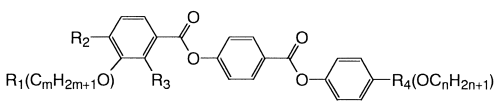
Experimental

Materials: 3-Hydroxy-2-methyl- and 3-hydroxy-4-methylbenzoic acids were purchased from Tokyo-kasei Co., and alkylated by Williamson synthesis with *n*-alkyl halides, giving the corresponding 3-alkoxy-2-methyl- and 3-alkoxy-4-methylbenzoic acids. All of these acids were non-mesogenic. The melting points for 3-ethoxy-2-methyl-, 3-hexyloxy-2-methyl-, 2-methyl-3-tetradecyloxy-, 3-ethoxy-4-methyl-, 3-hexyloxy-4-methyl-, and 4-methyl-3-tetradecyloxybenzoic acids are 00, 00, 00. 00. 00. and 00 °C, respectively. The materials were obtained by esterification of these acids and 4-(4-alkoxyphenoxy-carbonyl)phenols according to the conventional method.[23]

The purities of the materials were checked by elemental analysis, HPLC with ODS column, and ^{1}H NMR spectroscopy.

Method: The transition temperatures and latent heats were determined using a Seiko SSC-5200 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 or a cooling rate of 5 °C/ min. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900), where the temperatures were calibrated by standard benzoic acid (mp = 122.4 °C).

The molecular-orbital parameters referenced in this paper were obtained by a semi-empirical molecular orbital calculation (CS Chem 3D Pro Version 4.0), where minimization of the total energy was achieved by an AM1 method.



Compounds **1** R_2=R_3=H
2 R_2=CH_3, R_3=H
3 R_2=H, R_3=CH_3

Fig. 3. Chemical structures of present compounds.

Results and Discussion

It has been reported that 4-(4-pentyloxyphenoxycarbonyl)phenyl benzoate shows a phase sequence of C·129·N·147·I (T/°C).[24] The methoxy compound (**1a**) shows a monotropic nematic–isotropic (N–I) transition at 68 °C, indicating that the introduction of a methoxy group at the R_1 position notably reduces the N–I transition temperature (79 °C). Ethoxy compounds (**1b** and **1c**) do not show any mesophase, even upon a rapid cooling process of the isotropic liquid; thus, the mesomorphic properties of **1** were estimated by extrapolating the N–I transition temperature of binary phase diagrams, as shown in Fig. 4.

In Fig. 4a 4-(4-pentyloxyphenoxycarbonyl)phenyl 4-bromo-3-ethoxybenzoate (**4**: R_1 = OC_2H_5, R_2 = Br, R_3 = H, R_4 = OC_5H_{11}, C·111·(Sm A·91·N·100)·I)[25] is used as a reference compound, since these compounds would have a similar chemical structure. The N–I transition temperature in the diagram shows a linear correlation against the molar concentration of the components, and extrapolation of the straight line gives 46 °C for the N–I transition temperature of **1b**. In the diagram the

