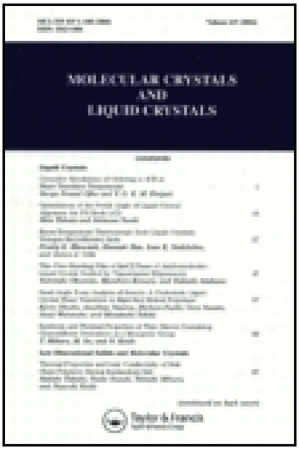

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Molecular Structure and Liquid Crystalline Properties: The Effect of the Terminal Hydroxy Group on Mesomorphic Properties

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Molecular Structure and Liquid Crystalline Properties: The Effect of the Terminal Hydroxy Group on Mesomorphic Properties

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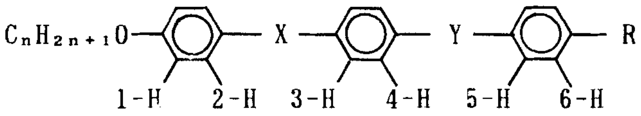
The thermal properties of 4-hydroxyphenyl 4-(4-alkoxybenzoyloxy)benzoates (1), 4-(4-alkoxyphenoxycarbonyl)phenyl 4-hydroxybenzoates (2), 4-(4-alkoxybenzoyloxy)phenyl 4-hydroxybenzoates (3), 4-hydroxyphenyl 4-(4-alkoxyphenoxycarbonyl)benzoates (4) and some related compounds have been examined. The nematic-isotropic and smectic A-nematic transition temperatures are compared with those of the related compounds having a methoxy group and a chlorine atom instead of the hydroxy group. The results indicate that the mesomorphic properties are almost independent of the hydrogen bonding at the terminal position. On the other hand, the effect of the hydrogen bonding is recognized in the smectic properties in some binary mixtures consisting of the hydroxy compounds and aryl acids. The effect of hydrogen bonding on mesomorphic properties is discussed.

INTRODUCTION

It is well known that some intermolecular interactions involving dipoles and induced ones are important in determining mesomorphic properties. In hydroxy compounds, the hydrogen bonding is also postulated to play some important role for the mesomorphic phenomena. Gray proposed that a hydroxy group is unfavorable for mesomorphic phenomena since intermolecular hydrogen bonding raises the melting point above the mesophase-isotropic transition temperature.[1] On the other hand, Schroeder *et al.* reported that 4-(4-hexyloxybenzoyloxy)phenyl 4-hydroxybenzoate and some related compounds show very high nematic-isotropic (N—I) transition temperature, and suggested the contribution of the associated complex by the hydrogen bonding.[2,3] Simultaneously, the formation of the smectic A phase is also discussed in terms of the hydrogen bonding.[3] Recently, we reported that the N—I transition temperatures of 4-hydroxyphenyl 4-alkoxybiphenyl-4′-carboxylates and 4-alkoxybiphenylyl 4-hydroxybenzoates are almost independent of the hydrogen bonding,[4] but the N—I and smectic A-nematic (S_A—N) transitions for the mixtures of the hydroxy compounds and the related acids show a non-linear behavior against the molar concentration due to intermolecular hydrogen bonding.[5]

Recently, it is reported that some liquid crystals having a diol group show an interesting polymesomorphism in the smectic phase due to the hydrogen bonding.[6]

In order to examine the effect of hydrogen bonding on the mesomorphic properties, we prepared some homologs of four related compounds, as shown below.



Compound	X	Y	R
1	-COO-	-COO-	OH
2	-OOC-	-OOC-	OH
3	-COO-	-OOC-	OH
4	-OOC-	-COO-	OH

(n = 8 - 10)

The mesomorphic properties are compared with those for two related compounds (*R* = OCH_3, Cl) since the methoxy group and the chlorine atom would have a similar volume to the hydroxy one, though the electronic properties are different. The effect of the hydrogen bonding is also discussed.

