Synthesis, characterization, electro-optical studies and crystal structure of a chiral mesogenic compound

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Synthesis, characterization, electro-optical studies and crystal structure of a chiral mesogenic compound

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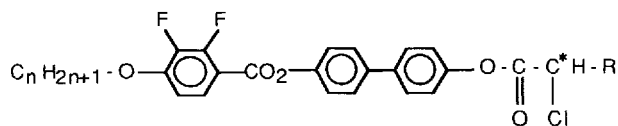MARIE-FLORE NABOR, CHRISTIAN DESTRADE and
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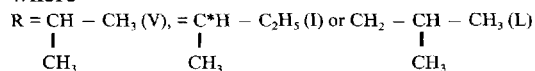A new series of chiral biphenyl derivatives presenting the following general sequence of phases $Cr \to S_C^* \to N^* \to I$ was synthesized and characterized. The mesomorphic properties were analyzed by optical microscopy, DSC and electro-optical measurements. This series presents a large temperature domain for the ferroelectric phase and large values for the spontaneous polarization (up to $200\,nC\,cm^{-2}$). For this series, the crystal structure of 4-[(2S)-2-chloro-3-methylbutanoyloxy]biphenyl-4-yl 4-undecyloxy-2,3-difluorobenzoate $(C_{35}H_{41}O_5F_2Cl)$ is described. This compound crystallizes in the monoclinic system and $P2_1$ space group with two independent molecules per asymmetric unit $(Z = 4)$. The cell parameters are the following: $a = 6.764(5)$, $b = 57.057(6)$, $c = 8.597(2)\,\text{Å}$ and $\beta = 99.08(1)°$; $\lambda(CuK\alpha) = 1.54178\,\text{Å}$, $R = 0.105$ for 2987 observed reflections. The independent molecules A and B adopt a parallel head-to-head arrangement which gives rise to sheets parallel to the $(x0z)$ plane with a thickness close to $28.5\,\text{Å}$ and having a permanent dipole moment. The tilt angle within a sheet is close to $40°$. Neighbouring sheets, generated by the 2_1 axis, are symmetric through the $(x0z)$ plane with an opposite tilt direction and dipole moment. The molecular arrangement is antiferroelectric-like. The crystal cohesion can be attributed to dipole-dipole forces and van der Waals interactions. The structure of the present compound is compared to that of a similar compound which differs only by the replacement of one of the two terminal methyl groups with an ethyl group.

1. Introduction

During the last decade, extensive chemical studies on the synthesis of new ferroelectric smectic compounds has yielded useful materials for applications and optical devices [1–7]. Recently some new ferroelectric liquid crystals having 2,3-difluoro lateral substituents have been reported. Such derivatives are low viscosity materials [8–10]. In order to satisfy the compromise between the existence of the ferroelectric S_C^* phase and the optimization of the electro-optic properties, a new series of chiral molecules with difluoro lateral substituents was synthesized and characterized [11] as follows.

We describe here the complete analysis of the mesomorphic properties of these compounds by microscopic observations, DSC and electro-optical measurements. Moreover, to understand better the molecular arrangement in the S_C^* phase and the transition $Cr \to S_C^*$, we have analyzed the crystal structure of the compound with $n = 11$ and $R = V$ and compared it with that of the other derivatives also exhibiting the S_C^* phase.

2. Synthesis
2.1. General

The materials studied were synthesized following the scheme:

where
R = CH − CH₃ (V), = C*H − C₂H₅ (I) or CH₂ − CH − CH₃ (L)
     | | |
    CH₃   CH₃   CH₃

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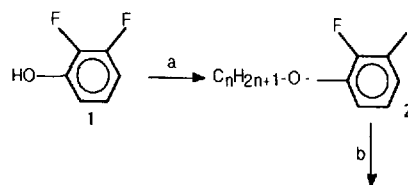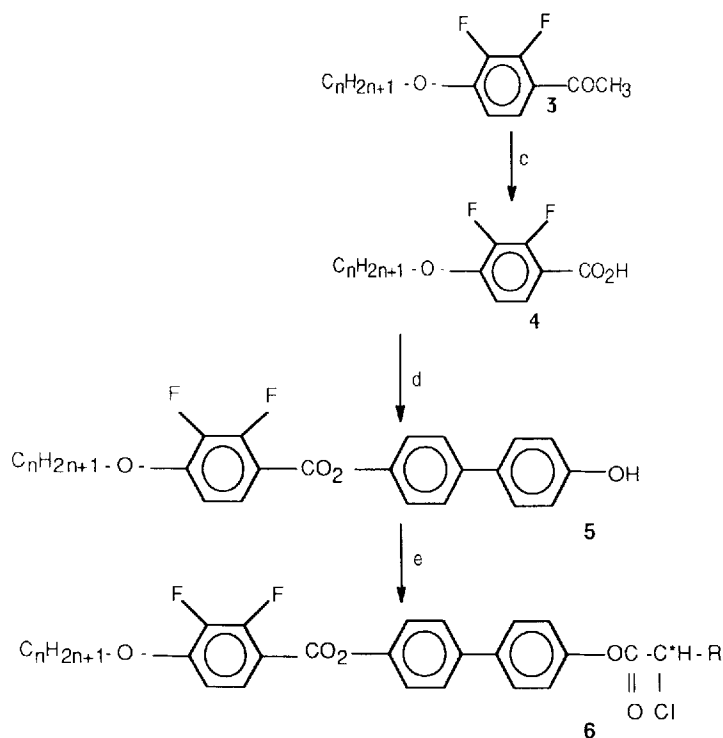
a: $C_nH_{2n+1}Br$, KOH, EtOH;
b: CH_3COCl, $FeCl_3$, CH_2Cl_2;
c: NaOH, Br_2, Dioxane, H_2O;
d: $SOCl_2$; HO- C_6H_4-C_6H_4-OH in excess, pyridine, toluene;
e: CH_2Cl_2, DMAP, R-CHCl-COOH, DCC.

The chemical structures of all compounds were checked by NMR (Bruker 200 MHz) and by Fourier Transform Infrared Spectroscopy (Nicolet MX^{-1}). The purity of intermediates and final products was checked by thin layer chromatography and by normal phase HPLC.

(2S)-2-chloro-3-methylbutanoic acid, (2S,3S)-2-chloro-3-methylpentanoic acid and (2S)-2-chloro-4-methylpentanoic acid were prepared according to literature methods [12].