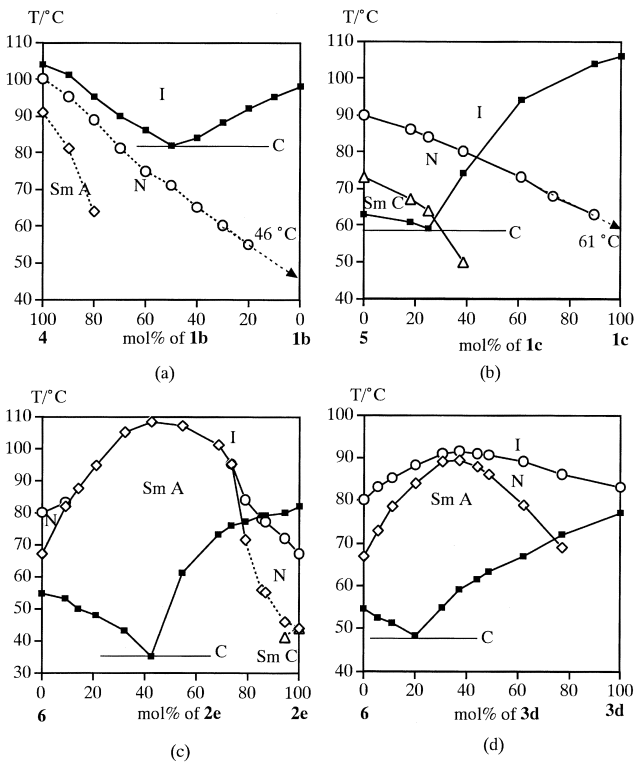


Fig. 4. Binary phase diagrams for the mixtures of (a) **4** (on left) and **1b** (on right), (b) **5** (on left) and **1c** (on right), (b) **6** (on left) and **2e** (on right), (d) **6** (on left) **3d** (on right). ○; N–I, △; Sm C–Sm A(N), ◇; Sm A–N(I), and ■; C–Sm C(N, or I) transitions. Sm C, Sm A, N, I, and C indicate smectic C, smectic A, nematic, isotropic, and crystal phases, respectively.

smectic A–nematic (Sm A–N) transition temperature steeply decreases with increasing concentration of **1b**.

Fig. 4b shows a phase diagram for a mixture of 4-octyloxyphenyl 4-octyloxybenzoate (**5**: C·62.5·Sm C·73.5·N·90.5·I)[26] and **1c**.

The N–I transition temperature in the diagram also shows a linear correlation against the molar concentration of both components, in spite of the notable difference in their LC cores. Extrapolation of the straight line gives 61 °C for the N–I transition temperature of **1c**. In this diagram, the smectic C–nematic (Sm C–N) transition temperature shows a steep reduction at around 40 mol% of **1c**, indicating that **1c** has difficulty to exhibit the Sm C phase. Considering the fact that 4-(4-octyloxyphenoxycarbonyl)phenyl benzoate and 4-(4-octyloxyphenoxycarbonyl)phenyl 4-ethoxybenzoate show the phase sequences of C·118·N·135·I and C·115·N·223·I,[27] respectively, substitution or the replacement of the ethoxy group at the R_1 position results in a notable reduction of the N–I transition temperature. Similarly, the virtual N–I transition temperatures for **1d**–**1g** were also estimated from corresponding binary phase diagrams.[28] The thus-obtained results are summarized in Table 1.

Although substitution of the methoxy or the ethoxy group at the R_1 position for compounds **1** resulted in a notable reduction in the N–I transition temperature, the effect of the lateral alkoxy group became weak upon ascending the homologs (**1a** > **1b** > **1d** ≈ **1g**). On the other hand, the effective order for the N–I transition temperature for $m = 5$ derivatives is **1f** > **1e** > **1d**, indicating that the long alkoxy group at the R_4 position enhances the N–I transition temperature.

Compounds **2a**–**2c** show a monotropic N phase, and the N–I transition temperatures are higher than the virtual N–I ones for **1**. For $m = 6$ derivatives, the N–I transition temperatures are almost independent of n (**2d**–**2f**). Compound **2e** shows a smectic phase exhibiting a schlieren texture, in addition to the N one. The smectic phase is assumed to be a C modification (Sm C). Compounds **2g**–**2i** do not show any mesophase because of rapid recrystallization during the cooling process of the isotropic solution.

Compounds **3a**–**3i** show the N phase; the Sm C phase is also formed by **3i**, exhibiting a schlieren texture under a homeotropic alignment. The N–I transition temperature gradually decreases with increasing m (**3b** > **3e** > **3h**).

For $m = 5$ (**1**) and $m = 6$ (**2** and **3**) compounds, broadly speaking, the effective order for the average N–I transition

Table 1. Transition Temperatures and Latent Heats for Compounds **1**–**3**

	Compounds				Transition temperatures °C							Latent heats kJ/mol	
	m	*n*	R_2	R_3	C		Sm C		N		I	mp	N–I
1a	1	5			·	101	—		(·	68)		48.9	0.7
1b	2	5	H	H	·	98	—		[·	46]	·	33.2	
1c	2	8			·	106	—		[·	61]	·	44.8	
1d	5	5			·	76	—		[·	22]	·	36.5	
1e	5	8			·	88	—		[·	43]	·	47.8	
1f	5	14			·	82	—		[·	51]	·	69.2	
1g	8	5			·	67	—		[·	23]	·	54.2	
2a	2	6	CH_3	H	·	100	—		(·	99)	·	36.9	1.4
2b	2	8			·	97	—		(·	94)	·	40.7	1.4
2c	2	14			·	96	—		—[a]		·	53.3	
2d	6	6			·	75	—		(·	64)	·	53.1	1.1
2e	6	8			·	82	(·	44[b]	·	67)	·	54.1	1.0
2f	6	14			·	76	—		(·	66)	·	67.6	1.1
2g	14	6			·	86	—		—		·	64.4	
2h	14	8			·	85	—		—		·	68.8	
2i	14	14			·	84	—		—		·	79.4	
3a	2	6	H	CH_3	·	98	—		·	109	·	33.9	0.7
3b	2	8			·	103	—		(·	100)	·	44.2	1.0
3c	2	14			·	102	—		(·	98)	·	49.4	0.7
3d	6	6			·	67	—		·	84	·	45.3	0.8
3e	6	8			·	77	—		·	83	·	42.5	0.9
3f	6	14			·	79	—		·	81	·	58.8	1.3
3g	14	6			·	81	—		(·	75)	·	61.2	0.6
3h	14	8			·	81	—		(·	74)	·	73.9	0.7
3i	14	14			·	81	(·	69[b]	·	80)	·	86.4	2.1

