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Stereochemical studies of optically active 2-hydroxy-5-alkyl-δ-valerolactone derivatives as chiral dopant for ferroelectric liquid crystals

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Both (2*S*, 5*R*)- and (2*R*, 5*R*)-2-hydroxy-5-alkyl-δ-valerolactone derivatives, *cis* and *trans*, respectively, show almost the same magnitude of spontaneous polarization (P_s) when added to a non-chiral smectic C mixture. The stereochemistry of these chiral dopants was studied using ^{1}H NMR. *Trans* derivatives seem to have a half-chair conformation with the 2, 5-diequatorial substituents and the *cis* derivatives have rather a flat conformation in solution. However in the liquid-crystalline phase, the *cis* and *trans* derivatives appear to change their conformation or the distribution of their conformations as the alkyl chain length is varied. The difference in the effect as a chiral dopant depends upon lateral interactions between chiral molecules through the solvent liquid crystal phase.

1. Introduction

Recently, a great deal of attention has been focused upon ferroelectric liquid crystals due to their potential as materials for application in high definition, flat panel displays and in optical processing devices.

One of the most important properties of ferroelectric liquid crystals for such applications is the response time, which depends upon the magnitude of spontaneous polarization (P_s), the effective viscosity (η_{eff}) and the applied electric field (E) [1]. In general, ferroelectric liquid crysals with short response times are prepared by doping non-chiral smectic C (S_C) mixtures, which have a low effective viscosity, with several kinds of chiral compounds. By making a chiral dopant with a very large P_s, we obtain a quick responding ferroelectric liquid crystal without altering its viscoelastic properties.

We have tried to make chiral dopants with a very large P_s and report the synthesis and properties of 2, 5-disubstituted δ-valerolactone derivatives as chiral dopants [2, 3]. In a previous paper [3], we showed that the sign of P_s was determined by the absolute configuration of the C-2 atom of the δ-valerolactone ring and that the values of P_s of ferroelectric liquid crystals containing 2 mol% of 2-(4′-octyloxybiphenyl-4-carboxy)-5-alkyl δ-valerolactones (1) with different relative configurations were almost the same.

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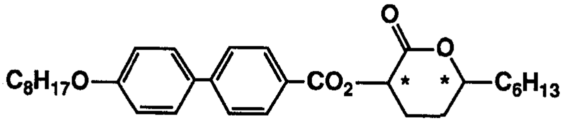
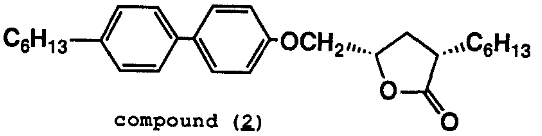
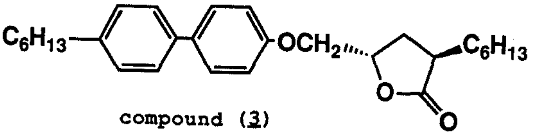


compound (1)

Sakaguchi *et al.* [4] have synthesized a series of γ-butyrolactone derivatives as chiral dopants for ferroelectric liquid crystals and reported that the value of P_s for a ferroelectric liquid crystal containing 2 wt% of these derivatives with the *cis* configuration (**2**) was about 10 times as large as that with the *trans* configuration (**3**).



compound (2)

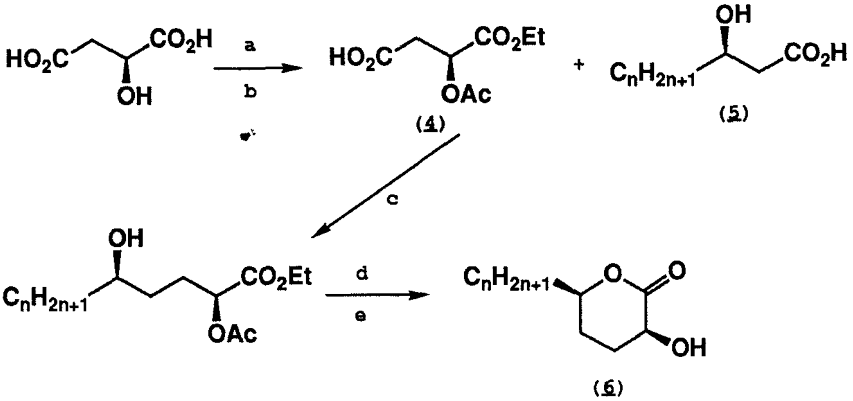


compound (3)

In this paper, we describe some new experimental results obtained by the addition of a series of *cis* and *trans* 2-(4′-octyloxybiphenyl-4-carboxy)-5-alkyl-δ-valerolactone derivatives to a non-chiral S_C mixture and further the NMR studies of these chiral compounds.