2.2. *4-Hydroxybiphenyl-4'-yl*
4-undecyloxy-2,3-difluorobenzoate (**5**)

To a solution of 18·6 g (0·1 mol) of 4,4'-dihydroxybiphenyl and 70 ml of pyridine in toluene (150 ml), a solution of 6·95 g (0·02 mol) of 4-undecyloxy-2,3-difluorobenzoyl chloride (obtained from the reaction between the corresponding benzoic acid [13] and thionyl chloride) in toluene (50 ml) was added dropwise during one hour. The mixture was heated under reflux for three hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was hydrolysed with 40 ml of concentrated sulphuric acid and 100 g of crushed ice. The solid was filtered off, washed with water and

treated with hot toluene. The excess of insoluble 4,4'-dihydroxybiphenyl was removed by filtration. The filtrate was evaporated and the product was recrystallised from absolute ethanol. Yield 5·7 g (55%). Cr—162→S_c—195→N—202→I IR (Nujol,cm^{-1}): 3380, 2910, 2840, 1730, 1500, 1290, 1210, 1090; ^{1}H NMR (200 MHz, solvent $CDCl_3$, standard TMS): 0·9 (t, 3H, CH_3), 1·2–1·9 (m, 18H, $9CH_2$), 2·9(s, 1H, OH), 4·3 (t, 2H, CH_2O), 6·9–7 (d, 2H arom.), 7·2 (m, 1H, arom.), 7·4(d, 2H arom.), 7·6(d, 2H arom.), 7·7 (d, 2H arom.), 7·9 (m, 1H arom.).

2.3. *4-[(2S,3S)-2-Chloro-3-methylpentanoyloxy]biphenyl-4'-yl 4-undecyloxy-2,3-difluorobenzoate* (**6**)

To a solution of 0·52 g (1 mmol) of 4-hydroxybiphenyl-4'-yl 4-undecyloxy-2,3-difluorobenzoate in CH_2Cl_2 (10 ml) were added 0·22 g (1·1 mmol) of dicyclocarbodiimide (DCC), 10 mg of N,N-dimethylaminopyridine (DMAP) and 0·17 g (1·1 mmol) of (2S,3S)-2-chloro-3-methylpentanoic acid. The mixture was stirred at room temperature overnight. After filtration the solvent was evaporated and the residue was purified by chromatography on silica gel with toluene as solvent. The desired product was recrystallized from ethanol. Yield 0·42 g (60%). IR (Nujol,cm^{-1}): 2900, 1750, 1730, 1500, 1280, 1200, 1090; ^{1}H NMR (200 MHz, solvent $CDCl_3$, standard TMS): 0·9 (t, 3H, CH_3), 1·3 (t, 3H, CH_3), 1·2(d, 3H, CH_3), 1·2–1·9 (m, 21H), 2·3 (m, 1H, CH–CH_3.), 4·15 (t, 2H, CH_2O), 4·4(d, 1H, CH–Cl), 6·9(d, 1H arom.), 7·2–7·65 (4d, 8H arom.), 7·9 (m, 1H arom.).

3. Mesomorphic properties

The phase behaviour, transition temperatures and enthalpies were determined by thermal microscopy and by differential scanning calorimetry. The liquid crystal transition temperatures and enthalpies for these new materials are summarized in table 1. All the compounds are mesomorphic and give chiral S_c^* and N* mesophases. The ferroelectric S_c^* phase is observed over the whole series within a large temperature domain varying from 45 to 76°C. Most compounds present a very short blue phase (BP) before the isotropic phase.

4. X-ray diffraction by the mesophase

In order to monitor the variation of the layer thickness with temperature and to correlate it with the results found in the crystalline state, X-ray diffraction by the mesophase was examined as shown in figure 3. The liquid crystal 4-[(2S)-2-chloro-3-methylbutanoyloxylbiphenyl-4'-yl 4-undecyloxy-2,3 difluorobenzoate was introduced in the isotropic phase into a 1 mm diameter Lindeman capillary. The sample was mounted on a Huber 2 goniometer. The temperature was

Table 1. Transition temperatures (°C) and enthalpies [kJ mol⁻¹].

n	R	Cr	S_C*	N*	BP	I
7	I	• 74·7 [16·08]	• 124·2 [1·7]	• 152·2 [0·7]ᵃ	•152·5	•
7	V	• 75 [18·15]	• 135·7 [1·6]	• 171·8 [0·6]	—	•
8	I	• 61·3 [13·05]	• 128·4 [1·4]	• 151·7 [0·8]	—	•
8	V	• 69·5 [23·01]	• 139·7 [1·4]	• 170·1 [0·86]ᵃ	• 170·2	•
9	I	• 84·6 [38·12]	• 131·3 [1·6]	• 148·4 [0·8]ᵃ	• 148·8	•
9	V	• 98·1 [49·2]	• 142·8 [1·4]	• 166·5 [0·82]ᵃ	• 166·8	•
10	I	• 75·3 [28·88]	• 132·5 [1·28]	• 146·9 [0·9]ᵃ	• 147·6	•
10	V	• 85·5 [24·67]	• 145 [1·25]	• 164·3 [1·07]ᵃ	• 164·6	•
10	L	• 72·4 [18·15]	• 136·6 [1·6]	• 140 [0·6]ᵃ	—	•
11	I	• 66·8 [36·57]	• 134·6 [1·19]	• 144·1 [1·01]ᵃ	•144·2	•
11	V	• 81·7 [16·01]	• 146·7 [1·15]	• 161 [0·88]ᵃ	•161·3	•
12	I	• 61 [42·50]	• 136·5 [1·23]	• 144 [1·17]ᵃ	•144·1	•
12	V	• 74·6 [26·96]	• 149·2 [1·04]	• 159·4 [1·22]ᵃ	•159·6	•
12	L	• 72·6 [23·50]	• 137·6 [1·20]	• 139·3 [1·12]ᵃ	—	•

ᵃ The sum of I–BP and BP–N* transition enthalpies.

controlled within 0·01°C accuracy. The CuK$_\alpha$ radiation from an 18 Kw rotating anode X-ray generator (Rigaku Ru-200) was selected by a flat pyrolitic graphite (0 0 2) monochromator. The resulting horizontal instrumental resolution was 10^{-2} Å^{-1}. The scattering profiles were fitted with the resolution function, and the accuracy on the Bragg position was estimated to be about 10^{-3} Å^{-1} or equivalently about 0·25 Å in direct space.

