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Three ring dioxanes as dopants enhancing the stability of the smectic C phase

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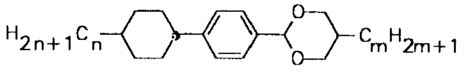
Searching for compounds which could be useful as modifiers of smectic C mixtures, we have synthesized four homologous series of three ring dioxanes, 2BBD, 5BBD, 2CBD, and 5CBD. Their phase transition temperatures and enthalpies were measured and their liquid crystal phases identified. Compounds belonging to series *n*-BBD form smectic B_{cr} phases for shorter alkyl chains, and smectic B_{cr} and A phases, for longer chains. Compounds belonging to the *n*-CBD series exhibit the smectic A phase, but those with longer alkyl chains have exclusively smectic B phases and those with short tails have other low temperature, highly ordered smectic phases. The compounds were added to smectic C mixture and it was found that some can be useful as dopants. Compounds with longer alkyl tails in the molecule are more suitable for this purpose; the type of ring in the core is less important.

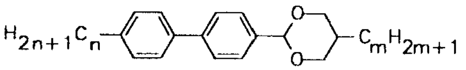
1. Introduction

Ferroelectric mixtures with controlled physical properties and a large temperature range of existence for the smectic C phase are more difficult to obtain than nematic mixtures. This is the result of both a limited number of compounds with the smectic C phase and the fact that not all of the compounds can be mixed one with another, because of the frequently occurring destabilization of the smectic C phase [1]. Therefore it is important to look for compounds which are not necessarily smectic C themselves, but which, when added to the mixture, widen the temperature range of existence of the smectic C phase. In previous papers [2, 3] we have shown that compounds not exhibiting the smectic C phase can be introduced to smectic C mixture in considerable amounts. These compounds not only do not cause destabilization of the smectic C phase but, in some cases even increase the upper temperature limit of existence of the smectic C phase. Such characteristics occur especially in terphenyl derivatives [3, 4]. Reasoning in this way we have started systematic investigations of structural elements of mesogenic molecules in order to find out which are responsible for the above mentioned behaviour, and at the same time to find compounds which would be appropriate as dopants.

In this paper we present results for two homologous series, derivatives of 1,3-dioxane of the general formulae



n-CBD series



n-BBD series

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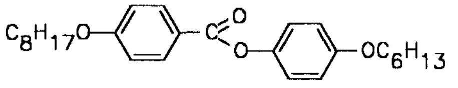
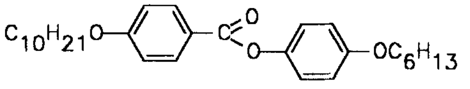
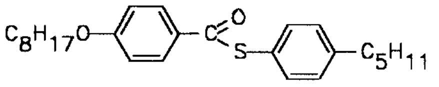
in which $n=2$ or 5 and m is varied from 2 to 10. The compounds were introduced in increasing amounts, as additional components, to a smectic C mixture of the compounds



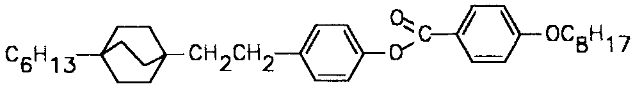
23·3 wt%



18·8 wt%



25·4 wt%

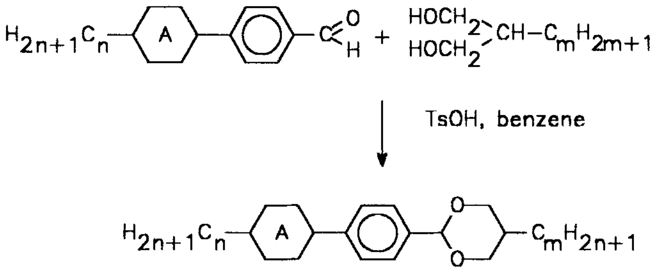


32·4 wt%

The basic mixture has the following phase transition temperatures: S_B 9 S_C 58·8 N 119·5 I (in °C).

