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New liquid-crystalline compounds with an intramolecular hydrogen bond

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New liquid-crystalline compounds with an intramolecular hydrogen bond are presented. They are derived from 2-methylalkanoic acid and resorcinol. The spontaneous polarization of the new compounds is larger than that of the analogues without the hydrogen bond. This paper details the method of synthesis and their physical properties.

1. Introduction

Since the discovery of ferroelectric liquid crystals [1] and the subsequent discovery of the surface-stabilized ferroelectric liquid crystal devices [2], much effort has been made to increase the spontaneous polarization. Two approaches are taken: enlargement of the dipole moment of the compound [3] and dampening of the dipole rotation [4].

Dipoles of ester or ether groups have been frequently used as sources of spontaneous polarization. However only a few compounds with a carbonyl group, whose dipole moment is larger than that of an ester group, have been reported to be ferroelectric, and their spontaneous polarization is fairly large [3]. Enlargement of the dipole moment has also been tried by using several dipoles. However, the spontaneous polarization strongly depends on whether they are aligned in the same or the reverse direction. In the former case, a large spontaneous polarization is expected. However, the latter case would give a much smaller spontaneous polarization. Only a few compounds have been found to show the enlarged spontaneous polarization [5].

Rotation of the dipole moment around the molecular axis considerably suppresses the spontaneous polarization. To dampen this rotation, positioning the dipole close to the asymmetric carbon [4] and elongation of the side chain [6] have been examined. The close positioning has been found to drastically increase the spontaneous polarization.

In order to utilize the large dipole moments of the carbonyl group and the hydroxyl group, as well as a positioned dipole close to an asymmetric carbon, we have focused our interest on 2-methylalkanoyl compounds with a hydroxyl substituent on the benzene ring, which forms an intramolecular hydrogen bond with the carbonyl group [7]. The intramolecular hydrogen bond is expected to align the two dipoles in the same direction and increase the spontaneous polarization.

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2. Experimental

The compounds were prepared according to the scheme shown in figure 1. Resorcinol was treated with (*S*)-2-methylalkanoic acid in the presence of zinc chloride to give the optically active phenols. The substituted phenols were then reacted in dichloromethane with 4′-alkyloxybiphenyl-4-carboxylic acid in the presence of dicyclohexylcarbodiimide (DCC) to give the compounds (*m*-A-*n*). The crude sample was purified using silica gel chromatography and recrystallization from ethanol. The compounds obtained were identified from IR and NMR spectra. A similar procedure was used for preparing analogous compounds [3] without the hydroxyl group (*m*-B-*n*).

The optical textures were observed using a Nikon XTP-11 polarizing microscope and the transition temperatures were determined using a Perkin–Elmer DSC-7 apparatus. NMR spectra were recorded on a Bruker MSL-400 (400 MHz) instrument. IR spectra were taken on a Hitachi 270-30 spectrometer. The spontaneous polarization was determined by the triangular wave method [8], using a sample cell that consists of two ITO-coated glass plates with rubbed polyimide. The electrode area in the sample cell was 100 mm^2. The distance between the glass plates was maintained by glass fibre spacers and was in the range of 10–18 μm. The liquid crystals were injected into the cell in the isotropic phase and cooled slowly.

