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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Jacobi, Andrea and Weissflog, Wolfgang(1997) 'Laterally 4-nitrobenzyloxycarbonyl substituted phenyl benzoates: The first two-ring mesogens with a lateral branch containing a phenyl ring', *Liquid Crystals*, 22: 2, 107 – 111

To link to this Article: DOI: 10.1080/026782997209469

URL: <http://dx.doi.org/10.1080/026782997209469>

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Laterally 4-nitrobenzyloxycarbonyl substituted phenyl benzoates: The first two-ring mesogens with a lateral branch containing a phenyl ring

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(Received 28 December 1995; in final form 18 August 1996; accepted 30 August 1996)†

The synthesis and properties of laterally 4-nitrobenzyloxycarbonyl substituted phenyl benzoates are described; these compounds represent the first two-ring mesogens having a phenyl ring in the lateral branch. The lengths of the terminal chains of the core carrying the branch have a great influence, as shown by the phase behaviour of two homologous series. Compounds having long alkyloxy groups exhibit enantiotropic smectic A phases. It should be emphasized that the mesophase thermal stability of these strongly branched derivatives can be higher than that of the laterally unsubstituted parent compound. Connecting two of the new mesogens by means of an aliphatic spacer results in a novel type of twin molecule.

1. Introduction

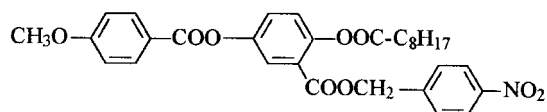
Terminally substituted two-ring compounds are the smallest molecules which are able to form the liquid crystalline state without additional association effects. The shape of two-ring mesogens corresponds to the classic rule first suggested by Vorländer [1]. Even small deviations from the rod-like geometry, for example as caused by an angled unit, by branched terminal chains or by lateral substituents, can result in a depression of transition temperatures or loss of mesophase stability [2, 3].

Starting from 4-*n*-octyloxyphenyl 4-*n*-octyloxybenzoate **1**, additional substituents in the 3-position of the phenolic as well as of the benzoic acid moiety cause a decrease in the clearing points. The larger the lateral group the lower the clearing temperature, as demonstrated by the few examples shown in table 1.

On the other hand, three-ring mesogens can be laterally substituted by long-chain groups [6–9], as well as by segments containing a phenyl ring, without loss of the mesophases. Suitable design of the molecules, especially the existence of electron-withdrawing substituents like cyano or nitro in the 4-position of the lateral aromatic ring linked by an odd-numbered spacer to the basic mesogenic moiety, can produce unexpectedly high clearing temperatures [10–13].

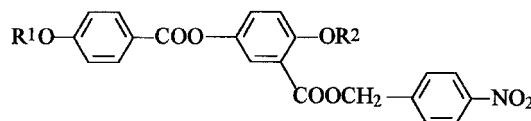
Having these facts in mind, the following question is

of interest: are two-ring molecules which are laterally substituted by a segment containing a phenyl ring able to form enantiotropic mesophases? Some years ago compound **5** was prepared by one of the authors [14]. A nematic phase could be detected only on strong supercooling to lower than 6°C. This unfavourable phase behaviour was the reason for the delay in additional activity in the investigation of derivatives having the constitution under discussion.



5 Cr 86 (N6) I

In this paper we would now like to present the synthesis and properties of new two-ring mesogens containing a 4-nitrobenzyloxycarbonyl segment according to formula **8**. The 4-nitrophenyl ring is attached to the 3-position of the phenolic unit by means of a three-membered spacer.



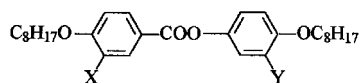
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2. Synthesis

