Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: J. C. Dubois & A. Béguin (1978): Influence of Lateral Substitution on Mesomorphic Properties of Phenyl 4-Benzoyloxybenzoate Derivatives, Molecular Crystals and Liquid Crystals, 47:3-4, 193-200

To link to this article: http://dx.doi.org/10.1080/00268947808083744

Mol. Cryst. Liq. Cryst., 1978, Vol. 47, pp. 193–200

Printed in Holland

Influence of Lateral Substitution on Mesomorphic Properties of Phenyl 4-Benzoyloxybenzoate Derivatives†

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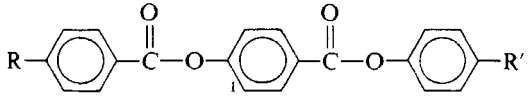
(*Received January 16, 1978; in final form April 13, 1978*)

A series of liquid crystalline phenyl 4-benzoyloxybenzoates with lateral bromo, cyano or methyl substituents have been prepared. The effect of these changes on the phase transitions of these compounds is discussed.

1 INTRODUCTION

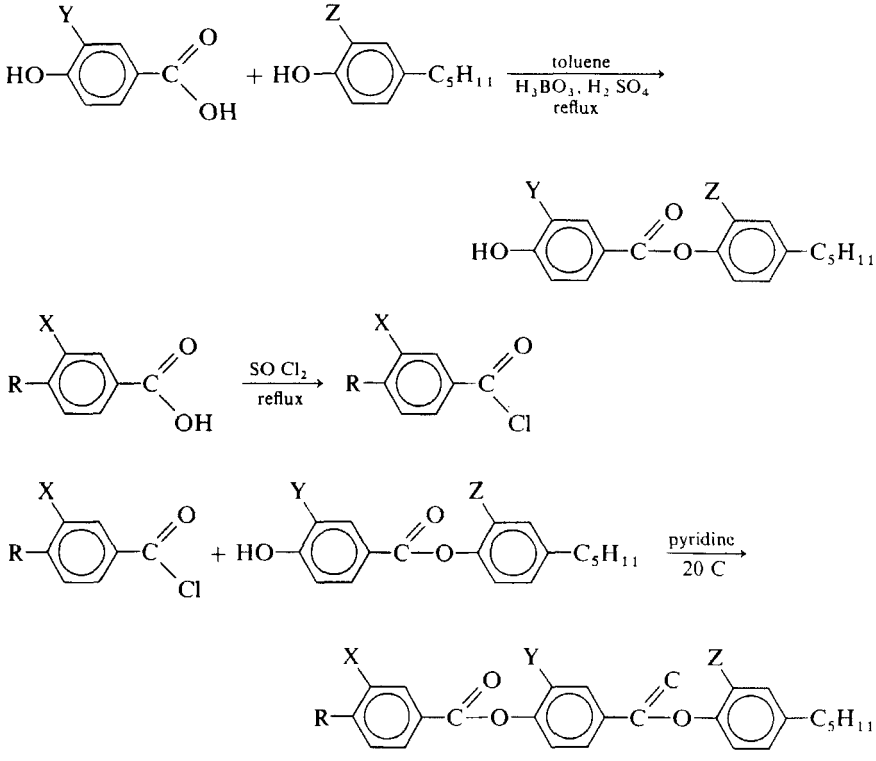
During the last few years, a large number of laterally substituted chloro and methyl derivatives of phenyl 4-benzoyloxybenzoate (1) have been synthesized.[1,2] However there is only one example of a cyano substituted compound belonging to this family.[3] In order to have a better understanding of the effect of the location and type of substituents on the mesomorphic properties of phenyl 4-benzoyloxybenzoates, we have prepared a number of derivatives of 1 with lateral substituents including several cyano substituted derivatives. This study, which concerns the preparation and the mesomorphic properties of these new compounds, is a continuation of some earlier work on derivatives of 1.[4]



† Presented at the Second Liquid Crystal Conference of Socialist Countries in Burgas (Bulgaria), September 1977.

2 RESULTS

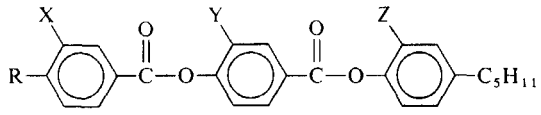
The bromo, chloro and methyl substituted phenyl 4-benzoyloxybenzoates were prepared by the route shown in scheme I. The cyano substituted compounds were prepared from the corresponding bromo derivatives by the action of cuprous cyanide in refluxing *N*,*N*-dimethylformamide. The details for the preparation of these compounds is given in the experimental section. Each compound was purified by chromatography on silica gel with a mixture of hexane and benzene (1 : 1) followed by recrystallization from ethanol. The structures were confirmed by infrared spectroscopy and elemental analysis. The purity of the final products was checked by thin layer chromotography and thermal analysis with a Perkin-Elmer DSC 1B. The transition temperatures were determined by differential scanning calorimetry. The smectic phases were identified by comparison to known reference compounds using the contact method.[5] The mesomorphic transition temperatures are given in Table I.