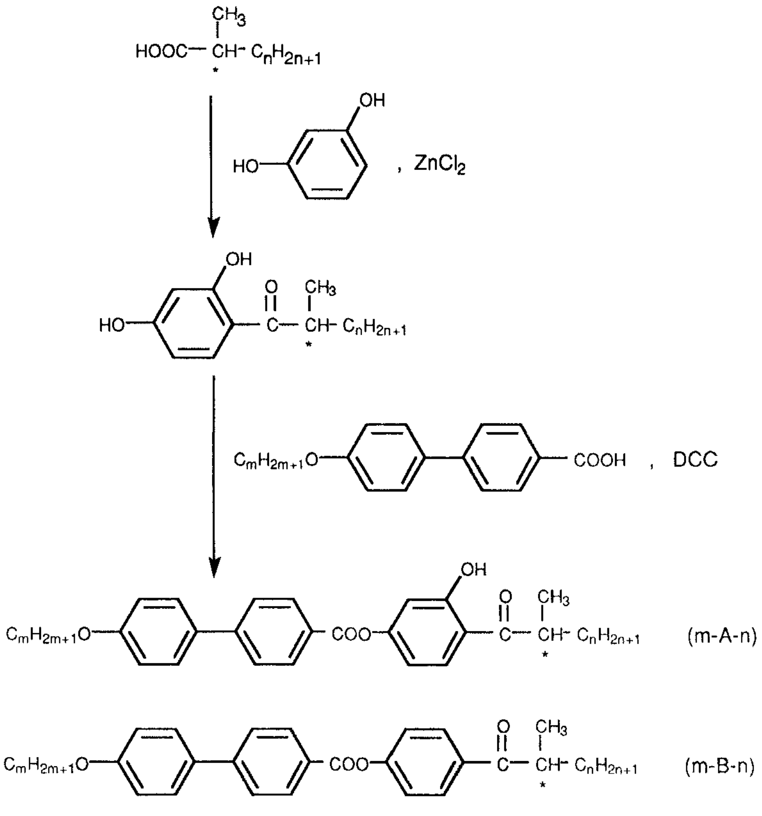


Figure 1. Synthetic method for the 3-hydroxy-4-(2-methylalkanoyl)phenyl esters (*m*-A-*n*) and analogous esters (*m*-B-*n*). * indicates an asymmetric carbon atom.

3. Results and discussion

3.1. *Transition temperatures*

Almost all of the compounds exhibit a phase sequence of crystal, chiral smectic C, smectic A, and isotropic liquid (C–S_C^*—S_A–I) on heating, and an additional higher order smectic phase on cooling. While compound 8-B-6 has been reported to show an anti-ferroelectric phase [3], no *m*-A-*n* compound showed an antiferroelectric phase. Table 1 lists the transition temperatures, tilt angles θ, and spontaneous polarization P_s for the compounds obtained.

The transition temperatures of compounds *m*-A-2 and *m*-B-2 are plotted against the carbon number *m* in the alkyl chain in figure 2. The melting points and the clearing points of the *m*-A-2 compounds are lower than those of the analogues *m*-B-2.

The clearing temperature of *m*-A-2 decreases with increasing *m*, while the transition temperature from S_C^* to S_A increases with *m* i.e., the thermal stability of the S_C^* phase increases with *m*. For *m*-B-2, however, both the transition temperature from S_C^* to S_A as well as the clearing temperature decrease slightly with *m*.

The lowering of clearing and melting points of *m*-A-2, compared to those of *m*-B-2, can be attributed to both the increase in molecular width due to the hydroxyl substituent on the benzene ring, and the resultant decrease in the intermolecular interaction in the S_A phase, and to the relaxation of the molecular packing in the crystal phase. If the hydroxyl group in *m*-A-2 forms an intermolecular hydrogen bond, the melting and clearing points of *m*-A-2 are expected to be higher than those of *m*-B-2. The results above imply no intermolecular hydrogen bond formation.

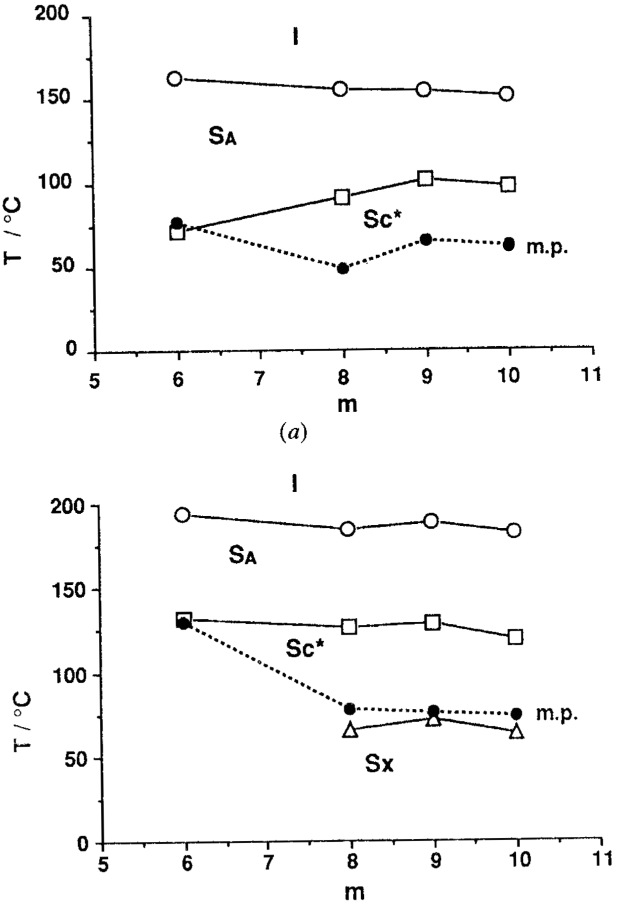
The transition temperatures of 8-A-*n* are plotted against *n* in figure 3. The transition temperature from S_C^* to S_A slightly increases with increasing *n*, though the clearing temperature falls with *n*. Thus, the temperature range of the S_C^* phase increases with *n*.