2. Experimental

Compounds from the series *n*-CBD and *n*-BBD were obtained by standard methods used for the synthesis of dioxanes [5, 6] (see scheme)

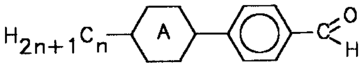


In the reaction, a mixture of *trans*- and *cis*-isomers is produced. The *trans*-isomer was isolated by crystallization using methanol containing triethylamine as solvent. The process was repeated until the transition temperatures, measured after purification, were the same. The purity of each compound was checked by liquid (column RP18, mobile phase methanol + 5 per cent of water) and gas chromatography (column Ultra 2, HP).

The aldehyde used as reactant was obtained by reduction of the nitrile using Raney alloy in formic acid. Reaction was complete after 1 hour and the yield was good (70–80 per cent). The aldehyde was purified by distillation. It is interesting to note that the aldehydes with shorter alkyl tails are low temperature nematics (see table 1), with clearing points lower (10 to 30°C) than for the corresponding cyano compounds [7]. The difference is bigger for phenylcyclohexanes than for biphenyl derivatives.

Phase transition temperatures and melting enthalpies were measured using a DSC-92 'SETARAM' microcalorimeter at a heating rate of 1°C min^{-1}. All other transition temperatures were measured by thermomicroscopy (TM) using a THM-600 LINKAM

Table 1. Phase transition temperatures for aldehydes of formula



n	A	C		N		I
2	Benzene	●	96–70	—		●
5	Benzene	●	16·5	24·5		●
2	Cyclohexane	●	−2	—		●
3	Cyclohexane	●	35–36	—		●
5	Cyclohexane	●	−10	●	22	●

programmable hot stage mounted on a polarizing microscope, 'Biolar' PZO, in the region of a phase transition the temperature was changed at the rate of 0·2°C min^{-1}.

The compounds under investigation are thermally unstable when heated above the clearing point. The decomposition products cause a lowering of the phase transition temperature measured during the cooling cycle. This was especially noticeable when DSC was used. We tackled this problem by using both techniques: DSC and TM. The transitions from solid to smectic are difficult to detect by TM, so for these we used the DSC.

Some of the compounds were examined by X-ray methods. The X-ray diffraction measurements were performed using a Guinier camera and $Co_{K\alpha 1}$ radiation or a Laue camera and Cu radiation, with the sample oriented by a magnetic field. Most investigated samples were thick (~0·2 mm) and freestanding; in some cases thin (~0·05 mm) freestanding samples were also used. The compounds whose phase transition temperatures were identified in this way were used for identifying the smectic phases of the other compounds by the miscibility method.

The upper temperature limit of existence of the smectic C phase in the mixture containing compounds from series CBD and BBD was measured using TM. The samples were prepared by weighing out small amounts of the base mixture and adding known amounts of the *n*-CBD and *n*-BBD compounds.

3. Results and discussion

Tables 2 and 3 show the phase transition temperatures for compounds of the *n*-BBD and *n*-CBD series. The temperatures given refer to heating cycles and denote the disappearance of the lower temperature phase.

Using the X-ray method we have discovered that compounds 2cbd6 and 2cbd7 have a crystalline smectic B phase (S_{Bcr}) and compounds 2bbd6, 2bbd7, 2bbd9, 2bbd10, 5bbd7, 5bbd10 have S_{Bcr} and S_A phases. Compound 5bbd3 has a B phase which is above a tilted phase manifesting itself by a mosaic texture. We failed to identify this phase. Compound 2cbd7 exhibits two smectic phases; the high temperature phase was identified as B and again in this case we were unsuccessful in identifying the monotropic, low temperature phase. The results of miscibility tests suggest however that it is a smectic E phase. We were unable to identify the phase revealed by compound 2cbd3; the texture of this unknown phase is shown in figure 1. Compounds belonging to series *n*-BBD reveal smectic B_{cr} phases for shorter alkyl chains and smectics B_{cr}, and A for longer chains. None of the compounds from series *n*-CBD has a smectic A phase; those with longer alkyl chains form exclusively the smectic B phase and those with short tails have other low temperature highly ordered smectic phases.