Brackets indicate a virtual transition temperature (see text). Parentheses indicate a monotropic transition temperature. a) The compound experienced an N–I transition before recrystallization on the cooling process. b) The latent heat could not be evaluated because of the recrystallization.

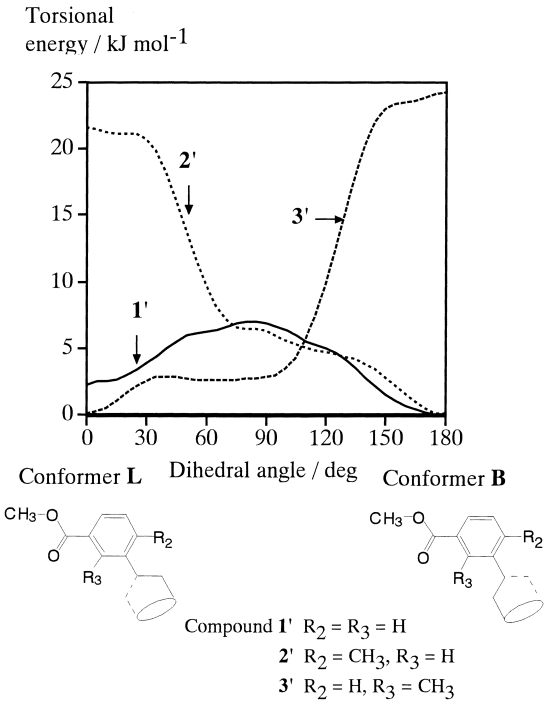


Fig. 5. Rotational barriers for ethyl 3-ethoxy- (**1′**), 3-ethoxy-2-methyl- (**2′**), and 3-ethoxy-4-methylbenzoates (**3′**). The heat of formation was calculated by MOPAC, where the lowerst energy was obtained by the AM1 method.

temperature is given by

$$\mathbf{3} > \mathbf{2} > \mathbf{1}.$$

In order to consider the conformational effect on the LC properties, we estimated the conformation of the long alkoxy group at the R_1 position by a semi-empirical molecular-orbital calculation (MOPAC); the results are shown in Fig. 5.

In the calculation, ethyl 3-ethoxy- (**1′**), 3-ethoxy-4-methyl- (**2′**), and 3-ethoxy-2-methylbenzoates (**3′**) were selected as model compounds of **1**–**3**, respectively.

For **1′**, the rotational freedom of the ethyl group around the Ph–O–C bond should be kept at the LC temperature because of the low rotational barrier (1.5 kcal/mol). In addition, because the energy difference between conformers **L** and **B** is only 0.5 kcal/mol, both conformers should alternate with each other and distribute equally in the gas and liquid phases. In the N phase, the observed N–I transition temperature should be given by a mathematical average of both conformers, supposing that both conformers have an ideal solution behavior;

$$T_{\mathrm{N–I,\,obs}} = \chi_{\mathrm{L}} \cdot T_{\mathrm{N–I,\,L}} + \chi_{\mathrm{B}} \cdot T_{\mathrm{N–I,\,B}}, \; (\chi_{\mathrm{L}} + \chi_{\mathrm{B}} = 1),$$

where χ_{L}, χ_{B}, $T_{\mathrm{N–I,\,L}}$, and $T_{\mathrm{N–I,\,B}}$ indicate the mole fractions of conformers **L** and **B**, and the N–I transition temperatures of the conformers, respectively. In such conditions, $T_{\mathrm{N–I,\,L}}$ should be higher than $T_{\mathrm{N–I,\,B}}$, according to a general requisite for the LC properties,

$$T_{\mathrm{N–I,\,L}} > T_{\mathrm{N–I,\,obs}} > T_{\mathrm{N–I,\,B}}.$$

In the AM1 calculation, because the energy difference between conformers **L** and **B** is 0.5 kcal/mol, the equilibrium constant for both conformers is estimated to be

$$\chi_{\mathrm{L}} \rightleftarrows \chi_{\mathrm{B}} \qquad K = 2.0 \text{ (at 373 K)}.$$