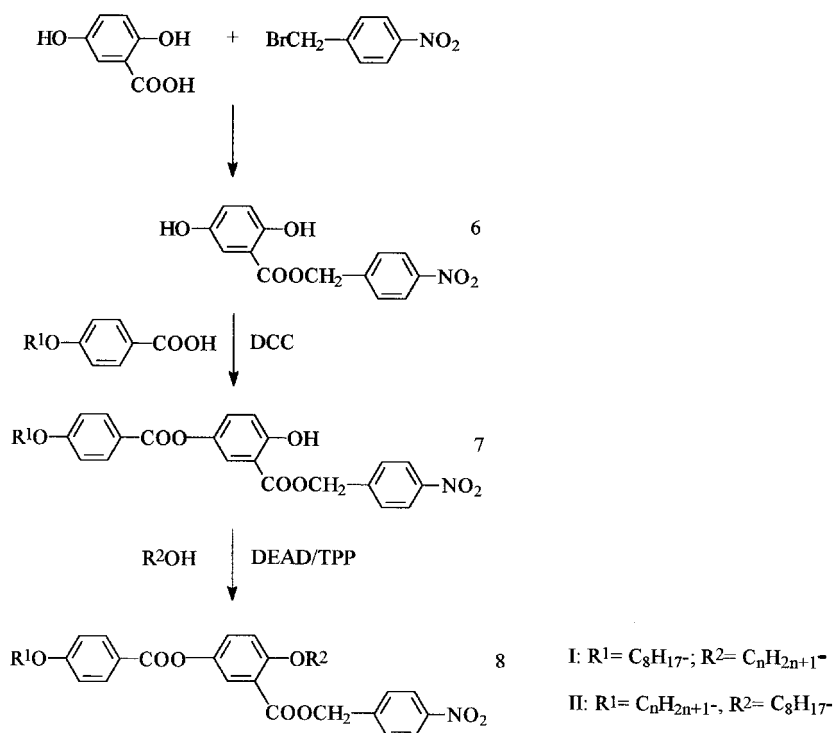
The reaction pathway to prepare the substances under discussion is given in the scheme.

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† Processing of this paper was severely delayed by loss of material in the post.

Table 1. Depression of the clearing temperature of 4-*n*-octyloxyphenyl 4-*n*-octyloxybenzoate by small lateral substituents.

Compound number	X	Y	Cr	S _C	S _A	N	I			
1 [4]	H	H	•	61	•	72	—	•	92.5	•
2 [5]	H	F	•	56	(•	55)	•	78	—	•
3	Cl	H	•	68	(•	55	—	•	65)	•
4	H	COOCH ₃	•	35	—	—	—	(•	30)	•



Scheme.

Esterification of gentisic acid with 4-nitrobenzyl bromide yielded 4-nitrobenzyl 2,5-dihydroxybenzoate **6**. Regioselective acylation of the hydroxyl group in the 5-position was achieved by reaction of the substituted benzoic acid in the presence of DCC according to the method of Stützer [15]. Etherification of the intermediates **7** with the corresponding alkanols using the Mitsunobu reaction [16] produced the desired compounds **8**.

3. Results

Surprisingly, the two-ring mesogens **8** with a 4-nitrobenzyloxycarbonyl segment in the lateral position can exhibit enantiotropic mesophases. However, the

length of the terminal alkyloxy chains is of an unusually great importance. Altogether about twelve or more methylene units seem to be necessary to observe liquid crystalline properties. To study the different influence of chain length at both terminal positions, two homologous series I and II, isomeric with one another, were prepared. In the first series, I (**8a–8i**), the chain near the lateral segment is varied, while in the second series, II (**8j–8s**), the alkyloxy group of the benzoic acid part is made longer. The transition points are listed in table 2. The trends in the smectic A–isotropic transition points of series I and II, together with the clearing temperatures of the laterally unsubstituted 4-*n*-octyloxyphenyl 4-*n*-alkyloxybenzoates (series III) are displayed in the figure.

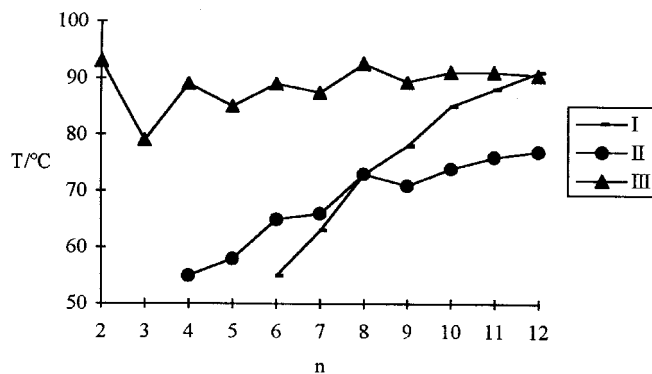
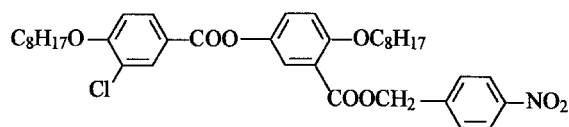


Figure. Comparison of the trends in the smectic A-isotropic transition points of series I (**8a-i**) and series II (**8j-s**) with the trends in the clearing temperatures of the laterally unsubstituted 4-*n*-octyloxyphenyl 4-*n*-alkyloxybenzoates III [**3b**] with increasing length of the alkyloxy group of the benzoate moiety.