The clearing temperature decreases rapidly with *n*, but does not depend strongly on *m*. This difference in the effect of the chain length means that the asymmetric group plays a major role in the liquid crystal phase stability, especially in the S_A phase.

Table 1. Properties of the 2-methylalkanoylphenyl esters.

	Transition temperature/°C					
Compound	Mp	$S_xS_C^*$	$S_C^*S_A$	S_AI	θ/°	P_s/nCcm^{-2}
6-A-2	77	(58)	(72)	163		—
8-A-2	49	(12)	96	155	17	73
9-A-2	65	(8)	101	154		69
10-A-2	62	(11)	97	151		57
8-A-6	35	(5)	96	132	20	146
8-A-8	38	(6)	86	124		86
8-A-10	49	(8)	77	121		71
6-B-2	130		131	194		56
8-B-2	78	(65)	126	184	17	53
9-B-2	76	(72)	129	189		52
10-B-2	74	(63)	119	182		50
8-B-6	79	(65)	139	153	24	108

Phases were identified by texture. P_s and θ were measured 10°C below the S_C^*–S_A transition temperature. MP = melting point; I = isotropic liquid; S_A = smectic A; S_C^* = chiral smectic C; S_x = unidentified smectic phase; θ = tilt angle; P_s = spontaneous polarization; ( ) parentheses = monotropic transition.



(*a*)

(*b*)

Figure 2. Transition temperatures of (*a*) *m*-A-2 and (*b*) *m*-B-2.

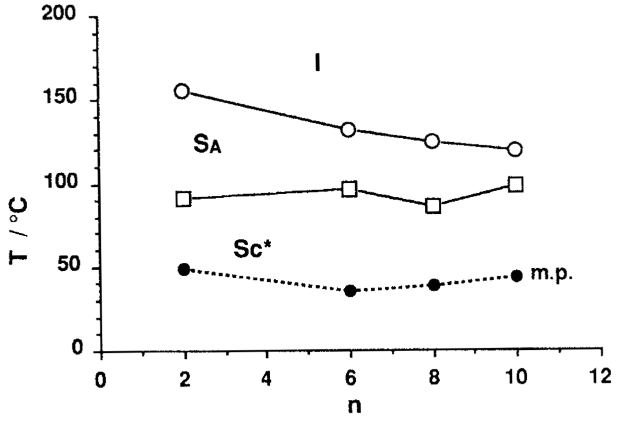
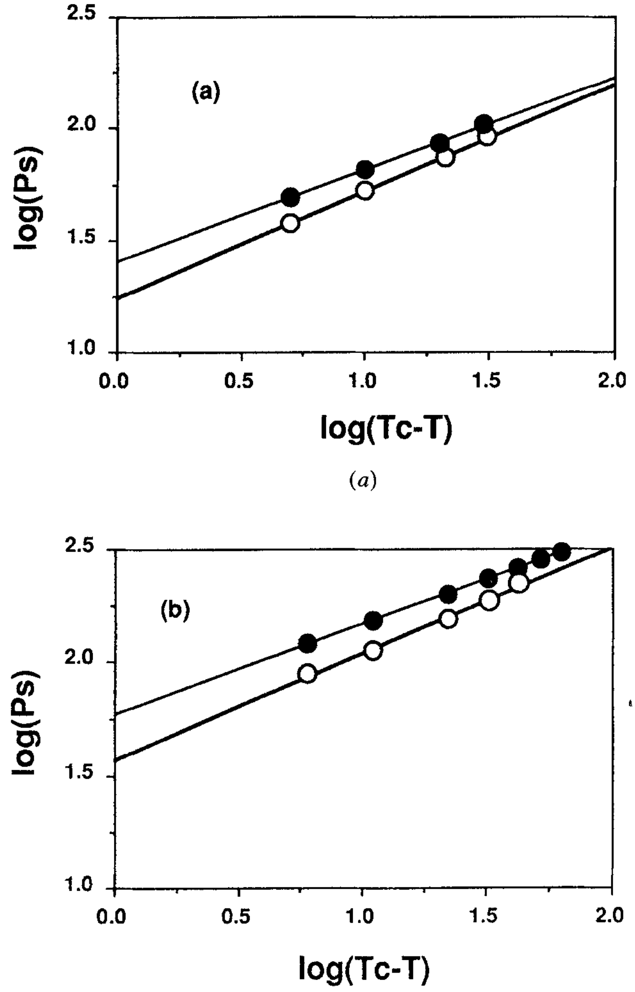


Figure 3. Transition temperatures of 8-A-*n*.