This fact indicates that conformer **B** is slightly preferable in liquid and gas phases. In anisotropic bulk states, such as LC phases, of course, the equilibrium might be affected by intermolecular interactions.

On the other hand, the rotational barrier for **2′** is so high that the ethyl group can not rotate readily, like **1′**. The rotational freedom of the ethyl group would be restricted in a limited range at the LC temperature. The MO calculation predicts that the ethyl group for **2′** distributes in the range between ca. 100 and $-100°$, where the co-planer conformation (180°) is the most preferable (conformer **B**). Thus, compounds **2** should keep a bent shape on average and be unfavorable for the appearance of LC properties. $T_{\mathrm{N–I,obs}}$ is given by

$$T_{\mathrm{N–I,obs}} = T_{\mathrm{N–I,B}} \; (\chi_{\mathrm{B}} = 1).$$

For compounds **3′**, the energy diagram resembles that of **2′**, while conformer **L** is the most preferable regarding energy. $T_{\mathrm{N–I,obs}}$ is given by

$$T_{\mathrm{N–I,obs}} = T_{\mathrm{N–I,L}} \; (\chi_{\mathrm{L}} = 1).$$

As a result, the effective order for the N–I transition temperature is expected to be $\mathbf{3} > \mathbf{1} > \mathbf{2}$.

In fact, the N–I transition temperature for compounds **3** is the highest of all, even though the methyl group at the R_3 position would increase the molecular breadth and distort the phenyl–COO bond. As mentioned above, however, the average N–I transition temperature for **2** is higher than that for **1**. It has been known that toluene has a polarizability (1.2 Å^3) and a dipole moment (0.37 D) along the longitudinal axis.[1] Therefore, the introduction of a methyl group at the R_2 position would enhance the N–I transition temperature. For example, it has been reported that the N–I transition temperature for 4-(4-octyloxyphenoxycarbonyl)phenyl 4-methylbenzoate (C·112·N·189·I) is higher than that of 4-(4-octyloxyphenoxycarbonyl)phenyl benzoate (C·118·N·135·I) by 54 °C.[29] Therefore, the increased polarizability anisotropy would be responsible for an enhancement of the N–I transition temperature for **2**.

One question is whether the alkoxy group at the R_1 position in conformers **L** and **B** would keep the zigzag conformation so that the entire molecule would maintain their linear and bent shapes, respectively. Certainly, the MO calculation predicts that in the hydrocarbon chain the zigzag conformation is the most stable regarding energy. Considering the fact that the energy difference between the trans and gauche conformers is ca. 0.9 kcal/mol, and the energy barrier for the rotation is 1.7 kcal/mol, the alkyl chain is assumed to maintain almost free rotation at the LC temperature, and that the gauche form also distributes (ca. 20% for each methylene unit at 100 °C). However, we have reported that in some aromatic ester compounds having long alkyl and/or alkoxy groups the layer spacings in the Sm A phase are in good agreement with the fully extended

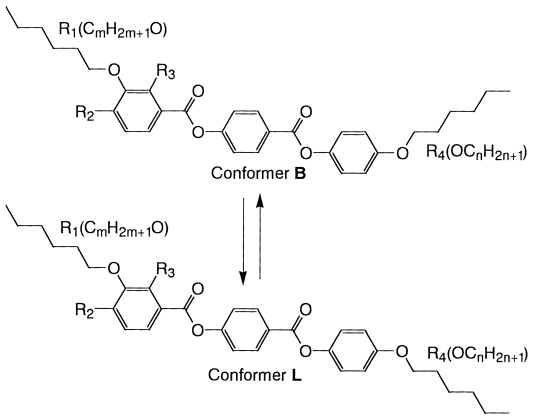


Fig. 6. Conformational isomerism formed from the long alkoxy chain at the R_4 position.

molecular lengths estimated by molecular-orbital calculations.[29] On the other hand, Weissflog et al. reported that in some 1,4-phenylene bisbenzoate compounds having a long lateral alkyl group at the central aromatic ring, the gauche form of the lateral hydrocarbon chain becomes preferential upon ascending the series, giving a calamitic shape of the molecular structure.[30–32] A similar disposition of the conformational equilibrium has been supposed in some 1,3- and 3,4-disubstituted phenylene compounds.[4] Therefore, we conclude that under anisotropic conditions, such as the LC states, the hydrocarbon chain gradually distorts so as to keep the linear and calamitic shape of the entire molecular shape upon extending the chain length by the outer physical forces.