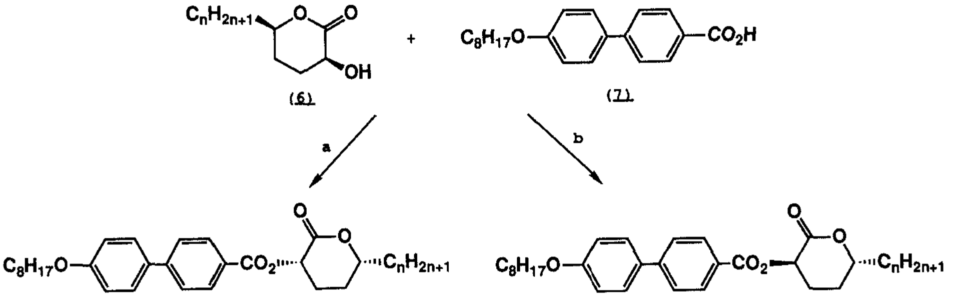
2. Experimental

The synthetic route of (2*S*, 5*R*)-2-hydroxy-5-hexyl-δ-valerolactone (**6**) is shown in scheme 1. (*S*)-2-Acetoxybutandioic acid 1-ethyl ester (**4**) was prepared from (*S*)-malic acid according to the method reported by Mori *et al.* [5]. Compound (**6**) was synthesized by the Kolbe electrolysis of compound (**4**) and (*R*)-β-hydroxy nonaic acid (**5**), followed by treatment with *p*-toluenesulphonic acid in benzene after removal of the protective groups. Similarly the (2*S*, 5*R*)-2-hydroxy-δ-valerolactones with different alkyl chains were synthesized from chiral β-hydroxy alkanoic acid and compound (**4**).



Scheme 1. Reagents: (a) AcCl, (b) EtOH, (c) e⁻, NaOMe, MeOH, (d) NaOH aq., (e) p-TsOH, benzene.

Both (2*S*, 5*R*)- and (2*R*, 5*R*)-2-(4′-octyloxybiphenyl-4-carboxy(5-alkyl-δ-valero lactone, the *cis* and *trans* configuration, respectively, were synthesized as shown in scheme 2. (2*S*, 5*R*)-Derivatives were synthesized from 4′-octyloxybiphenyl-4-carboxylic acid (**7**) and compound (**6**) with dicyclohexyl carbodiimide (DCC) and *N*,*N*-dimethylaminopyridine (DMAP) as a dehydrating catalyst in dichloromethane. (2*R*, 5*R*)-Derivatives were synthesized from compound (**6**) and compound (**7**) with triphenylphosphine (PPh_3) and diethyl azodicarboxylate as catalysts in benzene. All the final products were purified by means of silica-gel column chromatography, followed by recrystallization from ethanol or hexane/diethyl ether.



Scheme 2. Reagents: (a) DCC, DMAP, CH_2Cl_2, (b) PPh_3, $(NCO_2Et)_2$, benzene.

The ferroelectric liquid crystal mixtures were prepared by adding 2 mol% of the chiral compound to the non-chiral S_C mixture which was composed of several kinds of 2-(4-alkyloxyphenyl)-5-alkylpyrimidines with the phase transition temperatures as follows [6]:

$$S_C\ 51^{\circ}C\ S_A\ 61^{\circ}C\ N\ 68^{\circ}C\ I.$$

The measurements of the phase sequence, transition temperatures, the magnitude and the sign of P_s and tilt angles were carried out in accordance with the procedures reported previously [2]. The specimen was placed between two indium-tin oxide (ITO) glass plates to form a cell. The glass surface was coated with a polyimide. The polyimide film thus formed was rubbed in one direction. The cell thickness was 2 μm and the applied squarewave voltage was ± 10 V. The response time used in this paper is defined as the time required for the optical transmittance through the cell to change from 0 per cent to 50 per cent at 25°C when the voltage was applied to the cell. The pitch of the helical structure of the chiral nematic (N*) phase was measured at 62°C using the Cano–Wedge method.