(*a*)

(*b*)

Figure 4. Temperature dependence of P_s in (*a*) 8-A-2 (●) and 8-B-2 (○) and (*b*) 8-A-6 (●) and 8-B-6 (○). T_C is the transition temperature from S_C^* to S_A.

Table 2. Calculated dipole moments and fitting parameters for $P_s = \alpha(T_C - T)^\beta$.

Compound	α/nC cm^{-2}	β	$\mu_\perp$/D
8-A-2	25·5	0·41	3·0
8-B-2	17·5	0·48	2·0
8-A-6	58·6	0·40	3·0
8-B-6	37·2	0·47	2·0

Parameters for the calculation of the dipole moment of the functional groups are as follows: Bond moments: C=O 2·3 D; C–O 0·74 D; O–H 1·51 D. Bond angles: C–C=O 120°; C–C–O 122°; C–O–H 109°. The depression of the dipole moment due to hydrogen bond formation is not considered. The long molecular axis is assumed to be the line connecting the carbonyl carbon and its attached phenyl carbon.

3.2. *Spontaneous polarization*

The sign of the spontaneous polarization of the compounds is negative, as was reported by the group of Bell Labs [9]. The introduction of the hydroxyl group has no effect on the sign.

The temperature dependences of the P_s of 8-A-2, 8-B-2, 8-A-6 and 8-B-6 are shown in a log–log form in figure 4. The results follow the relation [6]

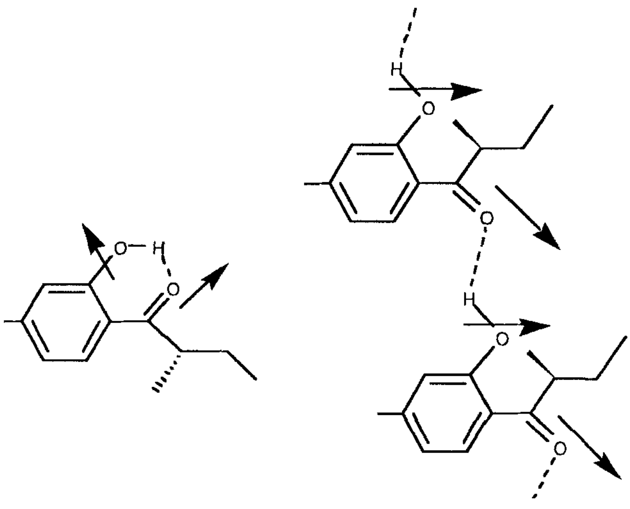
$$P_s = \alpha(T_C - T)^\beta,$$

where T_C is the transition temperature from S_C^* to S_A.

In figure 4, the points are experimental data and the lines demonstrate a least squares fit to $P_s = \alpha(T_C - T)^\beta$. It is seen that the power-law fit works very well for these compounds. The fit parameters are given in table 2. The dipole moment around the asymmetric carbon is calculated by adding the individual bond moment vectors. The perpendicular components ($\mu_\perp$) are also given in the table.

The α value for 8-A-2 and 8-A-6 is 50 per cent larger than that of 8-B-2 and 8-B-6, respectively. Since α is a material constant depending on the anisotropic distribution of the molecular dipoles, *m*-A-*n* compounds have a larger dipole moment and/or a larger anisotropic distribution. A simple interpretation can be given if the hydroxyl group forms an intramolecular hydrogen bond with the carbonyl oxygen, as shown in figure 5 (*a*). In this case, the total dipole moment perpendicular to the long molecular axis is calculated to be 3·0 D, 50 per cent larger than that of compounds without the hydroxyl group, 8-B-2 or 8-B-6 (2·0 D). A smaller value (2·5 D) is obtained for the case when the two polar groups form intermolecular hydrogen bonds, as shown in figure 5 (*b*).