Another question is which conformations are preferable in the alkoxy group at the other terminal position, as shown in Fig. 6.

As can be seen from Fig. 6, the relative conformation of the alkoxy group at the R_4 position also affects the entire molecular shape. Because both conformers are equivalent regarding energy, they might distribute equally in the liquid and gas phases. Strictly speaking, the MO results suggest that the energy difference between two conformers is ca. 0.1 kcal/mol, probably due to the electrostatic interaction between the nearest ester linkage and the ether oxygen. It is assumed, however, that the linear conformation is preferential under anisotropic conditions, such as smectic phases, if there is no energy difference between the bent and linear conformations. For example, we reported in a previous paper that in a homologous series of 4-alkoxyphenyl and 4-alkylphenyl 4-(4-octyloxybenzoyloxy)benzoates and the related ester compounds, the layer spacings in the Sm A phase are close to the calculated longitudinal lengths for the most linear conformers (**L**), rather than the bent (**B**) conformers.[29]

Therefore, we assume that the conformational disposition of the alkoxy group attached at the 4 position is affected by the inter-molecular conditions, and that conformer **L** is preferential in the LC phases.

In order to characterize the smectic properties of the present compounds, some binary phase diagrams for the mixtures were examined; the results are shown in Figs. 4c and 4d. Fig. 4c shows a phase diagram for a mixture of 4-cyano-4′-octyloxybiphenyl (**6**: C·54.5·Sm A·67·N·80·I)[33] and **2e**, where **6** was used as a typical polar LC material.

The binary mixture shows an enhanced Sm A phase with a broad maximum at around 20–60 mol% of **2e**, where the maximum Sm A–I transition temperature is 109 °C at ca. 50 mol% of **2e**. A similar enhancement of the Sm A–N(I) transition temperature was observed for a mixture of **6** and **3d**, where the maximum transition temperature was 90 °C.

Generally, the enhancement of the Sm A–N(I) transition temperature in a binary mixture has been interpreted in terms of intermolecular polar interactions involving the dipole[34,35] or an electron donor and an acceptor one.[36–39] The effect of the molecular shape on the Sm A thermal stability in binary mixtures has been discussed in detail.[40–42] We have supposed that the difference in the molecular shape of both components in connection with the molecular packing in the Sm A phase is also important for the phenomena.[43]

Gray et al. reported that 3-alkoxy-4-R-naphthalene-7-carboxylic acids (**7**) show an interesting substituent effect on the N–I transition temperature;[44,45] the results are cited in Table 2.

In these systems, introduction a lateral substituent apparently enhances the N–I transition temperature and facilitates the formation of the Sm C phase, opposite to the general tendency of LC materials.[1] An attempt has been made to interpret the abnormal substituent effect in terms of the increased dipole moment along the longitudinal direction.[44,45] The enhanced Sm C properties have also been interpreted in terms of an increased dipole moment along the transverse direction.[46]

In fact, the dipole moments along both directions increase by substitution, as shown in Table 3, though the magnitude is not necessarily reflected on the LC properties.

Aromatic carboxylic acids exhibiting LC properties are known to form hydrogen-bonded dimers. The entire molecular shape of the hydrogen-bonded dimers is determined by the relative orientation of the hydrogen-bonded dimer, giving two critical conformers, **L** and **B** (Fig. 7).

Therefore, we estimated the conformation of the alkoxy group by an MO calculation; the results are shown in Fig. 7 and Table 3. As shown in the table, the substituents notably affect the equilibrium constant for the conformation of the hy-

Table 2. Transition Temperatures of 3-Alkoxy-4-*R*-naphthalene-7-carboxylic Acids

m	Transition temperatures (T/°C)			
	R = H	R = Cl	R = Br	R = I
5	N·199·I	N·208·I	N·207·I	N·198·I
6	N·198.5·I	Sm C·160.5·N·207·I	N·203.5·I	N·195·I

For R = H, Br, and I compounds, the Sm C phase commeces from *m* = 9, 7, and 8 homologs, respectively.