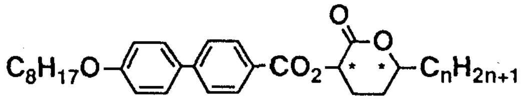
^1H NMR spectra were obtained with a Hitachi R-90H spectrometer and a JEOL GSX-400 spectrometer using $CDCl_3$ and acetone-d^6 solution and TMS as an internal reference.

3. Results and discussion

The melting points and liquid-crystalline properties of all the compounds synthesized in this paper are tabulated in table 1.

The melting points of compounds with the *cis* configuration were much higher than those with the *trans* configuration regardless of the alkyl chain length at the C-5 position. The S_C^* phase was observed for only the (2*R*, 5*R*)-5-hexyl derivative (**8**). The N* and monotropic S_C^* phases were observed for the (2*R*, 5*R*)-5-butyl derivative (**10**). And the monotropic *N** phase was observed for the (2*R*, 5*R*)-5-propyl (**12**) and ethyl

Table 1. Melting points and liquid-crystalline properties of the synthesized compounds.



Compound	Chain length *n*	Absolute configuration	p T_u/°C	S_C^*	Phase transition temperature/°C	N*		I
8	6	2*R*, 5*R*	111	●	128	—		●
9	6	2*S*, 5*R*	152	—		—		●
10	4	2*R*, 5*R*	116	(●	114)	●	118	●
11	4	2*S*, 5*R*	153	—		—		●
12	3	2*R*, 5*R*	124	—		(●	119)	●
13	2	2*R*, 5*R*	124	—		(●	107)	●
14	2	2*S*, 5*R*	138	—		—		●
15	1	2*R*, 5*R*	120	—		—		●
16	1	2*S*, 5*R*	132	—		—		●

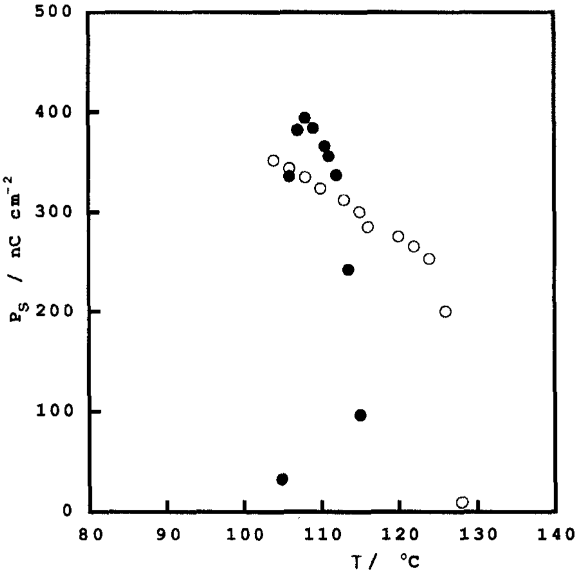


Figure 1. Temperature dependence of the magnitude of P_s of compounds (**8**) (○) and (**10**) (●).

(**13**) derivatives. These tendencies have been observed in other analogous series. All the compounds with the (2*S*, 5*R*)-configuration, which had the *cis* configuration, and the (2*R*, 5*R*)-5-methyl (**15**) derivative did not show any mesophase. This may result from the conformational difference between the (2*R*, 5*R*)-δ-valerolactone and (2*S*, 5*R*)-δ-valerolactone. The temperature dependence of the magnitude of P_s for compounds (**8**) and (**10**) is shown in figure 1.

The magnitude of P_s for compounds (**8**) and (**10**) was very large and the sign of P_s and the helical senses of the N* phase of these compounds were negative and left-handed, respectively.

Table 2. Ferroelectric properties of the ferroelectric liquid crystal mixtures containing 2 mol% of optically active 2-(4-octyloxybiphenyl-4-carboxy)-5-alkyl-δ-valerolactones.