EXPERIMENTAL

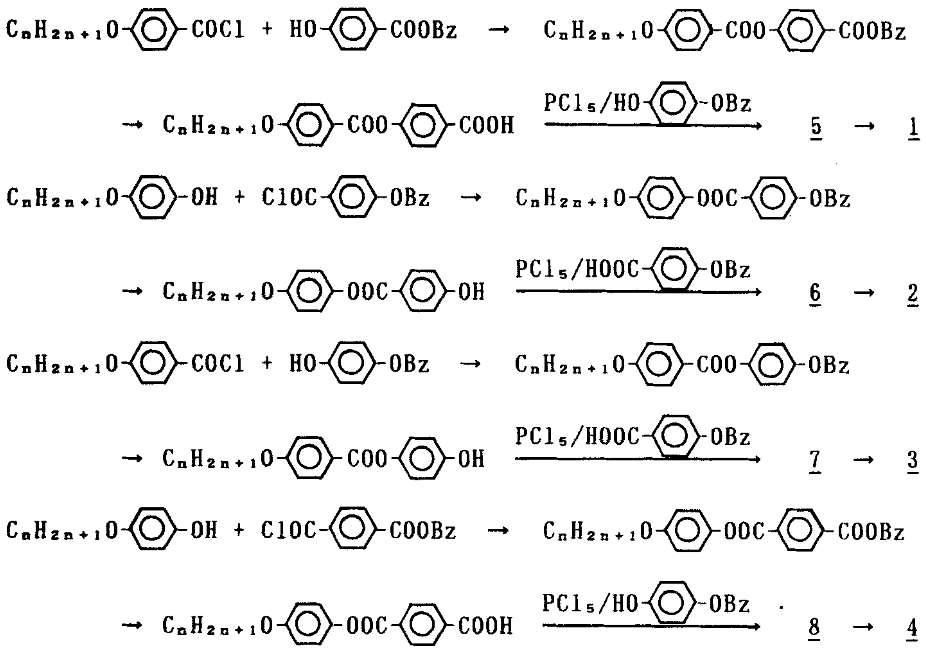
Compounds 1 – 4 were prepared according to Scheme I, and the methods were already reported in an earlier paper.[7]

In Scheme I, the benzyl group was removed by catalytic hydrogenation with palladium-carbon (10 w/w%) in a mixed solvent of toluene and acetic acid.[7] Compounds 5 – 8, the benzyl derivatives of 1 – 4, respectively, are mesogenic, and the transition temperatures and the elemental analyses are shown in Table II.

The products were identified by elemental analysis and ^{1}H-NMR, and the elemental analysis data are shown in Table III.

METHOD

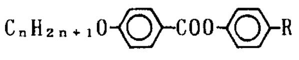
Transition temperatures were determined by using a Nikon POH polarizing microscope fitted with a Mettler FP-52 heating stage. Infrared spectra were recorded by a Japan-spectroscopic FT-IR-3 spectrometer. NMR spectra were taken by a Nihon-denshi JEOL JNM-GSX-400 spectrometer.



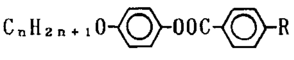
SCHEME I

TABLE I

Transition temperatures for compounds 9 and 10 (T/°C)



Compound 9



Compound 10

		Compound 9			Compound 10		
n	R	C	N	I	C	N	I
8	OH	·	107 -	·	·	160 -	·
9		·	111 (· 90)	·	·	153 -	·
10		·	112 (· *1)	·	·	148 -	·
8	OCH_3	·	82 (· 76)	·*2	·	64 · 78	·*2
8	Cl	·	76 · 77	·*2			

Parentheses indicate a monotropic transition. *1A nematic phase was formed on the cooling stage. *2Reference 8.

RESULTS

The transition temperatures for compounds 9 and 10, the synthetic intermediates of 3 and 2, respectively are shown in Table I.