The α value for 8-A-6 and 8-B-6 is double that of 8-A-2 and 8-B-2, respectively, due to the rotational hindrance of the longer alkyl chains. In spite of the difference in α, β is the same for the compounds with the same core. The smaller β value, that is, the smaller temperature dependence of P_s in the 8-A-*n* series may be due to the stronger rotational dampening, which is present even at higher temperatures.



(*a*) (*b*)

Figure 5. Probable molecular configuration around an asymmetric carbon with (*a*) an intramolecular and (*b*) an intermolecular hydrogen bond.

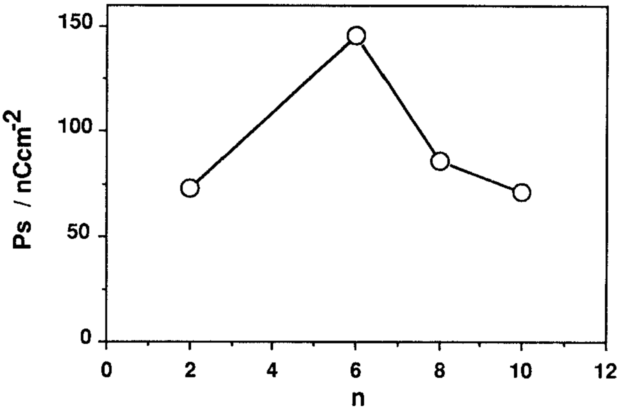


Figure 6. P_s dependence on the alkyloxy carbon number n in 8-A-n. P_s is measured at 10°C below the S_C^*–S_A transition.

The spontaneous polarization versus n in the 8-A-n series is shown in figure 6. P_s increases with n from $n=2$ to a maximum at $n=6$. The increase in rotational hindrance around the asymmetric centre is thought to be the origin of the increase in P_s with n [6, 10]. The hindrance effect, however, seems to saturate after $n=6$. The decrease in P_s with n at $n>6$ may be due to other reasons such as the increased molecular weight.

3.3. *Intramolecular hydrogen bond*

The transition temperatures and the P_s measurements seem to support the existence of an intramolecular hydrogen bond between the hydroxyl group and the carbonyl group in the m-A-n series. Some spectroscopic results are shown in this section.

The ^1H NMR spectrum for 8-A-2 in chloroform-d solution is shown in figure 7. The hydroxyl proton is found to be shifted to low field by $\delta = 12{\cdot}8$ ppm from the tetramethylsilane internal standard. This shift is attributed to the electron withdrawing effect of the carbonyl oxygen, indicating the hydrogen bond formation. If the observed shift were due to intermolecular hydrogen bonds, the peak would shift to a higher field upon dilution. This δ value is found to be unchanged on dilution with chloroform-d. The same amount of shift was observed in dimethylsulphoxide-$d6$ solution, which is more polar than chloroform-d. Thus, at least in these solutions, the intramolecular hydrogen bond is formed between the hydroxyl group and the carbonyl group.

The IR (kBr) spectrum for a homologous mixture consisting of m-A-n series compounds is shown in figure 8. The mixture consists of the compounds shown in table 3 and is in the S_C^* phase at room temperature. The OH stretching vibration cannot be identified in the spectrum; it should overlap with the CH stretching vibration, and the size of the shift implies that it is due to the strong hydrogen bond, i.e. the

Table 3. Liquid crystal mixtures of m-A-n compounds.

Compounds	Contents/%
8-A-6	52
9-A-6	27
8-A-2	21

The mixture shows a phase sequence of S_C^* 93°C S_A 132°C Iso. It did not crystallize at room temperature.