Table 2. Phase transition temperatures (°C) and melting enthalpies (cal mol^{-1}) for compounds from series *n*-BBD.

	n	*m*	C_1		C_2		C		S_{X1}		S_{Bcr}		S_A		N		I
2bbd2	2	2			●	45·4	●	89·3 4790							●	147	●
2bbd3	2	3					●	112·4 4560							●	163	●
2bbd4	2	4	●	54·5 340	●	57·4 590	●	93·1 4260			●	72·9†			●	157·8	●
2bbd5	2	5					●	107·4 4910			●	98·6†			●	169·1	●
2bbd6	2	6					●	101·7 4800			●	117·0†	●	117·7	●	155·2	●
2bbd7	2	7					●	77·8 3550			●	130·3‡	●	130·9‡	●	156·2	●
2bbd8	2	8					●	33 1070			●	134·9‡	●	136·9‡	●	150·7	●
2bbd9	2	9					●	79·4 2800			●	136·9‡	●	141·2	●	150·4	●
2bbd10	2	10					●	73·7 3530			●	135·2‡	●	139·8‡	●	143·8	●
5bbd2	5	2			●	39·2 740	●	81·6 2590			●	83·3			●	143·9	●
5bbd3	5	3					●	85·4 5960	●	(80·5)§	●	86·2			●	162·9	●
5bbd4	5	4					●	48·4 4260			●	94·1			●	161·3	●
5bbd5	5	5					●	77			●	107‡	●	119·6‡	●	159	●
5bbd6	5	6					●	69·1 4690			●	122·5‡	●	136·6‡	●	160·5	●
5bbd7	5	7			●	26 490	⊙	43·0 1990			●	140·8‡	●	153·4	●	165·8	●
5bbd8	5	8			●	40·7 150	●	47 2520			●	138·9‡	●	153·1‡	●	159·5	●
5bbd9	5	9					●	49·4 5650			●	142·7‡	●	154·8‡	●	156·6	●
5bbd10	5	10					●	47·2 6000			●	142·5‡	●	154·4‡			●

† Mosaic texture, ‡ Fan texture, § Mosaic texture with large domains.

Table 3. Phase transition temperatures (°C) and melting enthalpies (cal mol^{-1}) for compounds of series *n*-CBD.

	n	*m*	C_1		C		S_{X1}		S_{X2}		S_{Bcr}		N		I
2cbd2	2	2			●	62							●	111	●
2cbd3	2	3			●	74·6 1420	●	82·5					●	133·8	●
2cbd4	2	4			●	68	●	73					●	124	●
2cbd5	2	5			●	75·0 5360					●	68·7	●	132·8	●
2cbd6	2	6			●	55·8 6300					●	80	●	120·7	●
2cbd7	2	7			●	45·5 5950			●	52·4‡	●	99†	●	124·3	●
2cbd8	2	8			●	65·2 7080					●	106·5†	●	119·1	●
2cbd9	2	9			●	47·0 3360					●	114·5†	●	120·8	●
2cbd10	2	10			●	53·3 5090					●	116·8†	●	117·3	●
5cbd2	5	2			●	73·3 4380							●	136·3	●
5cbd3	5	3	●	45·3 1590	●	72·4 2960							●	157·3	●
5cbd4	5	4	●	53·8 3570	●	65 3200							●	151	●
5cbd5	5	5			●	54·0					●	83†	●	155·1	●
5cbd6	5	6			●	69·8 2100					●	111†	●	147·4	●
5cbd7	5	7			●	54·5 6370					●	142			●
5cbd8	5	8			●	46·6 6750					●	135·1†	●	144·9	●
5cbd9	5	9			●	57·4 6420					●	140·5†	●	143·4	●
5cbd10	5	10			●	55·8 7260					●	143·7†			●

† Mosaic texture, ‡ Marble texture.