FLC‡ no.	*Dopant* no.	Phase transition temperature/°C									P_s nC cm^{-2}	τ_{0-50} μs	Pitch of N* μm	θ/°
		C		S_C^*		S_A		N*		I				
1	**8**	●	2·5	●	53	●	60	●	67	●	−2·4	195	R–10·1	21·0
2	**9**	●	2·6	●	53	●	59	●	67	●	+4·2	126	L– 4·3	22·3
3	**10**	●	1·4	●	54	●	60	●	68	●	−3·1	154	R– 5·8	20·0
4	**11**	●	2·4	●	55	●	59	●	67	●	+3·1	161	L– 4·7	19·0
5	**12**	●	3·1	●	52	●	60	●	68	●	−2·9	154	R– 5·8	20·0
6	**13**	●	2·4	●	55	●	59	●	67	●	−2·9	149	R– 7·6	19·7
7	**14**	●	1·2	●	50	●	58	●	67	●	+3·8	126	L– 5·1	19·0
8	**15**	●	2·9	●	54	●	58	●	66	●	−2·0	192	R–10·1	17·0
9	**16**	●	2·4	●	50	●	59	●	67	●	+4·4	108	L– 4·3	22·5

† R means right-handed, and L left-handed.

‡ FLC: ferroelectric liquid crystal.

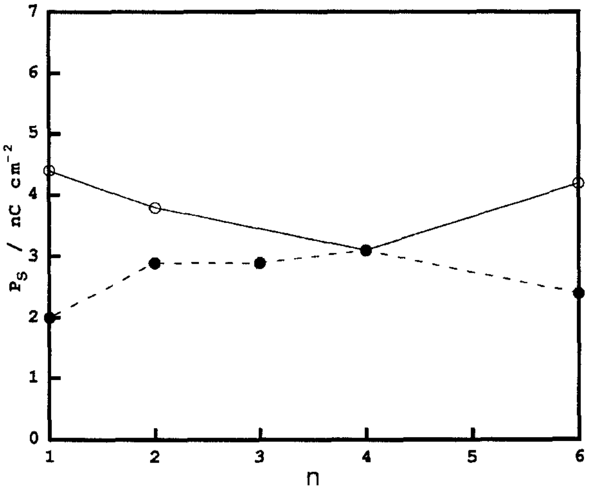


Figure 2. The relationship between the magnitude of P_s and the alkyl chain length, n, of chiral dopants with different relative configurations. ○ *Cis* δ-valerolactones, ● *trans* δ-valerolactones.

The phase transition temperatures, the sign and the magnitude of P_s, the response time, the pitch of the helical structure of the N* phase, and the tilt angle of the ferroelectric liquid crystals with these chiral dopants are listed in table 2.

The phase transition temperatures of these ferroelectric liquid crystals were almost the same as those of the non-chiral S_C mixture. The relationship between the alkyl chain length of C–5 and the magnitude of P_s of these are shown in figure 2. In a series of ferroelectric liquid crystals with the *trans* δ-valerolactone derivatives, the largest magnitude of P_s was obtained with $n=4$. Whilst in a series of ferroelectric liquid crystals with the *cis* δ-valerolactone derivatives, the minimum magnitude of P_s was observed also for $n=4$.

In spite of Sakaguchi's observation with ferroelectric liquid crystals containing the γ-butyrolactone derivatives [4], there was little difference in the magnitude of P_s for those compounds containing the δ-valerolactione derivatives with different relative configurations. It is said that a γ-butyrolactone ring has rather a flat and rigid structure than a δ-valerolactone ring. This may be a reason why these chiral γ-lactones with different relative configurations gave ferroelectric liquid crystals a different magnitude of P_s as a consequence of a different interaction with the S_C^* phase as proposed by Koden *et al.* [7].

We have tried to study the conformation of *cis* and *trans* δ-valerolactones using ^{1}H NMR. It is said that the unsubstituted δ-valerolactone exists as two non-equivalent conformational forms with similar energies; a half chair and a classical boat. The molecular mechanics approach had suggested that the half chair form was favoured by 2·26 kJ mol^{-1} in the gas phase [7]. Even when the molecule has two substituents at the C–4 and C–5 positions, its flexibility made it difficult to detect one conformation as the most stable [8]. As shown in table 3, the chemical shifts (δ) for the C–2 hydrogen of *cis* lactones were shifted to low field compared with that of *trans* lactones. On the other hand, the chemical shifts for C–5 hydrogens of both isomers were almost the same. Both *cis* and *trans* lactones exhibited different sets of vicinal coupling constants ($J_{2,3}$) for C–2 hydrogen; $J_{2,3}$ of H(2)–H(3) were about 9 Hz and 10 Hz for *cis* isomers and about 7 Hz and 11 Hz for *trans* isomers. When NMR spectra were measured at different

Table 3. ^{1}H NMR data of the δ-valerolactone derivatives.