SCHEME I

TABLE I

esomorphic transition temperatures of phenyl 4-benzoyloxy benzoates



d decrease of the clearing point ΔT°C of these compounds with regard to the corresponding no-bstituted one's.[1]

mpound umber	Ring substituent R	X	Y	Z	Transition temperatures °C K	S_C	S_A	N	I	ΔT °C
1[1]	C_7H_{15}	H	H	H	76	—		104	169	0
2[1]	C_8H_{17}	H	H	H	79	—		117	161	0
3	$C_8H_{17}O$	H	H	H	85	102		152	186	0
4	CH_3O	NO_2	H	H	135	—		—	151	73
5	CH_3	Br	H	H	113	—		—	121	78.5
6	C_3H_7	Br	H	H	76	—		—	118	70
7	C_6H_{13}	Br	H	H	57	(48)		—	117	52
8	C_7H_{15}	Br	H	H	58	(50)		—	117	52
9	C_8H_{17}	Br	H	H	57	(48)		—	104	57
10	CH_3O	Br	H	H	125	—		—	163	61
11	C_2H_5O	Br	H	H	117	—		—	176	—
12	C_4H_9O	Br	H	H	124	—		—	167	42.5
13	$C_7H_{15}O$	Br	H	H	121	(94.5)		—	153	—
14	$C_8H_{17}O$	Br	H	H	125	(100.5)		—	150	36
15	CH_3	CH	H	H	113	—		—	123	76.5
16	C_3H_7	CN	H	H	80	—		(76)	110	78
17	C_6H_{13}	CN	H	H	117	—		(115)	120.5	48.5
18	C_7H_{15}	CN	H	H	104.5	—		122	122.5	46.5
19	C_8H_{17}	CN	H	H	87	—		120.5	—	40.5
20	CH_3O	CN	H	H	123	—		—	158	66
21	C_2H_5O	CN	H	H	112	—		124	171	—
22	C_4H_9O	CN	H	H	102	—		160	170	39.5
23	$C_5H_{11}O$	CN	H	H	83	—		162	165	33.5
24	$C_7H_{15}O$	CN	H	H	75.5	100		166	—	—
25	$C_8H_{17}O$	CN	H	H	82	100		167	—	19
26	C_6H_{13}	H	Br	H	50	—		—	108.5	60.5
27	C_7H_{15}	H	Br	H	55	—		—	109	60
28	C_8H_{17}	H	Br	H	54	—		—	102.5	58.5
29	$C_8H_{17}O$	H	Br	H	70	—		—	133	53
30	C_8H_{17}	H	CN	H	97	—		—	113	48
31	$C_8H_{17}O$	H	CN	H	99	—		—	136	50
32	C_8H_{17}	H	H	CH_3	92.5	—		—	120	41

TABLE I (*continued*)

Compound number	Ring substituent				Transition temperatures °C									
	R	X	Y	Z	K		S_C		S_A		N		I	
33	C_8H_{17}	Br	H	CH_3	.	61.5	—		—		.	68	.	9
34	$C_7H_{15}O$	Br	H	CH_3	.	89.5	—		—		.	113	.	
35	$C_8H_{17}O$	Br	H	CH_3	.	95	—		—		.	112.5	.	7
36	C_8H_{17}	CN	H	CH_3	.	84.5	—		(.	61)	(.	64)	.	9
37	$C_7H_{15}O$	CN	H	CH_3	.	101.5	—		.	116	.	116.5	.	
38	$C_8H_{17}O$	CN	H	CH_3	.	72.5	(.	41)	.	112	—		.	7
39	$C_8H_{17}O$	Br	Cl	H	.	93	—		—		.	106	.	8
40	$C_8H_{17}O$	Br	CN	H	.	89	.	93.5	—		.	113	.	7
41	$C_8H_{17}O$	CN	Cl	H	.	130	—		—		—		.	