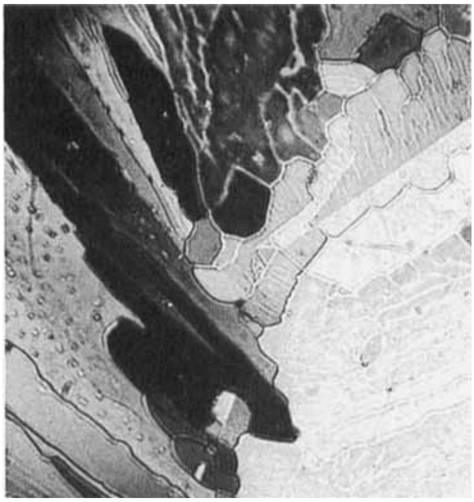
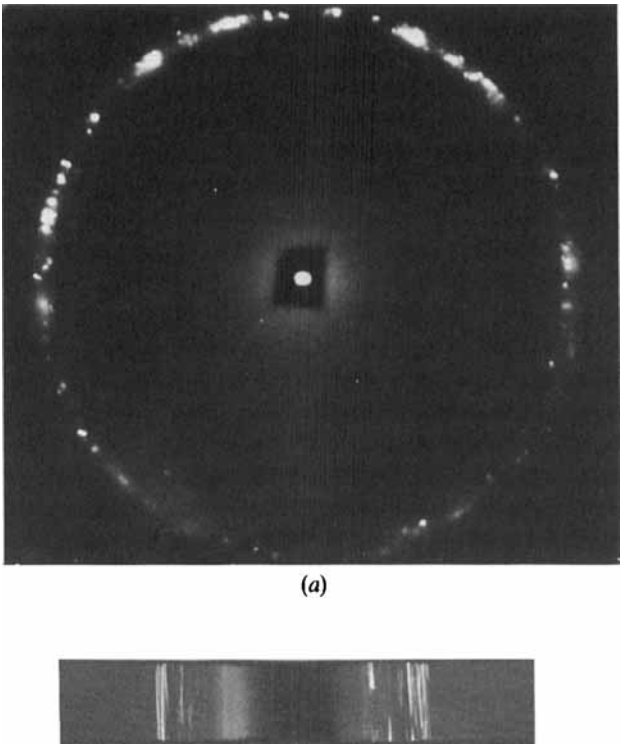


Figure 1. Photograph of the texture (crossed polarizers) for 2cbd3 at 81°C.



(*a*)

(*b*)

Figure 2. X-ray diffraction pattern of compound 2cbd6 (*a*) thin film (Laue) and (*b*) thick film (Guinier; inner ring).

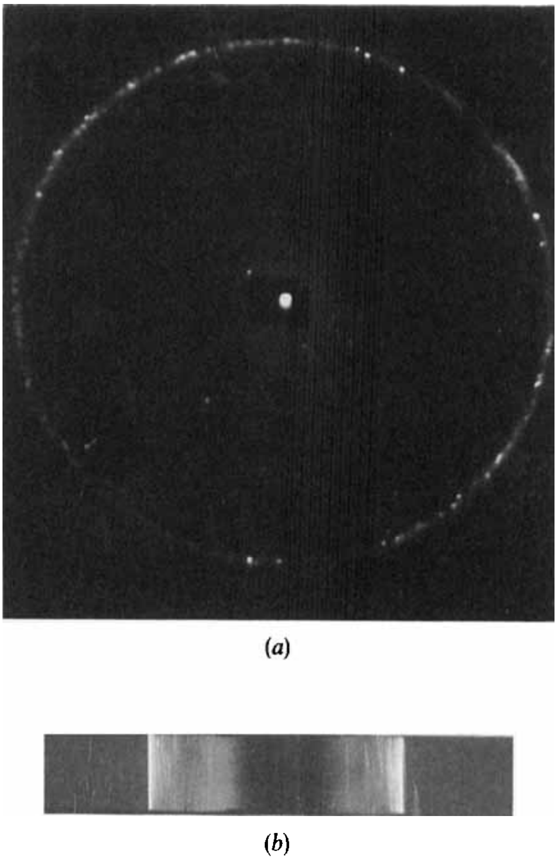


Figure 3. X-ray diffraction pattern of compound 2cbd7 (*a*) thin film (Laue) and (*b*) thick film (Guinier; inner ring).

Compound 2cbd6 as well as compound 2cbd7, has a smectic B_{cr} phase; however, the B phase for compound 2cbd6 is more crystalline, see figures 2 and 3. In the case of compound 2cbd6, the width of the diffraction ring (ΔQ) is smaller and the modulation in a χ scan also indicates long-range orientational order. These two compounds therefore differ in crystallinity and crystallite size. It is interesting that two neighbouring members from the same homologous series reveal such a great difference in the molecular organization of the smectic B layer.