The layer thickness was close to 30 Å in the S_C^* phase (29·95 Å at $T = 90°$C) and increased regularly on approach to the S_C^*–N* phase transition.

The maximum tilt angle ($\cos\theta = d_{S_C^*}/L$ with $L = 38·7$ Å) was estimated to be equal to 39·2°. (L is the estimated molecular length of the molecule in its most extended form).

5. X-ray collection and crystal structure determination

5.1. *Experimental*

Suitable crystals of 4-[(2S)-2-chloro-3-methyl-butanoyloxy]biphenyl-4′-yl 4-undecyloxy-2,3 difluoro-benzoate ($C_{35}H_{41}O_5F_2Cl$) were grown from ethanol/chloroform solutions at 293 K. The crystal setting, cell parameters and data collection were made with a CAD-4

Enraf-Nonius diffractometer, equipped with a graphite monochromator for the CuK$_\alpha$ radiation ($\lambda = 1·54178$ Å). Twenty-five reflections with angles between 21° and 41° were used for the crystal setting and least-squares refinement of the cell parameters: $a = 6·764(5)$, $b = 57·057(6)$, $c = 8·597(2)$ Å and $\beta = 99·08(1)°$, monoclinic system, $P2_1$ space group ($Z = 4$), two independent molecules per asymmetric unit. The volume of the cell is 3276 Å^3, the molecular weight is 614·14 g mol^{-1} and the calculated density is 1·247 g cm^{-3}. The linear absorption coefficient $\mu = 1·467$ mm^{-1}. Data collection was performed using ω-2θ scans, $\theta_{max} = 55°$ (($7 \geqslant h \geqslant 0$), ($60 \geqslant k \geqslant 0$), ($9 \geqslant l \geqslant 9$)).

Three standard reflections ((-3 9 1), (1 18 $-$2) and (1 15 $-$3)) were measured every three hours. No significant decrease in these reference reflections was noticed during data collection; the minimum and maximum transmission factors were 0·87 and 0·997; the experimental correction of absorption was measured with the ψ scan technique [14]. There were 6763 reflections measured, of which 4150 were independent. Finally 2998 reflections can be considered as observed ($I > 2·0\sigma(I)$).

The structure was solved using the Mithril package [15], which led to the positions of two-thirds of the non-hydrogen atoms. The missing atoms were located with some difficulty after successive Fourier syntheses. Atomic parameters were refined under constraints thanks to the Shelx76 package [16] with anisotropic thermal parameters for the non-hydrogen atoms, minimizing ($|Fo| - |Fc|$)^2 with unit weights. Hydrogen atoms were introduced into theoretical positions [17] riding on the carbon atoms to which they are attached [16]. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1974, vol. IV). The final reliability factor was $R = 0·105$. This high value can be attributed to rather high atomic thermal motions and probably some disorder.

5.2. *Structure analysis*

The fractional coordinates and the equivalent Beq (Å^2) factors are given in table 2. The labelling of non-hydrogen atoms is presented along with a stick-and-ball representation of the molecule in figure 1. For the sake of clarity, atomic numbers run from C1 to C42 for the molecule A and C51 to C92 for the molecule B. The phenyl rings are designated as Φ_{1A} (C1 to C6), Φ_{2A} (C10 to C15), Φ_{3A} (C20 to C25), Φ_{1B} (C51 to C56), Φ_{2B} (C60 to C65), Φ_{3B} (C70 to C75).

5.3. *Molecular conformation*

The alkoxy chains of both molecules (O31 to C42 and O81 to O92) are quasi-planar and differ by less than 10° for A and 5° for B from a fully extended conforma-

Table 2. Fractional coordinates and equivalent isotropic thermal parameters B_{eq} $(\text{Å}^2) = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_i\cdot a_j$ for the compound with $n=11$ and R = V.