Lengthening of the aliphatic chain located in the vicinity of the lateral segment causes a clear increase in the mesophase thermal stability, beginning at 55°C for the hexyloxy derivative **8c** up to 91°C for the dodecyloxy homologue **8i**. The slope of the clearing curve of the series II is lower and the transition points show a small alternation. The crossing of both curves gives indications of the different influence of the two terminal chains on the packing of these molecules in the anisotropic state.

The enantiotropic phase behaviour and the relatively high clearing points of the longer chain derivatives **8f-8i** are unexpected. Furthermore, the dodecyloxy derivative **8i** (S_A 91 I) exhibits a higher mesophase stability compared with the laterally unsubstituted parent compound, 4-*n*-dodecyloxyphenyl 4-*n*-octyloxybenzoate (N 88.5 I) [17]. These relationships between the molecular structure and the mesophase behaviour demonstrate that the liquid crystalline state of the new compounds cannot be explained in terms of the length-to-breadth ratio of the molecules. But, the shape and flexibility of the molecules allow the formation of a high density packing like a 'molecular puzzle' which exhibits an anisotropic direction of the molecular long axes.

To investigate the influence of the constitution of the new mesogens on the phase behaviour, different variations in the chemical structure were made. For example, we synthesized a compound with a second lateral substituent or branch. This further substitution of compound **8e** by chlorine, yielding **9**, is accompanied by a decrease of the smectic A-isotropic phase transition by 28 K.



9 Cr 80 (S_A 45) I

However, from another point of view, substitution of the 4-*n*-octyloxyphenyl 3-chloro-4-*n*-octyloxybenzoate **3** (S_C 55 N 65 I) by the bulky 4-nitrobenzoyloxy carbonyl segment, likewise giving **9**, causes a decrease in mesophase thermal stability of 20 K only. Therefore, multiple substitution of two-ring mesogens is possible without loss of the liquid crystalline properties and this should be investigated in future work.

Introduction of a second strong polar group by using 4-cyanobenzoic acid produces substance **10**, unfortunately showing a high melting point and a low tendency for supercooling.

Table 2. Phase transition behaviour of the 4-nitrobenzyl 2-*n*-alkyloxy-5-(4-*n*-octyloxybenzoyloxy)benzoates **8a-8i** (table 2 (a)) and of the isomeric 4-nitrobenzyl 2-*n*-octyloxy-5-(4-*n*-alkyloxybenzoyloxy)benzoates **8j-8s** (table 2 (b)). In each table, *n* represents the number of carbons in the group R^2 .

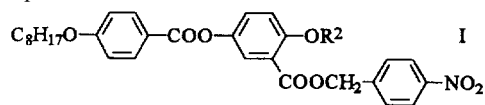


Table 2 (a)

Compound number	<i>n</i>	Cr	S_A	I		
8a	4	•	81	—	•	
8b	5	•	94	—	•	
8c	6	•	74	(• 55)	•	
8d	7	•	86	(• 63)	•	
8e	8	•	79	(• 73)	•	
8f	9	•	71	•	78	•
8g	10	•	68	•	85	•
8h	11	•	66	•	88	•
8i	12	•	65	•	91	•

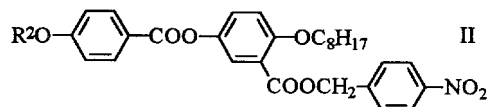
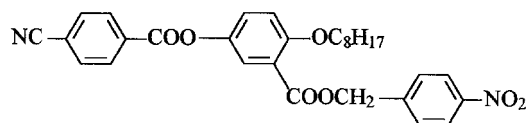


Table 2 (b)

Compound number	<i>n</i>	Cr	S_A	I		
8j	2	•	84	—	•	
8k	3	•	82	—	•	
8l	4	•	87	(• 55)	•	
8m	5	•	87	(• 58)	•	
8n	6	•	78	(• 65)	•	
8o	7	•	76	(• 66)	•	
8e	8	•	79	(• 73)	•	
8p	9	•	76	(• 71)	•	
8q	10	•	72	•	74	•
8r	11	•	80	(• 76)	•	
8s	12	•	66	•	77	•



10 Cr 130 I

Connection of two of the new laterally aryl branched mesogens by means of an aliphatic spacer leads to twin molecules. For example, reaction of the intermediate **8g** with 1,12-dodecandiol yielded substance **11**.

Comparing the clearing temperature of the twin **11** (S_A 75 I) with its half part, substance **8c** (S_A 55 I), we observe an increase in mesophase thermal stability of 20 K caused by the twinning link. Compounds like **11** represent a novel type of twin system and the influence of the length, constitution and position of the spacer on the mesophase behaviour and other properties is at present being investigated.