Compound	Absolute configuration	Chain length n	δ/ppm		$J_{2,3}$	Hz
			C_2-H	C_5-H		
8	2*R*, 5*R*	6	5·47	4·50	6·6	11·5
9	2*S*, 5*R*	6	5·70	4·48	9·0	10·0
10	2*R*, 5*R*	4	5·44	4·44	7·4	10·0
11	2*S*, 5*R*	4	5·69	4·42	9·0	9·0
12	2*R*, 5*R*	3	5·43	4·45	6·8	11·0
13	2*R*, 5*R*	2	5·45	4·42	7·6	10·1
15	2*R*, 5*R*	1	5·48	4·61	7·5	10·8
16	2*S*, 5*R*	1	5·56	4·66	9·0	10·4

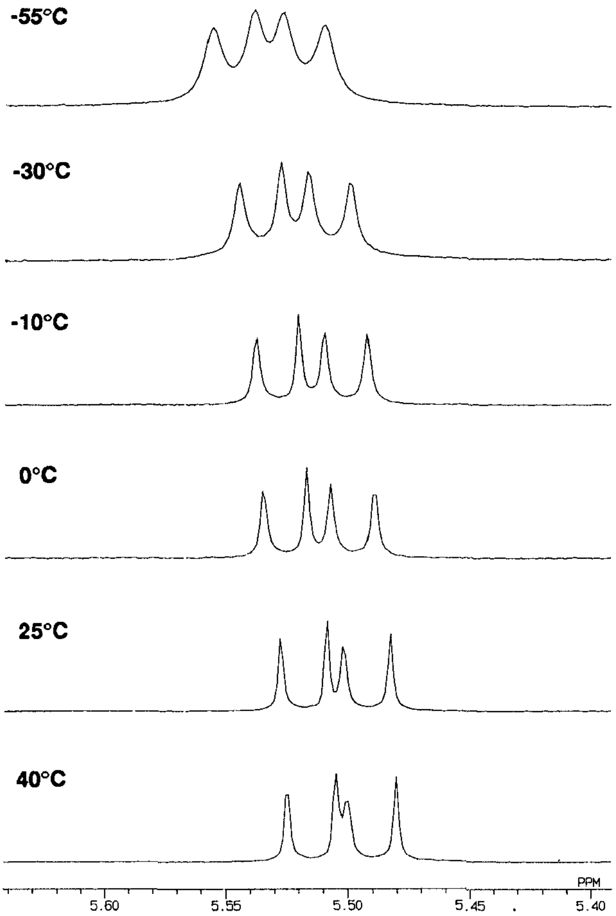


Figure 3. ^{1}H NMR spectra of C_2-H of compound **9** at different temperatures ranging from −55°C to 40°C.

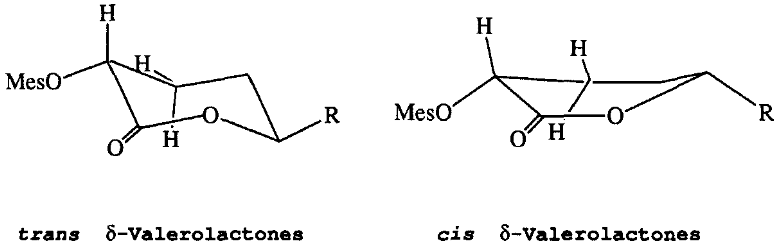


Figure 4. Possible structure of *trans* and *cis* δ-valerolactones in solution.