	Molecule A					Molecule B			
Atom	x/a	y/b	z/c	B_{eq}	Atom	x/a	y/b	z/c	B_{eq}
C1	1·834(2)	0·5729(3)	0·147(2)	5·56	C51	1·309(2)	0·5732(3)	0·659(2)	4·42
C2	1·980(2)	0·5578(3)	0·216(2)	5·03	C52	1·471(2)	0·5614(3)	0·735(2)	5·87
C3	1·947(3)	0·5390(3)	0·302(2)	6·02	C53	1·450(2)	0·5422(3)	0·830(2)	5·70
C4	1·763(2)	0·5347(3)	0·348(2)	5·36	C54	1·258(2)	0·5345(3)	0·837(2)	3·98
C5	1·606(2)	0·5481(4)	0·272(2)	7·55	C55	1·100(2)	0·5478(3)	0·772(2)	5·63
F105	1·419(1)	0·5453(2)	0·303(2)	9·09	F255	0·912(1)	0·5425(2)	0·786(1)	7·97
C6	1·642(3)	0·5680(3)	0·187(2)	6·00	C56	1·121(2)	0·5646(3)	0·667(2)	4·84
F106	1·470(1)	0·5805(2)	0·125(1)	8·32	F256	0·974(1)	0·5786(2)	0·605(1)	7·12
C7	1·755(2)	0·5134(3)	0·447(3)	6·50	C57	1·218(3)	0·5135(3)	0·949(2)	6·63
O8	1·886(2)	0·5008(3)	0·501(2)	11·56	O58	1·370(2)	0·5066(3)	1·034(2)	8·86
O9	1·560(2)	0·5088(2)	0·456(1)	6·05	O59	1·042(2)	0·5052(2)	0·931(2)	6·78
C10	1·509(2)	0·4889(3)	0·545(2)	5·96	C60	1·002(2)	0·4865(3)	1·021(2)	3·69
C11	1·630(3)	0·4771(5)	0·666(3)	12·24	C61	1·116(3)	0·4660(3)	1·039(3)	9·02
C12	1·555(4)	0·4571(5)	0·730(4)	14·36	C62	1·057(3)	0·4458(3)	1·117(3)	8·14
C13	1·360(2)	0·4496(3)	0·681(2)	4·03	C63	0·884(2)	0·4484(3)	1·180(2)	5·35
C14	1·239(2)	0·4600(4)	0·563(3)	8·53	C64	0·777(2)	0·4688(3)	1·157(2)	5·13
C15	1·322(2)	0·4790(3)	0·502(3)	8·67	C65	0·823(2)	0·4887(3)	1·070(2)	6·45
C20	1·295(2)	0·4278(3)	0·759(2)	4·43	C70	0·795(2)	0·4283(3)	1·257(2)	4·65
C21	1·405(3)	0·4165(3)	0·884(2)	7·36	C71	0·888(3)	0·4070(3)	1·270(3)	9·79
C22	1·334(3)	0·3959(3)	0·947(3)	9·41	C72	0·825(3)	0·3868(4)	1·335(3)	9·91
C23	1·138(2)	0·3893(4)	0·909(2)	5·79	C73	0·663(3)	0·3903(3)	1·407(2)	5·96
C24	1·045(3)	0·3976(3)	0·768(2)	7·73	C74	0·577(3)	0·4119(4)	1·430(3)	9·89
C25	1·112(4)	0·4184(4)	0·700(3)	10·16	C75	0·641(3)	0·4304(3)	1·343(3)	10·76
O16	1·061(2)	0·3711(2)	0·972(2)	7·26	O66	0·591(3)	0·3702(2)	1·496(1)	5·01
C17	1·142(2)	0·3496(4)	0·980(2)	6·24	C67	0·416(3)	0·3612(3)	1·449(2)	7·38
O18	1·276(2)	0·3442(3)	0·917(2)	8·31	O68	0·326(2)	0·3666(3)	1·327(2)	9·01
C19	1·011(2)	0·3311(3)	1·050(2)	5·63	C69	0·375(2)	0·3403(3)	1·551(2)	6·21
C126	0·753(1)	0·3374(1)	1·0174(8)	9·85	C176	0·1256(9)	0·3334(1)	1·5080(7)	9·23
C27	1·073(3)	0·3076(3)	1·044(2)	6·56	C77	0·525(2)	0·3201(4)	1·555(2)	7·03
C28	1·012(3)	0·2975(5)	0·882(2)	8·00	C78	0·524(4)	0·3099(4)	1·378(3)	9·45
C29	1·002(3)	0·2914(5)	1·159(2)	8·74	C79	0·467(3)	0·3003(3)	1·665(3)	7·69
O31	1·829(1)	0·5922(2)	0·062(1)	5·03	O81	1·331(1)	0·5918(2)	0·562(1)	6·13
C32	2·034(2)	0·6002(3)	0·042(2)	6·13	C82	1·518(2)	0·6000(3)	0·552(2)	5·80
C33	2·013(2)	0·6202(3)	−0·074(2)	5·78	C83	1·509(2)	0·6206(3)	0·445(2)	5·17
C34	2·218(2)	0·6297(3)	0·081(2)	6·43	C84	1·724(3)	0·6307(3)	0·437(2)	5·73
C35	2·234(2)	0·6505(3)	−0·191(2)	5·07	C85	1·709(2)	0·6496(3)	0·316(2)	5·60
C36	2·435(2)	0·6599(3)	−0·179(2)	4·46	C86	1·928(2)	0·6611(3)	0·304(2)	6·08
C37	2·438(2)	0·6804(3)	−0·305(2)	4·39	C87	1·942(3)	0·6801(3)	0·208(2)	6·53
C38	2·642(2)	0·6911(3)	−0·298(2)	4·82	C88	2·156(2)	0·6907(4)	0·208(2)	7·69
C39	2·669(3)	0·7109(3)	−0·411(2)	6·26	C89	2·155(2)	0·7102(3)	0·093(2)	4·94
C40	2·874(3)	0·7215(3)	−0·390(2)	5·67	C90	2·367(3)	0·7203(3)	0·096(2)	6·45
C41	2·879(3)	0·7426(4)	−0·509(3)	8·76	C91	2·384(3)	0·7400(3)	−0·012(2)	7·21
C42	3·072(3)	0·7516(4)	−0·511(3)	10·93	C92	2·593(3)	0·7515(4)	−0·003(3)	9·29

tion. The most significant torsion angles which entirely define the molecular conformations are given in table 3.

The first phenyl groups Φ_{1A} and Φ_{1B} are planar. The biphenyl groups $(\Phi2-\Phi3)_A$ on one side, and $(\Phi2-\Phi3)_B$ on the other side are planar and make an angle of $32\cdot1°$ and $35\cdot7°$ with the difluorobenzoate A and B groups. Due to the two different values of the torsion angles around the bond O9–C10 and O59–C60 (see table 3), the biphenyl rings of adjacent A and B molecules have non-parallel contacts: the angle between their mean

planes is close to $58\cdot4°$, whereas the mean planes of the $\Phi1_A$ and $\Phi1_B$ make an angle of $7°$. Similar characteristics were observed for other chiral biphenyl molecules [18].

The alkyloxy chains of molecule A (O31 to C42) and molecule B (O81 to C92) are parallel with a mean distance between them of $5\cdot9$ Å. This is also true for the benzoate groups of molecules A and B. Such a parallel arrangement has been observed for a non-chiral smectogenic compound [19,20]. The alkoxy chains have the same length in both molecules ($13\cdot83(3)$ Å for A and
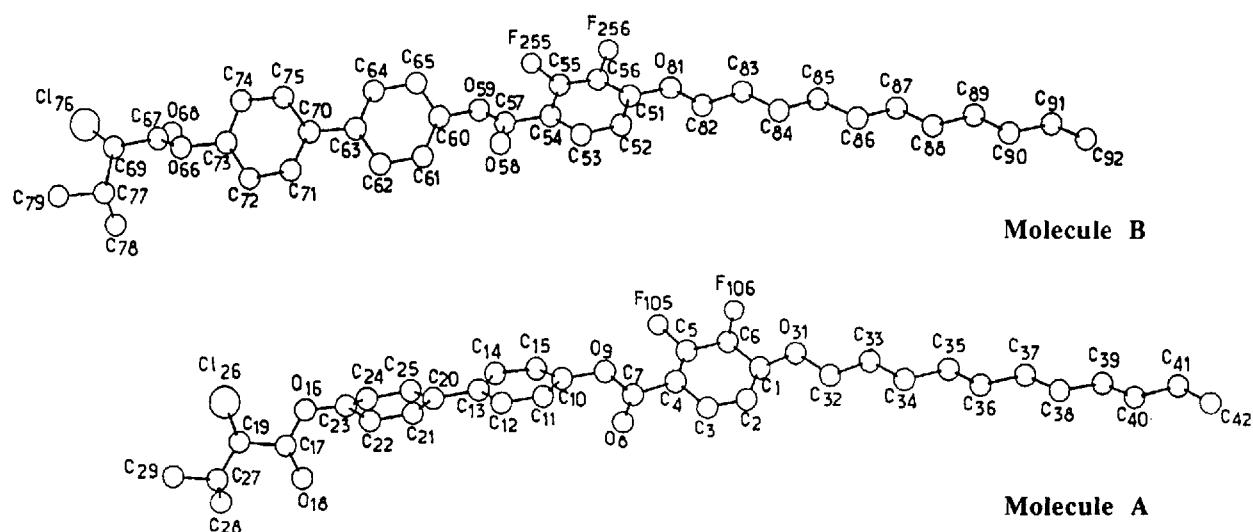
Figure 1. Stick-and-ball representation of the two independent A and B molecules of compound $n=11$, R = V with atomic labelling.