Figures 4–7 show the upper temperature limit of existence of the smectic C phase versus the concentration of the compounds in the mixture. Generally, the stability of the smectic C phase increases with increasing alkyl chain length. There could be defined two groups of the dopants: one with destabilization and one with stabilization of the smectic C phase. The first group consists of compounds with shorter alkyl chains in their molecules and the second of compounds with longer tails. The limiting length depends on the rigidity of the core and the length of the second alkyl terminal group.

In the case of the 2CBD series (see figure 4), the enhancement of the smectic C phase is observed in the case of dopants with nonyl and decyl alkyl tails. In the 5CBD series, enhancement starts from the homologue with a hexyl tail (see figure 5), 2BBD series (see figure 6), from the heptyl homologue and in the 5BBD series (see figure 7) from the hexyl homologue.

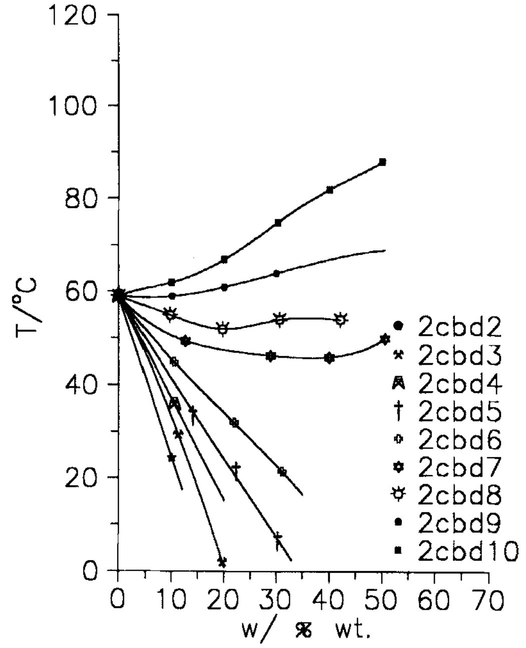


Figure 4. The upper temperature limit of existence of the smectic C phase versus the concentration of 2CBD homologue in the mixture.

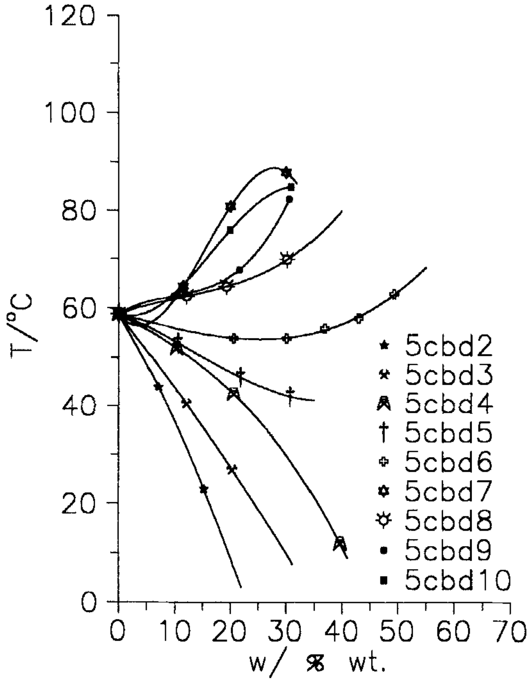


Figure 5. The upper temperature limit of existence of the smectic C phase versus the concentration of 5CBD homologue in the mixture.

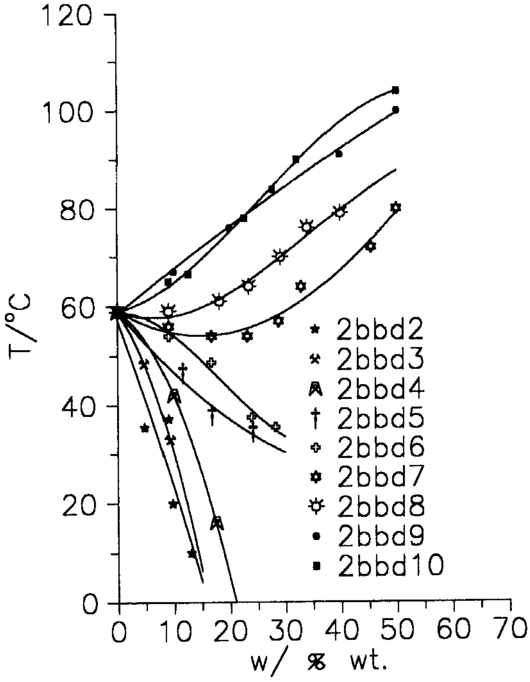


Figure 6. The upper temperature limit of existence of the smectic C phase versus the concentration of 2BBD homologue in the mixture.

