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Substituent Effects on Mesomorphic Properties of Some Liquid Crystals with 4-Nitrobenzene at the Terminal Position

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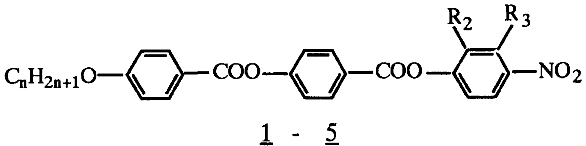
This paper describes the thermal properties of 4-nitrophenyl 4-(4-alkoxybenzoyloxy)benzoates and 4-*N*-[(4-alkoxybenzoyloxy)benzylidene]-4-nitroanilines that have an additional methyl, normal alkoxyl, or hydroxyl substituent on the nitrophenyl group. Methyl and methoxyl groups adjacent to the nitro group reduced the liquid crystalline properties, and derivatives with a long alkoxyl group at the 2 position are nonmesogenic. On the other hand, a hydroxyl group at the 2 position rather enhances the nematic and smectic properties, although a hydroxyl group has a similar volume to the methyl one. The results are discussed in terms of the steric effects of the substituent and electrostatic circumstances around the nitro group.

Liquid crystals with a polar terminal group such as a nitro or a cyano group are useful materials for display devices. In addition, polar liquid crystals are known to show interesting polymesomorphism involving monolayer (S_{A1}), bilayer (S_{A2}), partially bilayer (S_{Ad}) type's smectic A and reentrant nematic (N_{re}) phases, where strong electrostatic interactions around the polar groups are supposed to be important for the phenomena.[1] The polymorphism and layer spacing in the smectic phases are known to be affected by a lateral substituent.[2,3] Previous papers also demonstrated that the polymesomorphism in polar liquid crystals is sensitively affected by the steric effect of lateral substituents,[4—7] and also the position of the polar group.[8—10]

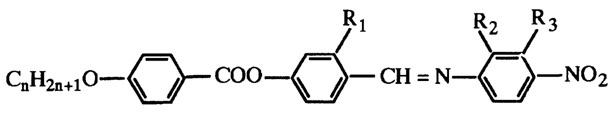
On the other hand, 2-methyl-4-nitroaniline and the related compounds are known to show nonlinear optical properties due to strong intramolecular charge-transfer interaction in the dissymmetric environments.[11] Especially, the substituents at 2 and/or 3 positions are important for dissymmetric arrangement of the molecules in the solid phase. From these results, we can assume that electrostatic and steric interactions around the polar group are important for the molecular arrangement not only in the liquid crystalline phases but also in the solid one.

This paper describes the effects of lateral substituents adjacent to the polar group on the mesomorphic properties of the related compounds shown below (Chart 1).



1 - 5

R_2 = H, CH_3
R_3 = H, OH, OCH_3 , CH_3



6 - 12

R_1 = H, OH
R_2 = H, CH_3
R_3 = H, OH, OCH_3 , OC_2H_5 , OC_4H_9

Chart 1.

In this work, we are mainly interested in the effects of substituents adjacent to the nitro group on the liquid crystalline properties, to develop novel liquid crystals with nonlinear optical properties.

Experimental

The esterification was done by the method described in a previous paper,[8] and the purity was checked by HPLC (Shimadzu LC-10S) where an ODS column were used, and elemental analysis.

Transition temperatures were measured with a Nikon POH polarizing microscope fitted with a Mettler FP-52 heating stage.

Results and Discussion

Transition temperatures of ester compounds **1**—**5**, and the related azomethine ones **6**—**12** are summarized in Tables 1 and 2, respectively.

The homologous series of **1** is known to show stable S_A as well as N phases when the alkoxyl group is suitably long, where the S_A phase has been known to have a partially bilayer arrangement.[8]

Compound **2**, with a hydroxyl group at the 2 position, has similar mesomorphic properties to **1**, where the S_A phase commences from the pentyloxy homolog. The smectic phase was characterized by the binary phase diagram, as shown in Fig. 1. In Fig. 1(1) the smectic phase of the nonyloxy homolog of **7** is miscible with the S_{Ad} phase of 4-(4-nitrobenzoyloxy)-4′-octyloxybiphenyl, where the S_A–N transition shows a linear correlation with the molar composition, and an N_{re} phase is observed below the S_A phase, indicating that the S_A phase of **7** intrinsically has an S_{Ad} nature. Incidentally, the homologous members of compounds, **10** and **11** show