Table 3. Significant torsion angles (°) with standard deviations in brackets for the compound with $n=11$ and R = V.

Molecule A		Molecule B	
C3–C4–C7–O9	−168(2)	C53–C54–C57–O59	−170(2)
C7–O9–C10–C15	−154(2)	C57–C59–C60–C65	−140(2)
C12–C13–C20–C25	−172(2)	C62–C63–C70–C75	−170(2)
C22–C23–O16–C17	−51(2)	C72–C73–O66–C67	−116(2)
C23–O16–C17–C19	−176(2)	C73–O66–C67–C69	−177(2)
O16–C17–C19–C27	172(2)	O66–C67–C69–C77	−59(2)
C17–C19–C27–C29	158(2)	C67–C69–C77–C79	179(2)
C17–C19–C27–C28	−79(2)	C67–C69–C77–C78	−60(2)
O16–C17–C19–Cl26	28(1)	O66–C67–C69–Cl76	168(1)
O18–C17–C19–Cl26	−139(1)	O68–C67–C69–Cl76	26(2)
Cl26–C19–C27–C28	64(1)	Cl76–C69–C77–C78	69(1)
Cl26–C19–C27–C29	−60(2)	Cl76–C69–C77–C79	−52(1)

13·81(3)Å for B) and make an angle close to 18·4° and 19·6°, respectively with the direction of the molecular core. The total length of molecules A and B in the crystal is, respectively, equal to 33·99(3) and 33·77(3)Å (distance C29...C42 for molecule A, C79...C92 for molecule B).

5.4. *Crystal packing and molecular arrangement*

Figure 2 (*a*) and 2 (*b*) show, respectively, the projection of the structure along the *x* axis on the *y*0*z* plane and the *z* axis on the *x*0*y* plane. The two independent molecules adopt a head-to-head arrangement where the directions of their molecular long axes are parallel. This very specific arrangement of molecules A and B in a given layer has the result that dipole moments of different polar groups like C=O and C–l are additive. There is a global dipolar moment which is probably not negligible in the O*x* direction. This arrangement gives rise to sheets

parallel to the *x*0*z* plane where molecules, when considering the core parts, are tilted relatively to the normal of the layer at an angle close to 38·6° (A) and 40·4° (B).

Neighbouring sheets show alternate inclinations of the molecules generated by the 2_1 axis lying along the *b* axis. This arrangement is antiferroelectric-like: a bilayered structure where the molecules in neighbouring layers tilt in the same or opposite sense, and where the transverse dipoles point up and down along the *c* axis (in the direction perpendicular to the tilt plane). The thickness of the sheets is close to half the crystallographic *b* parameter, close to 28·5Å. These different values are in agreement with those observed for the smectic S_c^* phase described above (see figure 3).

The interactions between parallel sheets are of the van der Waals type and very weak. Numerous interactions of a van der Waals type between the parent molecule (*x, y, z*) and the neighbouring molecules (*x, y, z*;
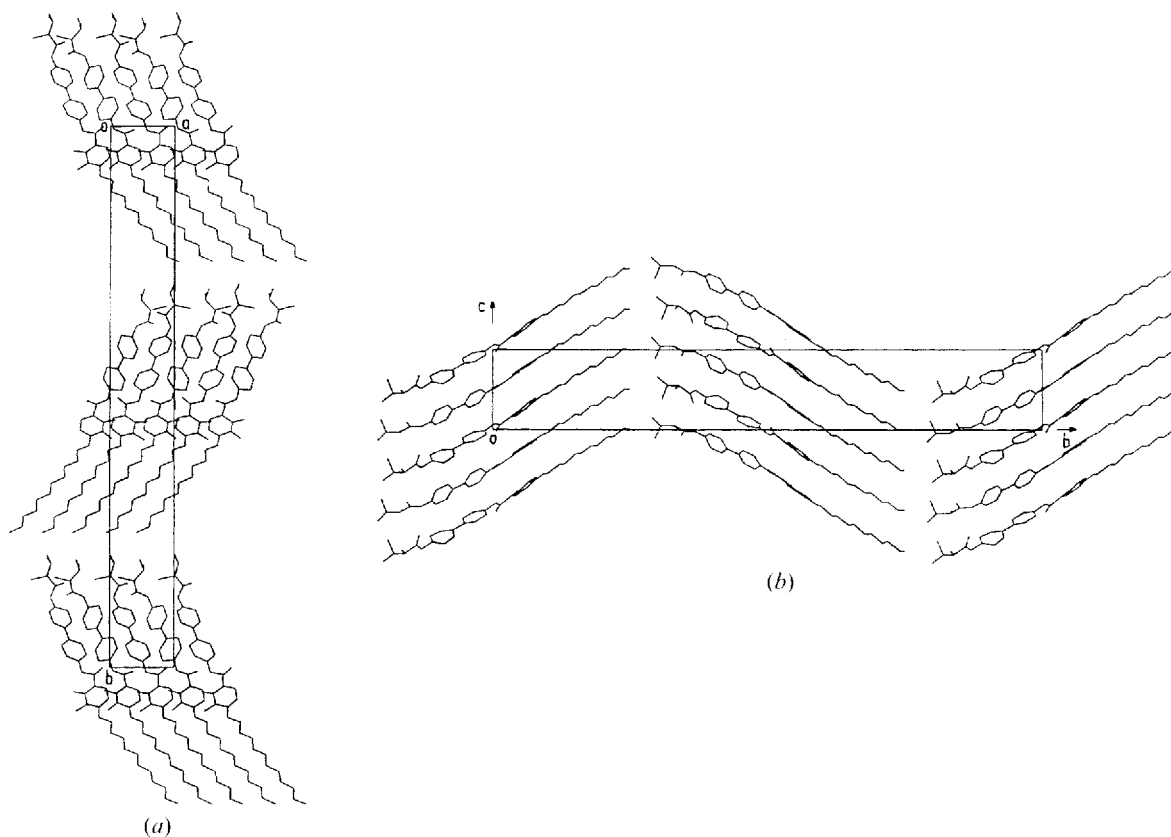
(*a*)

(*b*)

Figure 2(*a*). Projection of the structure along the z axis, on the ($x0y$) plane.