TABLE II

Transition temperatures (T/°C) and elemental analyses (%) for compounds **5**–**8**

			Transition temperatures					Elemental analyses	
Compound	n	R	C	S_C	S_A	N	I	C	H
5	8	OBz	·	140 (· 132)	-	· 218	·	76.1	6.55
	9		·	135 · 136	-	· 211	·	76.1	6.78
	10		·	127 · 147	-	· 208	·	76.5	6.90
6	8		·	147 -	· 200	· 219	·	76.1	6.48
	9		·	147 -	· 202	· 218	·	76.3	6.55
	10		·	141 -	· 205	· 216	·	76.3	6.82
7	8		·	150 -	-	· 223	·	76.0	6.51
	9		·	154 -	-	· 217	·	76.1	6.58
	10		·	155 -	-	· 213	·	76.7	6.81
8	8		·	192 -	· 206	· 222	·	75.9	6.54
	9		·	187 -	· 207	· 216	·	76.2	6.52
	10		·	183 -	· 207	· 213	·	76.5	6.88

Parentheses indicate a monotropic transition. The elemental analyses for the octyloxy, nonyloxy, and decyloxy homologs were: C; 76.1, H; 6.57 calcd. for $C_{35}H_{36}O_6$, C; 76.3, H; 6.76 calcd. for $C_{36}H_{38}O_6$, and C; 76.5%, H; 6.94% calcd. for $C_{37}H_{40}O_6$, respectively.

The benzyl derivatives of compounds **1**–**4**, **5**–**8**, are mesogenic, and the transition temperatures and the elemental analyses are summarized in Table II.

Transition temperatures and elemental analyses for compounds **1**–**4** are summarized in Table III.

IR studies of compounds **1**–**4**: IR spectra in non-polar solvents such as carbon tetrachloride were impossible to record because of low solubility. The IR spectral data in Table IV were taken by the KBr disc method.

The absorption maxima around 3500 and 3400 cm^{-1} arise from the stretching vibrations of the isolated and hydrogen-bonded hydroxy groups, respectively. Compound **2** shows two absorption maxima at 3452 and 3373 cm^{-1}, separately. On the other hand, compound **3** shows only a broad maximum at 3405 cm^{-1}.

The trend in Table IV should be dependent on the state of the crystalline phase, and different from that in the liquid crystalline phases. Infrared spectra for the hexyloxy homolog of compound **3** in the liquid crystalline phase were studied by Schroeder *et al.*[3]

NMR studies of compounds **1**–**4**: In order to estimate the acidity of the terminal hydroxy groups, the NMR spectra for the octyloxy homologs of compounds **1**–**4** were recorded in 6D-DMSO, and the results are summarized in Table V.

Binary phase diagrams of acid and phenols: Binary phase diagrams for the mixtures of 4-(4-octyloxybenzoyloxy)benzoic acid and the phenolic compounds are shown in Figure 1.

In Figure 1a, the minimal N—I transition temperature evaluated from a contact method is 198°C.

In Figure 1b, the induced S phases around the center of the diagram show a schlieren texture, but the phase is discontinuous with the S_C phase at ca. 70 mol% of the acid. The maximal S—S_A and S_A—N transition temperatures evaluated by

TABLE III

Transition temperatures (T/°C) and elemental analyses (%) for compounds 1–4

			Transition temperature				Elemental analyses	
Compound	n	R	C	S_A	N	I	C	H
1	8	OH	·	160 -	· 211	·	72.5	6.44
	9		·	158 -	· 207	·	72.9	6.67
	10		·	154 -	· 203	·	73.3	6.99
	8	OCH_3	·	107 · 122	· 226	·*1		
		Cl	·	123 · 200	· 209	·*1		
2	8	OH	·	183 · 189	· 207	·	72.4	6.38
	9		·	176 · 197	· 202	·	73.1	6.75
	10		·	173 · 201	-	·	73.3	6.89
	8	OCH_3	·	101 -	· 214	·*1		
		Cl	·	119 · 185	· 214	·*1		
3	6	OH	·	175 -	· 315	·*2		
	8		·	183 -	· 220	·	72.6	6.42
	9		·	173 -	· 214	·	72.9	6.75
	10		·	175 -	· 211	·	73.1	6.95
	8	OCH_3	·	124 -	· 224	·*1		
		Cl	·	168 -	· 217	·*1		
	6	NH_2	·	191 -	· 207	·*2		
4	8	OH	·	215 -	· *3	·	72.5	6.45
	9		·	211 -	· *3	·	73.0	6.56
	10		·	211 -	· *3	·	73.2	7.01
	8	OCH_3	·	167 -	· 218	·*1		
		Cl	·	195 · 222	-	·*1		