The substances under discussion are the first two-ring mesogens having a segment containing a phenyl ring in a lateral position. Because of their very nonconventional molecular shape, the compounds represent liquid crystals of a new architecture [18]. To study the structure of the smectic phases in detail, X-ray investigations must be done. Unfortunately, none of the new compounds shows a nematic phase above the smectic phase, as required for preparation of oriented samples. Therefore, our efforts are now directed at preparing such derivatives exhibiting a nematic-smectic polymorphism. Furthermore, nematic phases would allow us to study the dielectric relaxation behaviour of the new mesogens.

4. Experimental

The purity of the new compounds was checked by elemental analysis and HPLC. ^1H NMR spectra were recorded using a WP 200 (Bruker) spectrometer, CDCl_3 serving as solvent and tetramethylsilane as internal standard (δ in ppm). Calorimetric measurements were carried out using a Perkin Elmer DSC 7. The transition temperatures given in the tables and the phase behaviour were determined using a polarizing microscope (Nikon Optiphot-2) in combination with a hot stage, THM 600/S and a temperature control unit, TP 92.

4.1. 4-Nitrobenzyl 2,5-dihydroxybenzoate (**6**)

A solution of 50 g (0.23 mol) of 4-nitrobenzyl bromide in 200 ml of dry acetone is added slowly with stirring to

35.6 g (0.23 mol) of 2,5-dihydroxybenzoic acid, 23.4 g (0.23 mol) of triethylamine and a catalytic amount of sodium iodide in 300 ml of dry acetone. After heating under reflux for 4 h, the mixture is poured into 800 ml of water; the precipitated product is then filtered off and recrystallized from ethanol. Yield 55 g (83%), m.p. 178°C. ^1H NMR (200 MHz, CDCl_3): δ =4.45 (s, 1H, $-\text{OH}$), 5.45 (s, 2H, $\text{COO}-\text{CH}_2-\text{Ar}$), 6.87–6.91 (d, 1H, Ar), 7.00–7.01 and 7.04–7.06 (d, 1H, Ar), 7.30–7.32 (d, 1H, Ar), 7.55–7.61 (d, 2H, Ar) 8.23–8.28 (d, 2H, Ar), 10.13 (s, 1H, H_2O).

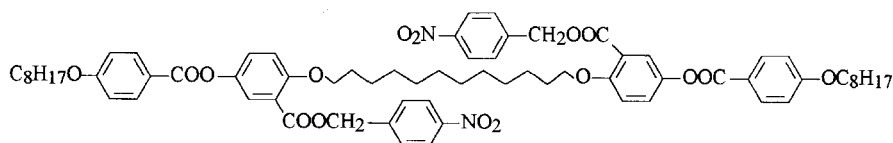
4.2. 4-Nitrobenzyl 2-hydroxy-5-(4-n-alkyloxybenzoyloxy)benzoates (**7a–k**)

A mixture of 5 g (0.017 mol) of **6**, 0.017 mol of 4-n-alkyloxybenzoic acid, 3.92 g (0.019 mol) of N,N' -dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4- N,N -dimethylaminopyridine (DMAP) in 100 ml of dry methylene dichloride is stirred for 48 h. After filtration of the precipitated urea through a short column of silica gel, the solution is washed with water, aqueous sodium hydrogen carbonate (5% w/v) and again with water. Then the organic phase is dried over sodium sulphate and the solvent evaporated. Recrystallization from ethanol yields the pure product. Yields are shown in table 3.

Representative of all the substances **7a–k**, the ^1H NMR data are given for **7g**. ^1H NMR (200 MHz, CDCl_3): δ =0.83–0.87 (m, 3H, CH_3), 1.27–1.45 (m, 10H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{O}$), 1.73–1.83 (t, 2H, $\text{CH}_2-\text{CH}_2-\text{O}$), 3.99–4.05 (t, 2H, $-(\text{CH}_2)_6-\text{CH}_2-\text{O}$), 5.45 (s, 2H, $\text{COO}-\text{CH}_2-\text{Ar}$), 6.92–6.97 (m, 2H, Ar), 7.01–7.06 (d, 1H,