3 DISCUSSION

The effect of lateral substitution on the mesomorphic properties of the phenyl 4-benzoyloxybenzoates can be discussed with regard to the following:

a) changes in clearing point (nematic-to-isotropic transition temperature)

b) type and range of the mesophase

c) changes in melting point.

a Effect of lateral substitution on the clearing point

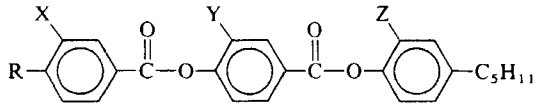
As expected, the introduction of a lateral substituent into the phenyl 4-benzoyloxybenzoate system results in a decrease in the clearing point. This decrease was approximately the same (45–55°C) for each substituent regardless of location. Compounds 23–25 in Table I are an exception to this generality. These compounds have an especially high negative dielectric anisotropy: for a mixture of 20% of one of these compounds and 80% of 4-pentylphenyl 4-methoxybenzoate whose dielectric anisotropy is near zero (molar ratio) at 22°C, the measured dielectric anisotropy is -1.7[4]. It seems that the strong dipole moment enhances the mesomorphic properties of these compounds. The decrease in the clearing point was found to be additive in that the sum of the decreases which can be attributed to each substituent is in relatively good agreement with the observed decrease in the clearing point for the disubstituted compounds (Table II).

b Effect of lateral substitution on the type of mesophase

The synthesized compounds exhibit only three types of mesophase: nematic, smectic A and smectic C. In each family smectic mesophases appear only with long alkyl or alkoxy chains.

TABLE II

Comparison of the decrease of the clearing point ΔT for disubstituted compounds of general formula



with regard to the sum of the decreases due to each substituent $\Delta T_1 + \Delta T_2$

R	X	Y	Z	ΔT°C	$(\Delta T_1 + \Delta T_2)$°C
C_8H_{17}	Br	H	CH_3	93	57 + 41 = 98
$C_8H_{17}O$	Br	H	CH_3	75.5	36 + 41 = 77
C_8H_{17}	CN	H	CH_3	97	40.5 + 41 = 81.5
$C_8H_{17}O$	CN	H	CH_3	64	19 + 41 = 60
$C_8H_{17}O$	Br	Cl	H	80	36 + 47.5 = 83.5
$C_8H_{17}O$	Br	CN	H	73	36 + 53 = 89

When the substituent is on the second aromatic ring, (Table I—compounds 26–31) there is only a nematic mesophase. The same results were obtained by J. P. Van Meter and B. H. Klanderman[1] with phenyl 4-benzoyloxy 2 or 3-chloro benzoates. The substitution on the middle of the molecule seems to be unfavourable to the smectic packing.

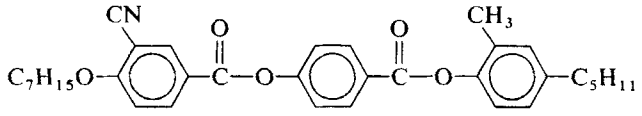
On the contrary a polar substituent on the first aromatic ring is favourable to the smectic arrangement as it can be seen in Table I (compounds 16–25, 36–38). The stabilization of the smectic mesophase, with regard to the equivalent unsubstituted compounds (Table I, compounds 1–3), can certaintly be attributed to very strong lateral interaction.

Another interesting point is the appearance of a smectic C phase for the bromo derivatives of phenyl 4-benzoyloxy benzoate (Table I, compounds 7–9), whereas the equivalent unsubstituted compounds (Table I, compounds 1–2) are only nematic and smectic A. These compounds do not possess the two oppositely directed, "outboard" dipoles associated with oxygen or nitrogen atoms which is the basis of the McMillan's model.[6] It is difficult to involve the dipole moment of Br for the occurrence of the S_C mesophase as the corresponding cyano derivatives (Table I—compounds 17–19) are only smectic A and do not possess a smectic C phase. In fact for these compounds, it seems that the size of the substituent is preponderant and that it is a steric effect on the smectic arrangement which promotes the smectic C phase.

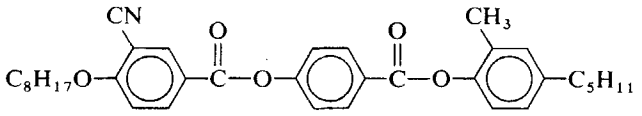
c Effect of lateral substitution on the melting point

One would expect that a lateral substituent will lower the crystal-to-mesophase transition temperature by creating a less efficient packing in the crystal

lattice. In fact, as it can be seen in Table I, it is difficult to find an absolute rule. Generally the bromo derivatives have lower melting point than the cyano derivatives. But we must remember the important part played by the crystalline structure as it is illustrated by the following example where K_1 is a crystalline transition:



K_1 73 K_2 101.5 S_A 116 N 116.5 I



K 72,5 S_A 122 I

4 CONCLUSION

We have studied the effect of lateral substituents, essentially bromo, cyano and methyl substituents on the mesomorphic properties of phenyl 4-benzoyloxybenzoates. The effect of a substituent is important on the clearing point and on the type and range of the mesophase. It seems that this can be explained essentially by the steric effect of the substituent and for a little part by electronic effects.