*1Reference 7, *2Reference 3. *3The correct transition temperature was not determined because of rapid decomposition in the nematic phase. The elemental analyses for octyloxy, nonyloxy, and decyloxy homologs were: C; 72.7, H; 6.54 calcd. for $C_{28}H_{30}O_6$, C; 73.1, H; 6.77 calcd. for $C_{29}H_{32}O_6$, and C; 73.4%, H; 6.99% calcd. for $C_{30}H_{34}O_6$, respectively.

TABLE IV

IR data for the octyloxy homologs of compounds 1–4

Compound	ν_{OH} (cm^{-1})	ν_{CO} (cm^{-1})
1	3482, 3378 (sh)	1731, 1713
2	3452, 3373	1733, 1711
3	3405	1729, 1705
4	3440, 3388 (sh)	1730

Sh indicates a shoulder peak.

a contact method are 164 and 201°C, respectively. For the mixture the minimal N—I transition temperature is 202°C.

DISCUSSION

It is well known that the hydroxy group of phenol is acidic (Ka, 2.06 × 10^{-10})[9] and forms the complex due to the hydrogen bonding. In the present compounds, the acidity of the hydroxy groups would vary with electronic interactions between

TABLE V

NMR data for the octyloxy homologs of compounds 1–4 (ppm. from internal TMS).

Compound	Chemical shift							Concentration (mol/l)
	1-H	2-H	3-H	4-H	5-H	6-H	OH	
1	7.08	8.10	7.50	8.20	7.13	6.82	9.50	0.001
2	6.99	7.20	8.20	7.49	8.02	6.95	10.59	0.001
3	7.12	8.08	7.33	7.33	7.96	6.94	10.53	0.001
4	7.01	7.12	8.30	8.30	7.24	6.83	9.54	0.001
4	7.01	7.12	8.30	8.30	7.24	6.83	9.54	0.01

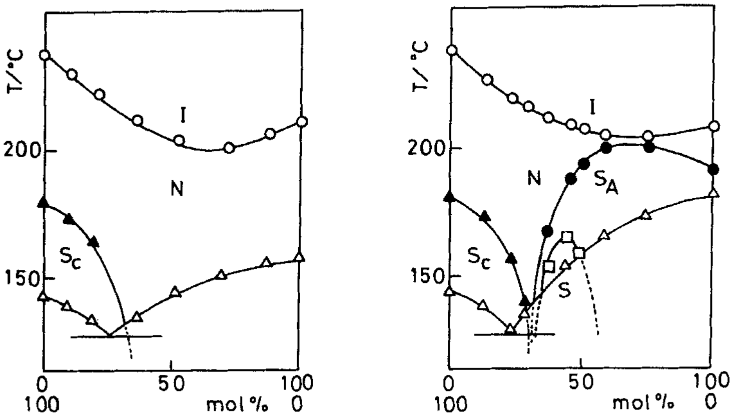


FIGURE 1 Binary phase diagrams for the mixtures of 4-(4-octyloxybenzoyloxy)benzoic acid (on left) and a) the octyloxy homolog of compounds 1 (on right), and b) 2. Dashed lines indicate a monotropic transition.

Compounds 1 and 4 Compounds 2 and 3

FIGURE 2 Electronic interactions between the hydroxy and carboxy groups.

the hydroxy group and the carboxy one at the para position, as shown in Figure 2.