Table 3. Physical Properties of 3-Alkoxy-4-*R*-naphthalene-7-carboxylic Acids

	R = H	R = Cl	R = Br	R = I
Bond length, C–R (Å)	1.100	1.719	1.881	2.149
Dipole moment, D (R–Phenyl)	0	1.69	1.70	1.70
van der Waals radii (Å)	1.1	1.8	1.95	2.15
Rotational barrier (kcal/mol)[a)]	0.9	2.2	3.5	4.7
Equilibrium const for conformer **x** and **y** at 373 K[b)]	3.4	5.2×10^{-2}	8.9×10^{-3}	1.9×10^{-3}

from Ref. 47. a) The values were calculated for 3-ethoxy-4-*R*-naphthalene-7-carboxylic acids by AM1 method. b) Calculated from Fig. 7.

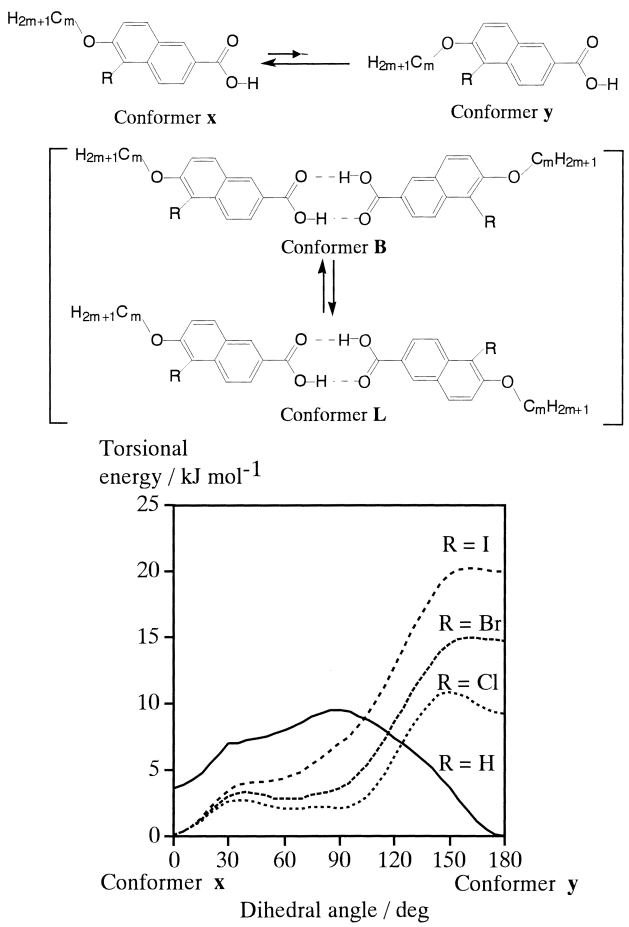


Fig. 7. Rotational barriers for 3-ethoxy-4-*R*-naphthalene-7-carboxylic acid. The heat of formation was calculated by MOPAC, where the lowest energy was obtained by the AM1 method.

drocarbon chain (conformers **x** and **y**). The MO calculation predicts that in hydrogen derivatives conformer **y** is slightly more stable compared with **x**. We can assume that both conformers co-exist in the LC states, and easily alternate wiyh each other, since the energy difference between two conformers and the rotational barrier is small. On the other hand, introducing a the substituent at the 4 position results in destabilizing conformer **y**, giving preferentially conformer **x**. It would be reasonable to assume that the N–I transition temperature for conformer **x** is higher than that for **y**, since the former is excellent in concerning the linearity of the entire molecular shape compared with the latter. Thereby, the substituent would increase the molecular breadth by the order of I > Br > Cl, as predicted by Gray et al.[44,45] An increase in the rigidity around the ether bond due to the steric hindrance between the alkoxy group and halogens is also responsible for an enhancement of the N–I transition temperature.

The change in the smectic properties is assumed to be also concerned with the change in the entire molecular shape due to introducing a substituent.

Conclusion

In compounds with a long lateral alkoxy group, the conformation of the alkoxy group is important in determining the LC properties. Both the linear and bent conformers exhibit LC properties. A similar conformational effect is assumed to be common in compounds with a longitudinal alkoxy group. We assume that the conformational effect is more important in determining the smectic properties in connection with the packing of molecules.

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