Table 1. Transition Temperatures of Compounds **1**—**5** (T/°C)

Compound	R_2	R_3	n	C		S_A		N		I
1[a)]	H	H	5	·	122	-		·	240	·
			6	·	118	·	152	·	238	·
			7	·	121	·	199	·	228	·
			8	·	114	·	210	·	224	·
2	H	OH	4	·	116	-		·	230	·
			5	·	106	·	141	·	221	·
			6	·	109	·	165	·	217	·
			7	·	124	·	184	·	211	·
			8	·	96	·	195	·	209	·
			9	·	99	·	201	·	209	·
			10	·	91	·	203	-		·
			11	·	94	·	195	-		·
3	H	CH_3	7	·	109	·	118	·	163	·
			8	·	88	·	142	·	161	·
			9	·	98	·	149	·	157	·
			10	·	86	·	155	·	156	·
			11	·	98	·	158	-		·
4	H	OCH_3	5	·	124	-		·	146	·
			6	·	128	-		·	144	·
			7	·	130	-		·	141	·
			8	·	122	-		·	140	·
			9	·	120	(·	112)	·	139	·
			10	·	118	·	134	·	139	·
			11	·	106	·	138	-		·
5	CH_3	H	8	·	91	-		·	175	·
			9	·	96	-		·	168	·
			10	·	82	-		·	169	·

Parentheses indicate a monotropic transition. C, S_A, N, and I indicate crystal, smectic A, nematic phases, and isotropic solution, respectively. a) from Ref. 8.

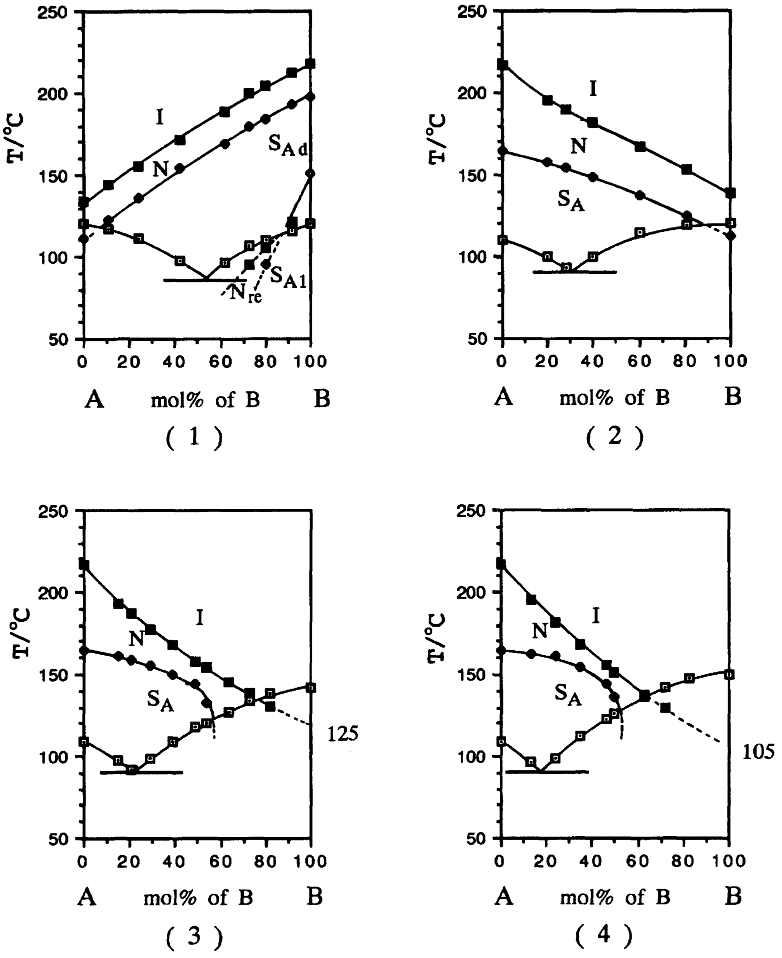
Table 2. Transition Temperatures of Compounds **6**—**12** (T/°C)