In compounds 2 and 3, the electron-withdrawing nature of the carbonyl group would decrease the electron density of the hydroxy group and increase the acidity, while the effect would be less in compounds 1 and 4. Considering a similar effect of the carboxy group at position X, the acidity of the hydroxy group would decrease in the order of 2 > 3 > 4 > 1. In fact, the chemical shift of the hydroxy group in 6D-DMSO shows an up-field shift of the same order. The IR spectrum in the solid phase shows two peaks; that is, a sharp band at ca. 3500 cm^{-1} due to the vibrational stretching of the free hydroxy group, and a broad band at ca. 3400 cm^{-1} due to that of the associated hydroxy group. As we can see from Table IV, compounds 2 and 3 form stronger associated complexes than 1 and 4. A similar trend is expected in the solution and the liquid crystalline phases. The presence of the hydrogen bonding in the liquid crystalline phases has been confirmed by IR spectroscopy.[3]

It is well known that hydrogen bonding enhances melting and boiling points. In fact, the hydroxy derivatives of compounds 9 and 10 have higher melting points by 25 and 97°C than the corresponding methoxy derivatives, respectively. For the octyloxy homologs of compounds 1–4, the melting points are higher by 53, 82, 51, and 48°C than the corresponding methoxy derivatives, and 37, 64, 7, and 20°C than the chloro ones, respectively. These results indicate that the terminal hydroxy group fairly enhances the melting point.

For the hydroxy derivatives of compound 9 the N—I transition temperatures are higher by ca. 15°C than those of the methoxy and chloro derivatives. Although compound 10 shows no nematic phase due to high melting points, it would be reasonable to assume that the N—I transition occurs at ca. 90°C similar to 9.

On the other hand, the N—I transition temperatures for the octyloxy homologs of compounds 1–4 are always lower than those for the methoxy and chloro derivatives except for that of the hexyloxy homolog of 3 which was reported by Schroeder *et al.*[2,3] As far as the present results are concerned, therefore, the hydrogen bonding of the terminal hydroxy group neither enhances nor reduces the N—I transition temperature. A similar trend has been found in the 4-*R*-phenyl 4-(4-trans-*n*-penylcyclohexyl)benzoate system.[10] The N—I transition temperature for the hydroxy derivative is higher by 5°C than that of the methoxy one.

In Table III, the transition temperatures of the amino derivative reported by Schroeder *et al.*[3] are also indicated. As we can see from the comparison, the N—I transition temperature of the amino derivative is quite reasonable, indicating that the hydrogen bonding of the terminal amino group also has no effect on the transition temperature.

In a previous paper, we reported that halogens at the terminal position tend to enhance the smectic A-nematic (isotropic) (S_A—N(I)) transition temperature, and the methoxy group decrease it due to the electronic nature of the substituents.[7]

The hydroxy group has an electron-donating nature similar to the methoxy one, so that these two compounds are expected to have similar smectic properties.

For methoxy and the chloro derivatives of compound 1 the ratios of the S_A—N to N—I transition temperatures are 0.79 and 0.98, respectively. Considering the fact that for the hydroxy derivatives the nematic phase recrystallized at ca. 130°C on the cooling stage, the S_A—N transition temperatures are fairly low similar to the methoxy derivative. For compound 2 the chloro derivative shows the S_A phase where the ratio of the S_A—N to N—I transition temperatures is 0.94, and the methoxy derivative is nematogenic. Interestingly, the hydroxy derivatives show the S_A phase, and the ratios of the S_A—N to N—I transition temperatures are fairly high (>0.96). Apparently, the terminal hydroxy group enhances the S_A—N transition temperature. For compound 3 all chloro, methoxy, and hydroxy derivatives do not show the S_A phase, indicating that the structural and electronic properties of the core portion are very unfavorable for the layer arrangement of the molecules.

For compound 4 the chloro derivative shows the S_A phase where the ratio of the S_A—N to N—I transition temperatures is 1.0, and the methoxy derivative is nematogenic and the virtual S_A—N transition temperature is fairly low. Similarly, the hydroxy derivatives show only the nematic phase. The S_A—N transition temperatures were not possible to estimate from the binary phase diagram, since the recrystallization of the nematic phase occurred at 205–210°C, and that the compounds easily decomposed in the nematic phase. Therefore, it is impossible to recognize the apparent effect of the hydroxy group on the S_A—N transition temperature.

Schroeder *et al.* have proposed the molecular arrangements in the nematic and smectic A phases, as shown in Figure 3.[2,3] The authors considered that the formation of complex [A], having a linear conformation is responsible for the enhancement of the N—I transition temperature, and complex [B] for S_A—N.