Figure 2(*b*). Projection of the structure along the x axis, on the ($y0z$) plane.

$-1 + x, y, 1 + z; 1 + x, y, z$) were noticed; the shortest of these are given in table 4. These interactions are located within the layers, whereas no particularly strong interactions were noticed between the layers. There is a segregation into three parts within the sheets, the long

Table 4. Shortest intermolecular distances noticed between neighbouring molecules of the compound with $n = 11$ and $R = V$.

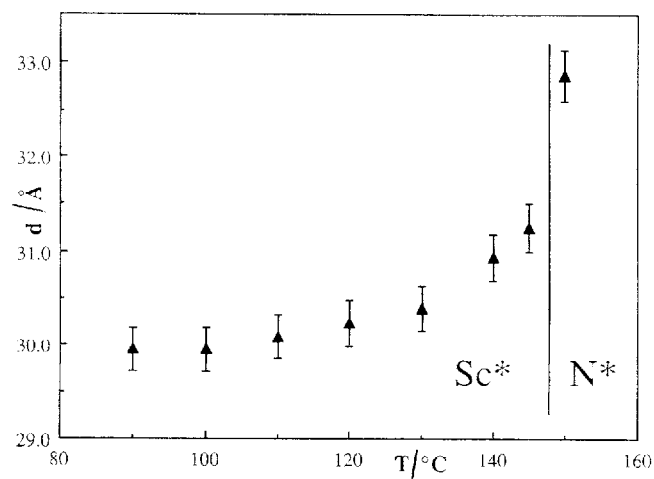|	
C20 (x, y, z).....C61 (x, y, z)	3·60
C53 (x, y, z).....C6 $(x, y, 1 + z)$	3·47
C64 (x, y, z).....C7 $(-1 + x, y, z)$	3·58
C65 (x, y, z).....C3 $(-1 + x, y, z)$	3·52
C74 (x, y, z).....C13 $(-1 + x, y, z)$	3·53
C2 (x, y, z).....F105 $(1 + x, y, z)$	3·03
C3 (x, y, z).....F105 $(1 + x, y, z)$	3·21
C3 (x, y, z).....C56 $(1 + x, y, z)$	3·49
O8 (x, y, z).....C15 $(1 + x, y, z)$	3·20
C4 (x, y, z).....C65 $(1 + x, y, z)$	3·57
O18 (x, y, z).....C126 $(1 + x, y, z)$	3·23
C32 (x, y, z).....F106 $(1 + x, y, z)$	3·13
C52 (x, y, z).....F255 $(1 + x, y, z)$	3·14
C53 (x, y, z).....F255 $(1 + x, y, z)$	3·21
O58 (x, y, z).....C65 $(1 + x, y, z)$	3·20
C82 (x, y, z).....F256 $(1 + x, y, z)$	3·28

Figure 3. X-ray diffraction of the mesophase and evolution of the layer thickness of the compound with $n = 11$ and $R = V$.

alkoxy chains giving rise to weak van der Waals interactions, the central cores with dipolar interactions involving especially the carboxylate groups, and the chiral

terminal parts $C^*H(Cl)-CH(CH_3)_2$ with dipolar interactions involving the C–Cl bond. This implies that at the transition, there is a greater or lesser rotation of sheets around the b axis giving a S_c^* helicoidal arrangement and probably corresponding to a small energy contribution.

5.5. *Comparison with the compound with $n = 11$ and $R = I$*

In this part, we compare this structure to that of a similar compound [21] which has the particularity of differing only in the chiral part (having an additional chiral centre). The latter crystallizes in the $P1$ space
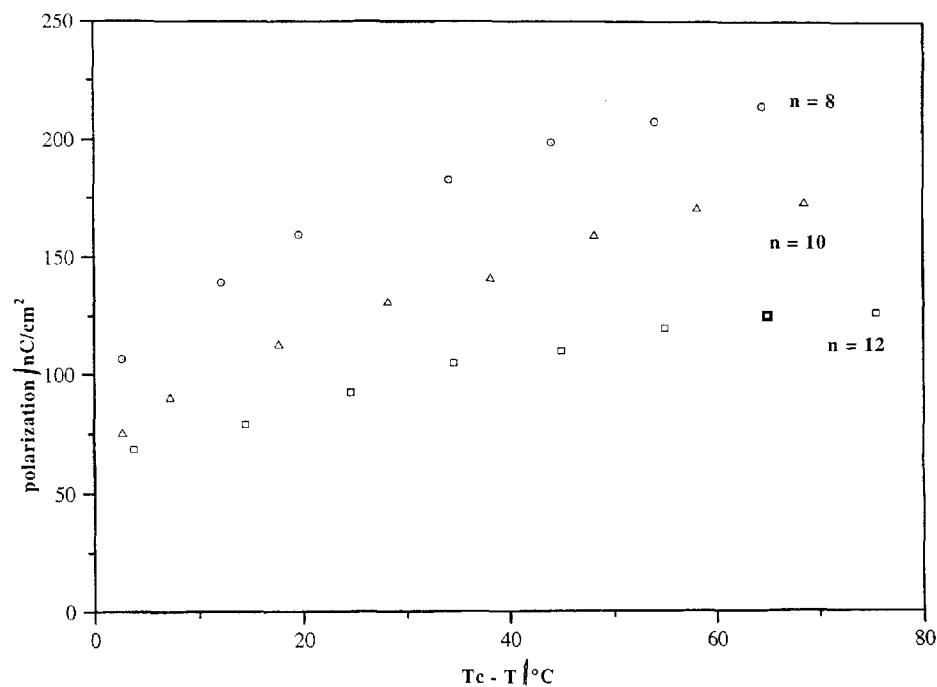