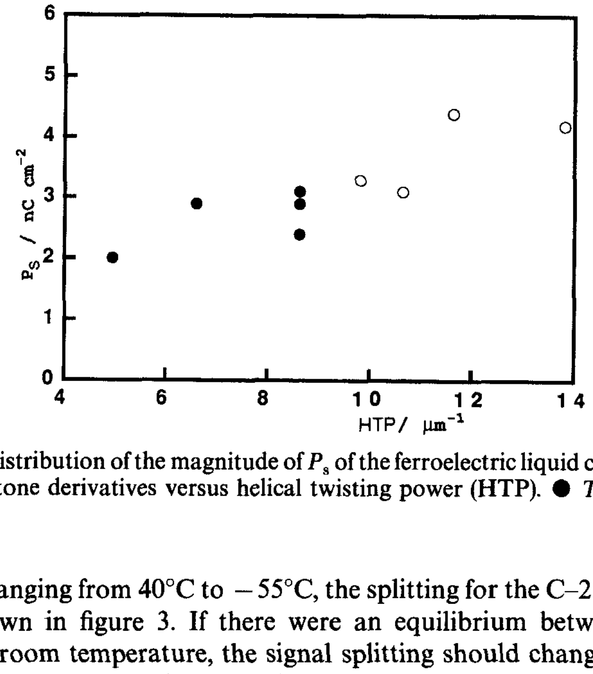


Figure 5. The distribution of the magnitude of P_s of the ferroelectric liquid crystal containing d-valerolactone derivatives versus helical twisting power (HTP). ● *Trans*, ○ *cis*.

temperatures ranging from 40°C to −55°C, the splitting for the C–2 hydrogen did not change as shown in figure 3. If there were an equilibrium between any different conformers at room temperature, the signal splitting should change as lowering the temperature. These observations implied the following facts: (1) *cis* and *trans* δ-valerolactones had different conformations is a solution and (2) *cis* and *trans* 2,5-disubstituted δ-valerolactones seemed to have only one conformer at room temperature. Although more experiments and molecular mechanics approaches are needed to elucidate the real stereochemistry for these isomers, it seemed that the conformations of the *trans* δ-valerolactones were a half chair with 2, 5-diequatorial substituents and those of the *cis* isomers rather a flat structure as shown in figure 4.

All ferroelectric liquid crystals examined here have N* phases with short helical pitches. In spite of numerous publications on the helical twisting power (HTP) induced by optically active molecules in nematic liquid crystals, there still lacks a general relationship between molecular structure and helical twist [9–11]. However it is well known that the helical twisting powers induced by the same optically active molecule have different values in different nematic solvents. Therefore, we consider the helical twisting power results from molecular interactions between the chiral dopants through the nematic liquid crystal. Walba and Clark explained the P_s by the hindrance of a rotating dipole close to the asymmetric carbon atom [12]. Since the magnitude of P_s of ferroelectric liquid crystals with the same chiral dopant is different in various solvent liquid crystals, the P_s seems to result from molecular interactions between chiral dopants through the solvent liquid crystals. Figure 5 shows the distribution of the magnitude of P_s versus helical twisting power.

Since the helical twisting power is observed in N* phase and P_s in the S_C^* phase, their molecular arrangements are of course different. Figure 5 indicates that the *cis* δ-valerolactone appears to have stronger molecular interactions making both the helical twisting power and P_s larger. This might result from rather a flat conformation of the *cis* δ-valerolactone in solution as discussed previously. But in the liquid-crystalline phase, especially in S_C^* the conformation of the distribution of some conformations of the *cis* δ-valerolactone might change by lengthening the alkyl chain since the magnitude of P_s becomes smaller by lengthening the alkyl chain as shown in figure 2. The *trans* isomers might also change their conformation in a liquid-crystalline phase, because their magnitude of P_s changes by varying the alkyl chain length. These studies show that δ-valerolactones adopt only one conformation in solution at room temperature but adopt different conformations in the liquid-crystalline phase because of the anisotropic rearrangement of the liquid-crystalline molecules. This fact and the difference in molecular interactions might be the reason why the magnitude of P_s of the *cis* isomers is little larger than that of the *trans* isomers.

For applications the response time is one of the most important properties of ferroelectric liquid crystals. As shown in table 2, the response time of a ferroelectric liquid crystal with compound (**16**) was as fast as 108 μs. However the response time was not inversely proportional to the magnitude of P_s because of the difference in the tilt angle.

In summary, from the stereochemical studies using ^{1}H NMR, δ-valerolactone derivatives adopt only one conformation in solution, but from ferroelectrical observations, their conformation or distribution of conformations might change by varying the alkyl chain length in a liquid-crystalline phase.

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