Certainly, the complex is expected to form preferentially the linear conformation due to anisotropic interactions in the nematic phase. However, the present results indicate that the formation does not affect the N—I transition temperature.

In general, liquid crystals have a rigid core involving linkage(s). The linkage determines the molecular properties such as linearity, rigidity, and polarizability which are very important in determining the N—I transition temperature. In the model of the complex, the hydrogen bonding (O—H—O) is equivalent to the linkage of usual liquid crystalline molecules.

The hydrogen bonding would enhance the N—I transition temperature, only when the hydrogen bonding specifically stabilizes the linear conformation, [A], and increases the rigidity of *the linkage*. However, it is difficult to expect that the hydrogen bonding stabilizes only the linear conformer, since the hydrogen atom of the hydrogen bonding has a spherical 1S orbital. In addition, it is well known that the linkage consisting of odd-number atoms reduces the linearity of the molecule. A similar argument can apply to the hydrogen bonding of the amino compound in Table III.[3]

Schroeder *et al.* have mentioned that conformer [B] enhances the S_A—N transition temperature.[2,3] Certainly, the hydroxy derivatives of compound 2 show high S_A—N transition temperature, while the methoxy derivative shows no S_A phase. At present, however, the smectic properties are impossible to correlate with the

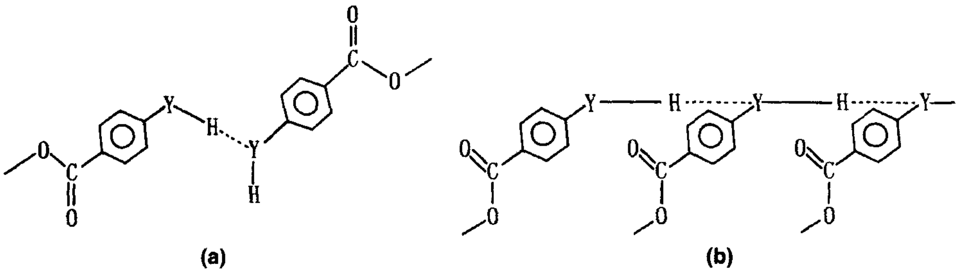
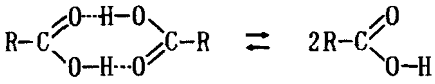


FIGURE 3 Molecular arrangements in nematic (a) and smectic A phases (b). Y indicates —O— or —NH—.

hydrogen bonding, since the apparent effect of the hydrogen bonding is not recognized in the other compounds.

In connection with hydrogen bonding, an interesting behavior is recognized in the binary phase diagram in Figure 1. The hydrogen bonding of acid and phenol may be roughly represented by:



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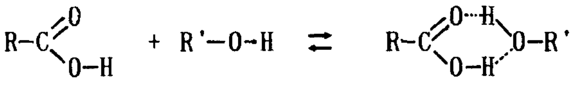

----(2)

It is well known that the acid dimer (Equation 1) is responsible for the formation of the stable nematic phase, where the linear conformation of the dimer is supported by *two hydrogen bondings*.[1] The non-linear behavior of the N—I transition temperature and the formation of the tilt S phase and enhancement of the S_A—N transition temperature around the center of the diagram (Figure 2b) may be concerned with the decomposition of the dimer (Equation 1) and recombination of the components (Equation 2).

Recently, some diol compounds are reported to show smectic phases having a bilayer arrangement,[6,12] and some cyclohexane-1,3-diol compounds show discotic properties.[12] As pointed out by the authors, the hydrogen bonding of two hydroxy groups would facilitate the anisotropic arrangement of the molecules.

A similar phenomenon is observed in some silane compounds, where the homologs show a discotic mesophase, while their molecular structures are not discotic.[13]

CONCLUSION

The hydrogen bonding arising from terminal hydroxy and amino groups of the present type rarely enhances the N—I transition temperature, since the hydrogen bonding does not give rise to anisotropic intermolecular interactions.

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