Figure 4. Evolution of spontaneous polarization as a function of temperature for the compounds with $n = 8$, 10, 12 and $R = I$.
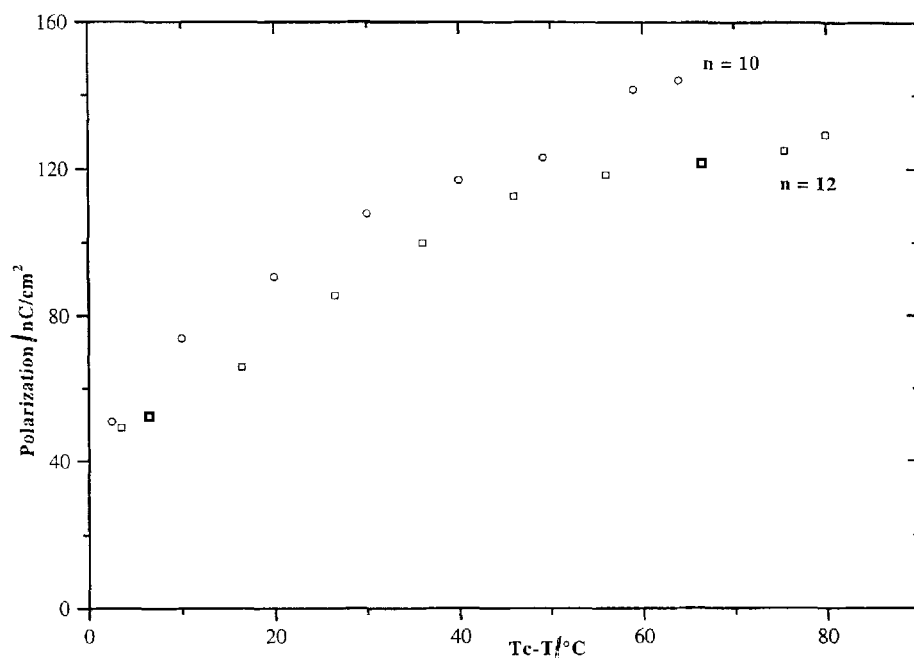

Figure 5. Evolution of spontaneous polarization as a function of temperature for the compounds with $n = 10$, 12 and $R = V$.
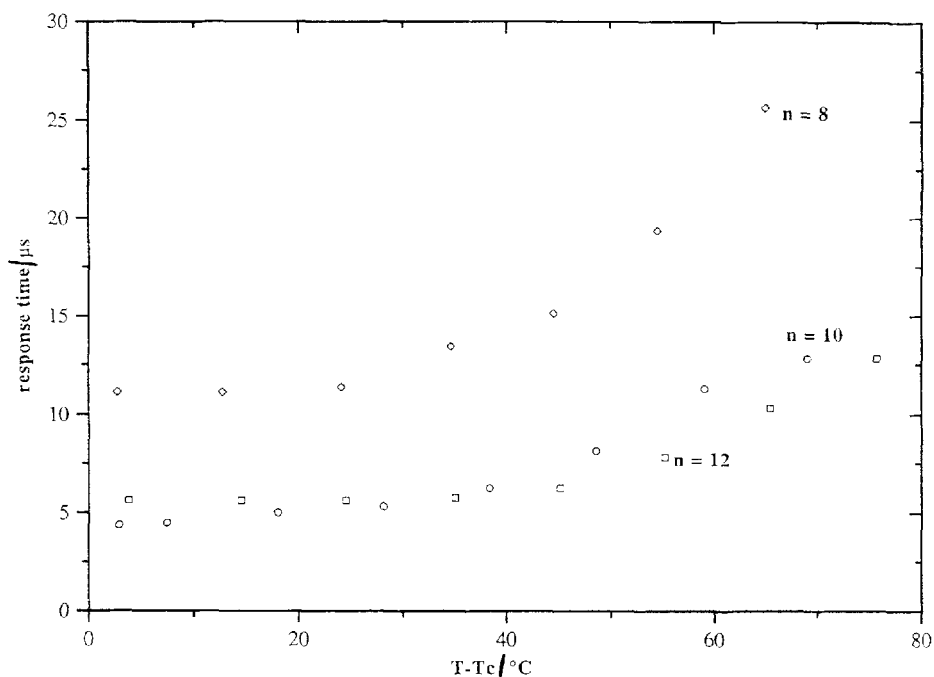
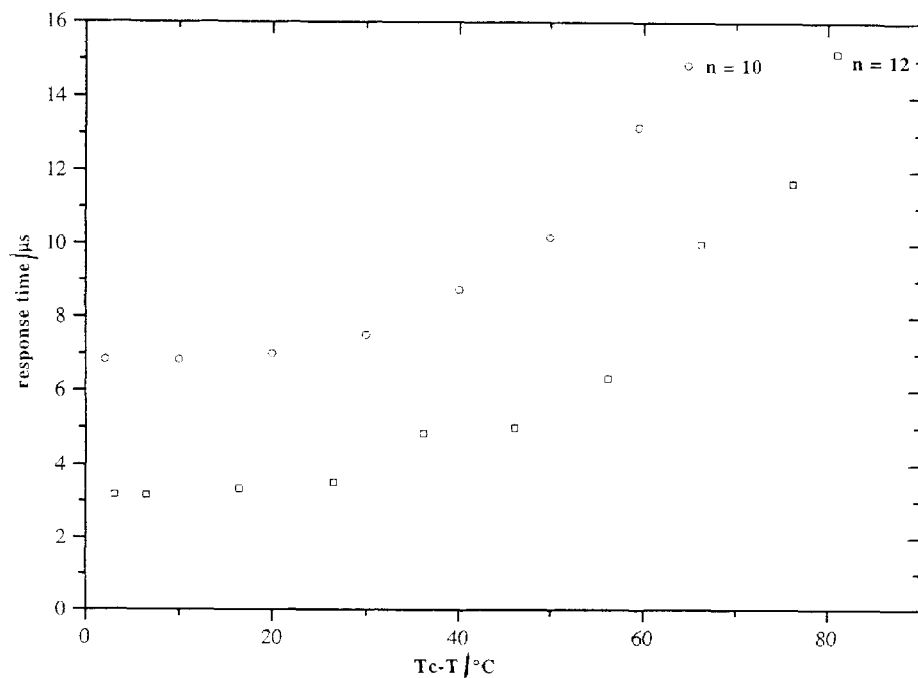Figure 6. Variation of response time with temperature for the compounds with $n = 8$, 10, 12 and R = I.