Table 3. Synthesis data for compounds **7a–k**

Compound number	R^1	m.p./°C	yield/%
7a	$\text{C}_2\text{H}_5\text{O}$	121	60
7b	$\text{C}_3\text{H}_7\text{O}$	121	64
7c	$\text{C}_4\text{H}_9\text{O}$	99	64
7d	$\text{C}_5\text{H}_{11}\text{O}$	88	68
7e	$\text{C}_6\text{H}_{13}\text{O}$	77	63
7f	$\text{C}_7\text{H}_{15}\text{O}$	66	62
7g	$\text{C}_8\text{H}_{17}\text{O}$	80	62
7h	$\text{C}_9\text{H}_{19}\text{O}$	72	69
7i	$\text{C}_{10}\text{H}_{21}\text{O}$	60	35
7j	$\text{C}_{11}\text{H}_{23}\text{O}$	68	52
7k	$\text{C}_{12}\text{H}_{25}\text{O}$	68	67

11 Cr 93 (S_A 75) I

Ar), 7.29–7.30 and 7.33–7.35 (d, 1H, Ar), 7.56–7.60 (d, 2H, Ar), 7.67–7.69 (d, 1H, Ar), 8.07–8.13 (d, 2H, Ar), 8.22–8.26 (d, 2H, Ar), 10.48 (s, 1H, H_2O –).

4.3. *4-Nitrobenzyl 2-hydroxy-5-(3-chloro-4-n-octyloxybenzoyloxy)benzoate 7n* and *4-nitrobenzyl 2-hydroxy-5-(4-cyanobenzoyloxy)benzoate 7o*

Preparation was effected as described for **7a–k** by reaction of **6** with 3-chloro-4-octyloxybenzoic acid and 4-cyanobenzoic acid, respectively.

7n: Yield 67%, m.p. 64°C. Elemental analysis: $\text{C}_{29}\text{H}_{30}\text{ClNO}_8$ (556.01 g mol^{-1}) calc. C 62.70, H 5.40, N 2.52, Cl 6.30; found C 62.79, H 5.48, N 2.47, Cl 6.41 per cent.

7o: Yield 73%, m.p. 162°C. Elemental analysis: $\text{C}_{22}\text{H}_{41}\text{N}_2\text{O}_7$ (418.36 g mol^{-1}) calc. C 63.15, H 3.37, N 6.70; found C 63.02, H 3.42, N 6.45 per cent.

4.4. *4-Nitrobenzyl 2-n-alkyloxy-5-(4-n-alkyloxybenzoyloxy)benzoates (8)*

To a mixture of 4 mmol of **7**, 6 mmol of *n*-alkanol and 1.95 g (7.5 mmol) of triphenylphosphine in 60 ml of dry diethylether/acetone (1:1), 1.1 ml (0.75 mol) of diethyl azoxydicarboxylate are added dropwise at 0°C under nitrogen. After stirring at room temperature over-night, the reaction mixture is washed with water, dried over sodium sulphate and the solvent evaporated. The crude products are purified by more than one recrystallization from ethanol. Yield 53–85% (the yields rise with increasing chain length of the alkanol used).

Representative of all the mesogens **8**, the ^1H NMR data are given for **8e**. ^1H NMR (200 MHz, CDCl_3): δ = 0.82–0.87 (t, 6H, 2x CH_3), 1.23–1.29 (m, 20H, 2x-(CH_2)₅-), 1.76–1.82 (t, 4H, 2x CH_2 - CH_2 - CH_2 -O-), 3.98–4.07 (t, 4H, 2x -O- CH_2 - CH_2 -), 5.41 (s, 2H, COO- CH_2 -Ar), 6.92–8.24 (m, 11H, Ar).

4.5. *4-Nitrobenzyl 2-n-octyloxy-5-(3-chloro-4-n-octyloxybenzoyloxy)benzoate 9* and *4-nitrobenzyl 2-octyloxy-5-(4-cyanobenzoyloxy)benzoate 10*

Starting from the intermediates **7n** or **7o**, respectively, the synthesis of **9** and **10** is carried out as described above for the compounds **8**. Yields: **9** 45%, **10** 60%.

4.6. *Twin mesogen 11*

To a mixture of 2.15 g (4 mmol) of **7g**, 0.6 g (3 mmol) of 1,12-dodecandiol and 1.95 g (7.5 mmol) of triphenylphosphine in 60 ml of dry diethylether/acetone (1:1), 1.1 ml (7.5 mmol) of diethyl azoxydicarboxylate are added dropwise at 0°C under nitrogen. After stirring at room temperature over-night, the reaction mixture is washed with water, dried over sodium sulphate and the solvent evaporated. The crude product is purified by column chromatography on silica gel using chloroform as eluent, followed by recrystallization from ethanol. Yield 0.23 g (10.3%).

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