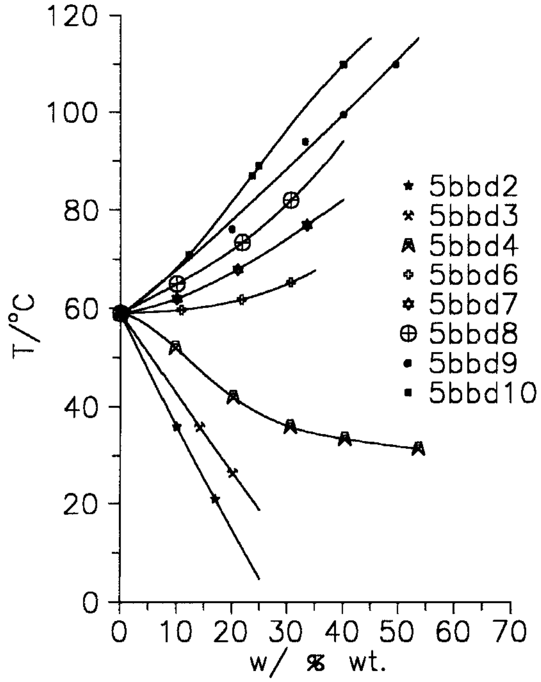


Figure 7. The upper temperature limit of existence of the smectic C phase versus the concentration of 2CBD homologues in the mixture.

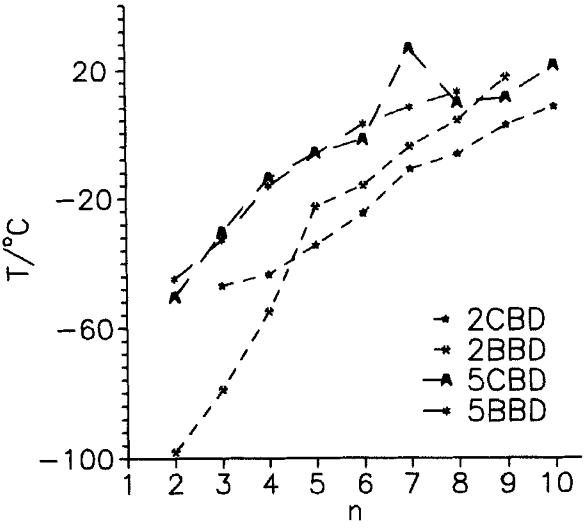


Figure 8. Change in the upper temperature limit of the smectic C phase of the mixture after doping with 20 wt% of the investigated compounds versus the length of the alkyl tail on the side of dioxane ring.

In the case of compounds from the series 2CBD (see figure 4), the lines separating the nematic and smectic C phases are straighter than in the case of the 5CBD compounds (see figure 5). The curves for compounds 5cbd7 and 5cbd10 differ in their character from the rest of the curves in figure 5. The different properties of these two compounds are also seen in their polymorphism (see table 2); these compounds do not form a nematic phase. It is interesting to note that only homologues with heptyl and decyl alkyl tails give rise to the observed irregularities.

Figure 8 shows the change in the S_C–N phase transition temperature, after doping the base mixture with 20 wt% of the investigated compounds, versus the length of alkyl tail on the side of the dioxane moiety. As we can see, the 2CBD compounds destabilize the smectic C phase more than the 2BBD compounds. But when the length of the alkyl chain on the side of the benzene or cyclohexane moieties increases, an influence of the nature of the ring for alkyls shorter than heptyl is not seen. Instead, some irregularities, seen also in the polymorphism of individual compounds, are seen. Generally, the length of the alkyl tail is more important than the nature of the ring.

4. Conclusions

Compounds which do not have the smectic C phase can be used as dopants of a smectic C mixture. The character of the core is important, but more important is the total length of the alkyl tails.

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