Compound	R_1	R_2	R_3	n	C		N_{re}		S_A		N		I
6[a)]	H	H	H	5	·	136	-		-		·	272	·
				6	·	139	-		·	192	·	265	·
				7	·	127	-		·	229	·	255	·
				8	·	131	-		·	245	·	251	·
7	H	H	OCH_3	7	·	130	-		-		·	142	·
				8	·	131	-		-		·	139	·
				9	·	121	-		(·	111)	·	134	·
8	H	H	OC_2H_5	6	·	149	-		-		-		·
				7	·	152	-		-		-		·
				8	·	150	-		-		-		·
				9	·	142	-		-		[·	125]	·
9	H	H	OC_4H_9	6	·	159	-		-		-		·
				7	·	163	-		-		-		·
				8	·	146	-		-		-		·
				9	·	152	-		-		[·	105]	·
10	H	CH_3	H	6	·	112	-		-		·	205	·
				7	·	100	-		-		·	201	·
				8	·	104	-		-		·	199	·
				9	·	117	-		-		·	190	·
				10	·	112	-		-		·	185	·
				11		92	(·	69)	·	153	·	173	
11	OH	CH_3	H	6	·	124	-		-		·	231	·
				7	·	119	-		-		·	200	·
				8	·	117	-		-		·	197	·
				9	·	119	·	122	·	160	·	196	·
12	OH	H	OC_2H_5	6	·	149	-		-		-		·
				7	·	142	-		-		-		·
				8	·	133	-		-		-		·
				9	·	126	-		-		(·	119)	·

Brackets indicate a virtual transition temperature extrapolated from the binary phase diagrams (see Fig. 1). N_{re} indicates a reentrant nematic phase. a) from Refs. 12 and 13.

and N_{re} phase. These facts suggest that the smectic A for these compounds has the S_{Ad} nature. In Fig. 1(2) the S_A phase for the hexyloxy homolog of **2** is miscible with the S_A phase of the nonyloxy homolog of **7**. The homologous series of **3**, with a methyl group at the 2 position, has less stable N and S_A phases than **1** and **2**, where the S_A phase probably commences from the heptyloxy homolog. The homologous series of **4** also has N and S_A phases. However, the beginning of the S_A phase is the nonyloxy homolog. The 3-methyl compound, **5**, has only an N phase, while the N–I transition temperatures are little higher than those of **3**.

The homologous series of **6** which is the parent compound of **7**—**12**, has N–I transition temperatures higher than those of **1**, and the S_{Ad} phase commences from the hexyloxy homolog. For 2-alkoxy compounds, only a methoxy compound, **7**, is mesogenic. The N–I transition temperatures for the nonyloxy homologs of **8** and **9** were estimated from the binary phase diagrams shown in Fig. 1(3) and (4). The nonyloxy homolog of **12** shows a monotropic N phase, where the N–I transition temperature is similar to the estimated transition temperature of **8**. The 3-methyl compounds, **10** and **11**, have the N phase, and the higher members have the S_A phase as well. For comparison, the N–I transition temperatures for compounds, **6**—**9** are given with those of the related compounds, **13** and **14**, and the results are summarized in Table 3. The trend of the N–I transition temperature for compound **13** is quite similar to that of the parent compound **14**, while the trend for compounds **6**—**9** is fairly different. The possible conformations of the terminal alkyl group are demonstrated in Fig. 2. Generally, the terminal alkyl group has two rotational isomers (Fig. 2(1)), where from the energy point of view both conformers are equivalent, and must be present in the isotropic solution and liquid crystalline phases. On ascending the series, both longitudinal and transverse lengths of the molecule would increase simultaneously so that the anisotropy of the molecular structure does not increase as much. As shown in Table 3, for the homologous series of compound **14**, the N–I transition temperature decreases gradually on ascending the series (30 °C from the methoxy to the octyloxy homolog). In compound **13**, the one conformer of the two should be prohibited due to steric interaction between the alkoxyl and adjacent nitro groups so that the rigidity of the long alkyl group may increase. In addition, the extension of



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

Fig. 1.

Table 3. N–I Transition Temperatures of Compound **13** and **14** (T/°C)

Compound R$_1$ (or R$_2$)	H	CH$_3$	OCH$_3$	OC$_2$H$_5$	OC$_4$H$_9$	OC$_8$H$_{17}$
6—**9** (R$_1$=NO$_2$)	251[a)]		139	[125]	[105]	
13 (R$_2$=NO$_2$)	134	147	171	178	172	164
14 (R$_2$=H)[b)]	141	199	224		211	194

X=COO for compounds **13** and **14** and CH=N for **6**—**9**. The values in the brackets were extrapolated from the binary phase diagrams. a) The value is for the nonyloxy homolog (from Ref. 12). b) from Ref. 14.