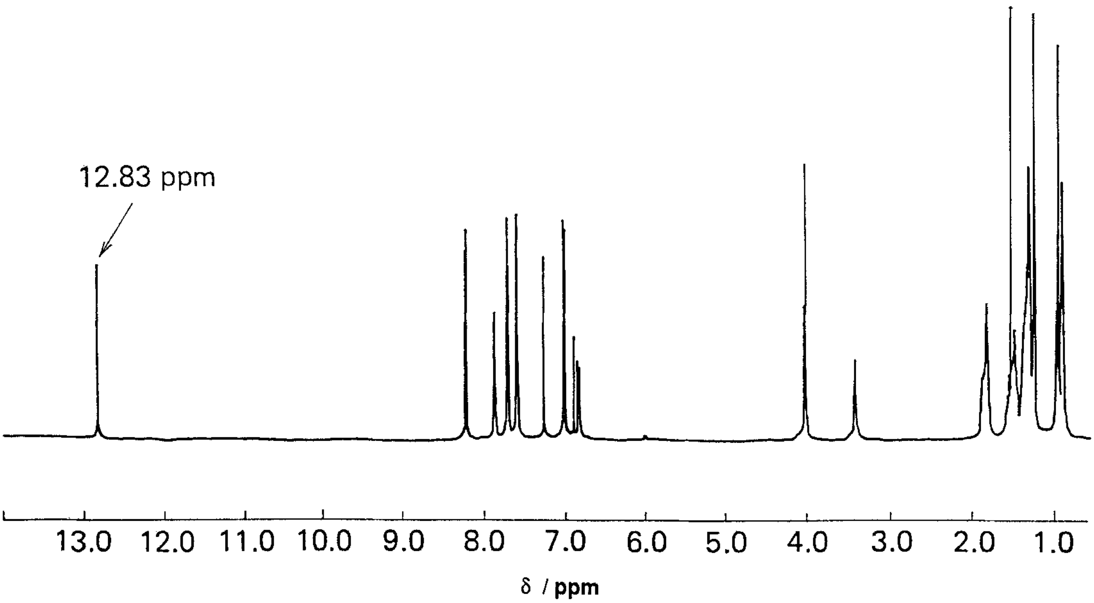


Figure 7. ^1H NMR spectrum of 8-A-2 in $CDCl_3$.

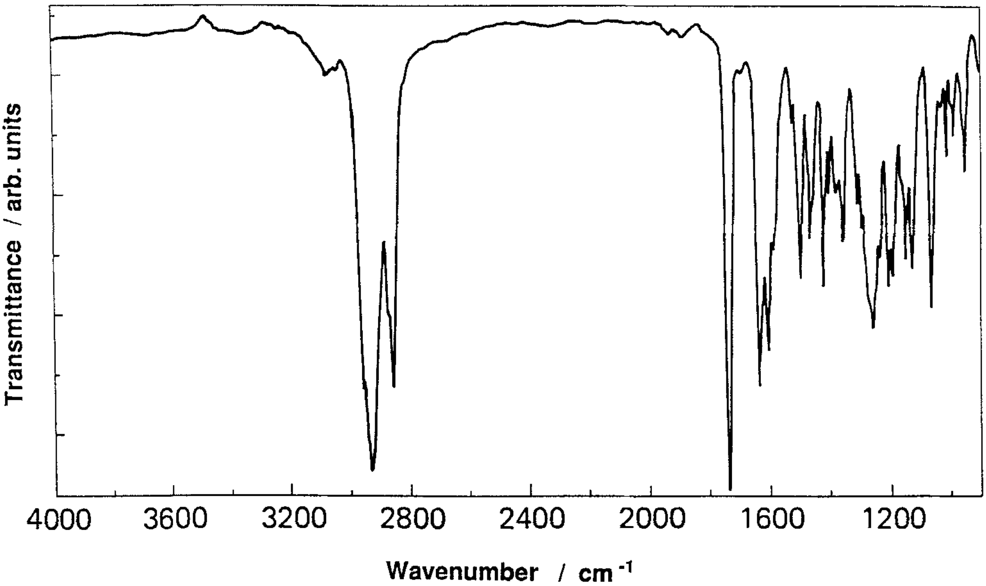


Figure 8. IR spectrum of an *m*-A-*n* mixture in the S_C^* phase.

intramolecular hydrogen bond. If the hydrogen bond were intermolecular, addition of a less polar material to the mixture would weaken the hydrogen bond according to the decrease in concentration. On dilution with a pyrimidine compound (*S*)-2-(4-methylhexyloxy)phenyl-5-octylpyrimidine), no clear change was observed in this wavelength region. Thus, in the *m*-A-*n* series, the intramolecular hydrogen bond is formed between the hydroxyl group and the carbonyl group.

4. Conclusion

We have shown that new liquid-crystalline compounds with a hydroxyl substituent on the benzene ring have a larger spontaneous polarization than the analogues without the hydroxyl substituent. Enlargement of spontaneous polarization can be attributed to intramolecular hydrogen bond formation between the hydroxyl substituent and the carbonyl group. We have also shown that the intramolecular hydrogen bond formation is confirmed by the results of transition temperature measurements and the spectroscopic study.

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