Figure 7. Variation of response time with temperature for the compounds with $n = 10$, 12 and R = V.

group with $Z = 2$, i.e. with two independent molecules A and B per asymmetric unit (calculated density equal to $1.306 \, \text{g cm}^{-3}$), but in this case, the molecules are anti-parallel (head-to-tail arrangement related by a pseudo-centre of symmetry). Such pairs give rise to sheets parallel to the $(x0y)$ plane. The orientation of the molecules in contiguous sheets is the same and the molecules

are tilted relatively to the normal of the layer by an angle close to $42°$. The layer thickness was $26.2 \, \text{Å}$. This molecular arrangement is a classical one and differs greatly from that of the structure established above for the compound with $n = 11$ and R = V. Numerous core-core interactions of the van der Waals type were detected within a given layer, but due to this arrangement,

interlayer interactions between atoms belonging to the terminal ethyl groups of the chiral parts were noticed. Moreover, the conformation of the molecules is different; thus for the compound with $n = 11$ and $R = I$, the mean planes of molecules A and B are parallel and the angle between the mean planes of the adjacent biphenyl groups is close to $1.5°$ (contrast $58.4°$ for the compound with $R = V$). It seems that this structure (compound with $n = 11$ and $R = I$) is more rigid and more compact and that the forces holding the layers together are stronger, thus explaining the difference in the enthalpies of transition (see table I) and in the density.

6. Electro-optic studies

A classical electro-optical method was used for the measurement of switching current, electric response time and apparent tilt angle. The samples were aligned in the bookshelf SSFLC planar geometry in cells with a thickness of $2.5\,\mu m$.

6.1. Spontaneous polarization

The spontaneous polarization P_s was calculated by integration of the switching current under an applied rectangular a.c. field. The field saturation value was $6\,V\,\mu m^{-1}$. Figures 4 and 5 represent the change in the spontaneous polarization P_s as a function of the temperature $T_c - T$, with T_c equal to $T_N^* - T_{SC}^*$, for homologues with $R = I$ and $R = V$ respectively. As expected, the values of the spontaneous polarization are very high and are almost identical for a given length of the

aliphatic chain. The compound with $n = 8$ and $R = I$ gives a $P_s > 200\,nC\,cm^{-2}$.

6.2. Electric response time

The electric response time, defined here as

$$\tau_g = \int_0^\infty i_p(t)\,dt/2i_p(\tau m)$$

[22,23] where $i_p(t)$ is the polarization current and τ_m the time between the field reversal and the maximum of the polarization, was measured using a field equal to $20\,V\,\mu m$. A classical behaviour was observed. The response time depends on the aliphatic chain length and on $T_c - T$: this correlates with the increase of the viscosity at lower temperatures.

These compounds present very interesting response time results (figures 6 and 7; the response time of the compound with $n = 12$ and $R = I$ or V increases slowly with temperature and reaches a maximum close to $15\,\mu s$ for T_c-T equal to $80°$. The behaviour of the compound with $n = 8$ and $R = I$ is slightly different and the response time is equal to $25\,\mu s$ for T_c-$T = 60°$.

6.3. Tilt angle

The tilt angle characterizes the optical contrast and should approach the ideal value of $22.5°$. The SSFLC cell is under an alternating field of low frequency, $0.1\,Hz$. The apparent tilt angle of the molecules was calculated from the difference between the extinction positions of the sample between crossed polarizers. The accuracy
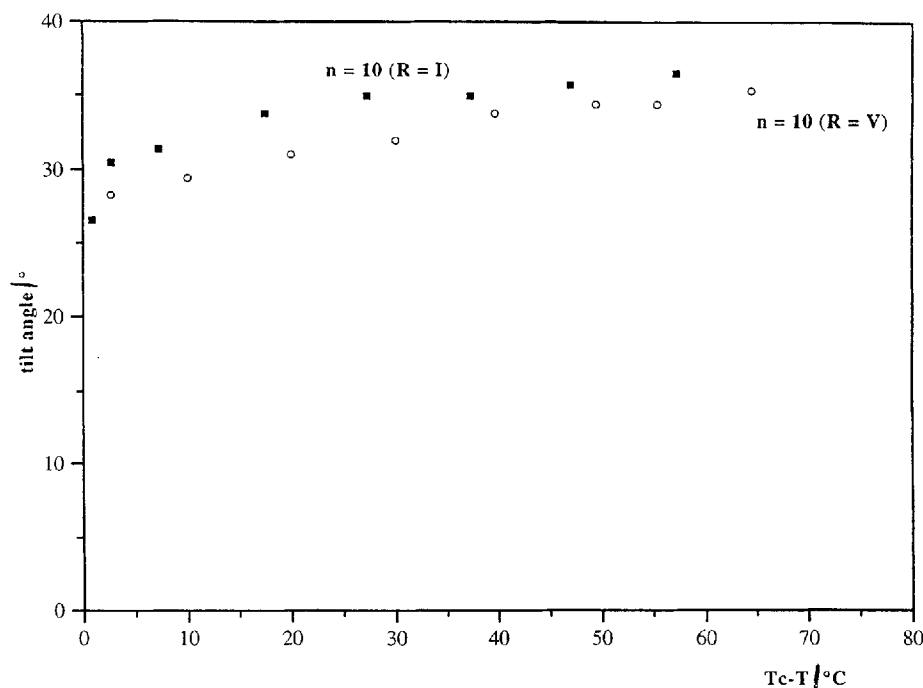

Figure 8. Variation of tilt angle with temperature for the compounds with $n = 10$ and $R = V$ or $R = I$.

was estimated to be equal to 0·5°. The tilt angle (figure 8), close to 35°, for these pure compounds is too high for classical device applications, but could be useful in ferroelectric liquid crystal twist cells [24].

7. Conclusion

Pure compounds with high values for the spontaneous polarization and short response times over a large temperature range were successfully synthesized. These compounds have rather remarkable electro-optic characteristics and could be used for preparing mixtures exhibiting the ferroelectric smectic C* phase at room temperature.

The crystal structures of two compounds belonging to this series have been solved. One is described here and presents a special arrangement. The crystal preceeding the mesophase adopts a layer structure where the molecules are tilted at an angle close to 40°, which is consistent with the phase sequence Cr→S_c^*→N*. The molecular packing in the structure must be controlled by the arrangement of the polar groups [25], and indeed, by changing the chiral part of the molecule (introducing a C_2H_5 group), so involving a supplementary chiral centre, the molecular arrangement differs greatly.

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