the alkoxyl group may increase the longitudinal length rather than the breadth around the alkoxyl group. In fact, the depression of the N–I transition temperature from the methoxy homolog to octyloxy one is only 7 °C, as shown in Table 3. On the other hand, these compounds have a large substituent at the lateral position, where the alkoxyl group extends toward the lateral direction of the molecule, as shown in Fig. 2(3). The conformer should be unfavorable for displaying the liquid crystalline properties. As is evident from Table 2, the alkoxyl group adjacent to the nitro group tends to enhance the melting point, and the N phase is formed only by the methoxy compound. The N–I transition temperatures extrapolated from the binary phase diagrams are gradually reduced on ascending the series. An interesting fact in Table 3 is that the N–I transition temperature tends to plateau, while the extension of the alkoxyl group would be the cause of the increase in the molecular breadth or the bend of the molecular structure. The hydroxy compound **2** has somewhat interesting mesomorphic properties. The introduction of the hydroxyl group gives rise to a little reduction of the N–I transition temperature, while the hydroxyl group would have a similar volume to the methyl one. There is no doubt that the steric effect of the hydroxyl group reduces the N–I transition temperature like the methl group. Therefore, the electrostatic effect of the hydroxy group adjacent to the nitro group enhances the N–I transition temperature. The hydroxyl group adjacent to the nitro group forms strong intramolecular hy-

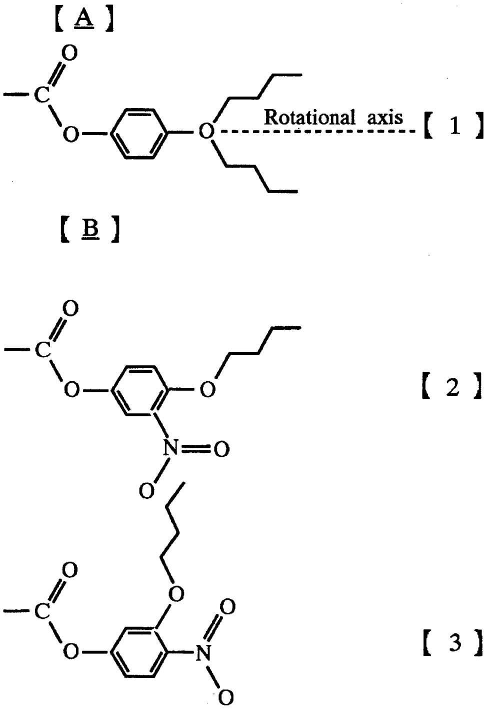


Fig. 2.

drogen bonding (IR: $\nu_{OH}=3300$—3400, $\nu_{NO_2,AS}=1485$, and $\nu_{NO_2,S}=1260\ cm^{-1}$ (KBr disc); PMR: $\delta=10.8$ ppm from TMS in $CDCl_3$ for the hexyloxy homolog of **2**). Changes in polarity and polarizability due to the intramolecular hydrogen bonding must be concerned in the enhancement of the N–I transition temperature.

Polar liquid crystals are known to show very complex polymesomorphisms in the liquid crystalline phases, where attractive interactions involving dipoles arising from the polar group are supposed to be important for the phenomena.[1] In these compounds the beginning of the smectic A phase and the ratio of S_A–N to N–I transition temperature are strongly dependent on the substituent. The dipole moments for nitrobenzene derivatives in benzene and the beginning of the S_A phase are summarized in Table 4. For the phenomena, both steric and electrostatic factors of the substituents must be taken into consideration. A bulky substituent at the 2 position such as a methoxyl group should interrupt the proximity of the nitro groups due to steric hindrance, weakening the polar interactions in spite of the large dipole moment. Considering thus, we can assume that the formation of the S_A phase is easy when the polarity of the nitrobenzene moiety is 3—4 D, and the terminal long alkoxyl group is indispensable for the formation when the polarity of the nitrobenzene core is large (>4 D). This indicates that the polar interactions are not always additive for the formation of the S_A phase.

Table 4. The Dipole Moments of Nitrobenzene Derivatives and Beginning of the S_A Phase

R	o-OH	o-CH$_3$	H	m-CH$_3$	o-OCH$_3$
Dipole moment (D)	3.14[a)]	3.82[b)]	3.96[c)]	4.23[d)]	4.87[e)]
Compound	**2**	**3**	**1** and **6**	**10**	**4** and **7**
Commencement of S_A phase (n=)	5	7 (or 6)	6	11	9

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The examination of nonlinear optical properties of these compounds is now underway.

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