5 EXPERIMENTAL

The detailed procedure for preparing the compounds described in this article is given below:

3-Bromo-4-alkylbenzoic acids

These were prepared by bromination of the corresponding alkylbenzoic acids in acetic acid according to the method of A. M. Fleifel.[7] The purification was different. After the reaction the product in suspension was filtered, washed with water and the acid dissolved in ethanol. The solution was discoloured with vegetal carbon and product recrystallized from ethanol/water.

3-Bromo-4-alkoxybenzoic acids

These were prepared by bromination of the corresponding alkoxybenzoic acids according to the method described by Späth, Pikl.[8]

3-Bromo-4-hydroxybenzoic acids

This compound was prepared on the same way that 3-bromo 4-alkoxybenzoic acids.

3-Chloro-4-hydroxybenzoic acid

This product is commercial and was obtained from "Merck."

4*n*-Pentyl-2-methylphenol

This compound was prepared by Friedel-Crafts acylation of o-cresol followed by Wolff-Kishner reduction of the corresponding pentanophenone according to the method described by W. R. Young, I. Maller and D. C. Green.[2]

Substituted phenyl 4-hydroxybenzoates

These compounds were prepared by the acid catalyzed esterification of phenols following the procedure of Lowrance.[9] For unsubstituted compounds the time of reflux was 24 hours. For 4-n-pentylphenyl 3-bromo-4-hydroxybenzoate the procedure was as follows. To a suspension of 21.7 g (0.1 mole) of 3-bromo-4-hydroxybenzoic acid and 18 g (0.11 mole) of 4-n-pentylphenol in 500 ml of toluene were added 0.5 g of concentrated sulfuric acid and 0.3 g of boric acid. The reaction mixture was heated under reflux for 100 h under a Dean-Stark trap. The solvent was then removed under reduced pressure and the product was washed with ligroin. The resulting 4-*n*-pentylphenyl 3-bromo-4-hydroxybenzoate was purified by column chromatography on silica gel using benzene as eluent and was then recrystallized from benzene to give 19.7 g (54,5%) of pure product, m.p. 153°C.

Substituted phenyl 4-benzoyloxybenzoates

These compounds were prepared by reacting the alkyl or alkoxybenzoic acid chloride, prepared by the reaction of the acid and thionyl chloride, with the corresponding phenyl 4-hydroxy benzoate in dry pyridine at 20°C, The solution was stirred two days long, then poured into a mixture of ice and sulphuric acid. The solide was extracted with benzene, the extract washed and dried over magnesium sulphate. The solvent was evaporated and the product purified by column chromatography on silica gel using benzene/hexane as eluent. Each ester was then recrystallized from ethanol.

Cyano-substituted phenyl 4-benzoyloxybenzoates

These compounds were prepared by reacting the corresponding bromo-substituted products with CuCN in dimethylformamide at reflux. The time of reflux was different according to the type of bromo-substituted compound, varying from one hour to seven and a half hours. The solution was then poured into a solution of ethylenediamine in water. The product was extracted with benzene, washed with water and dried over magnesium sulphate. The solvent was evaporated and the product purified by column chromatography on silica gel using benzene/hexane as eluent. Each ester was then recrystallized from ethanol.

We are giving below two examples of this reaction.

Synthesis of 4-*n*-*pentylphenyl* 4-(3-*cyano*-4-*n*-*butoxybenzoyloxy*) *benzoate* A suspension of 2.7 g (0.005 mole) of 4-*n*-pentylphenyl 4-(3-bromo-4-*n*-butoxybenzoyloxy) benzoate and 0.55 g (0.006 mole) of cuprous cyanide in 10 ml of dimethylformamide was heated under reflux for 6 hours. The solution was then cooled and poured into a solution of 5 g of ethylenediamine in 60 ml of water. The solid was extracted with benzene (3 × 100 ml) and the extract washed with water and dried over magnesium sulphate. The solvent was evaporated and the product purified by column chromatography on silica gel using benzene/hexane as eluent and was then recrystallized from 50 cc of ethanol. 1.3 g (53.5%) of pure product was obtained.

Synthesis of 4-*n*-*pentylphenyl* 4-(3-*cyano*-4-*n*-*octyloxybenzoyloxy*) 3-*chloro-benzoate* Starting from 4-*n*-pentylphenyl 4-(3-bromo-4-*n*-octyloxybenzoyl-oxy) 3-chlorobenzoate the procedure was the same as previously described. The time of reflux in DMF was 90 min and the yield was 25%.

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