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Helmut Hartung[a]; Frank Hoffmann[a]; Cornelia Stützer; Wolfgang Weissflog
[a] Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Halle, Saale, Germany

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Unsymmetrically disubstituted mesogens with a phenyl ring containing lateral branch. Crystal and molecular structure of smectogenic 4-nitrobenzyl 2-(3-chloro-4-*n*-octyloxybenzoyloxy)-5-(4-*n*-octyloxybenzoyloxy)benzoate

by HELMUT HARTUNG* and FRANK HOFFMANN
Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie,
Mühlpforte 1, D-06108 Halle (Saale), Germany

CORNELIA STÜTZER and WOLFGANG WEISSFLOG
Max-Planck-Gesellschaft, Arbeitsgruppe Flüssigkristalline Systeme, Mühlpforte 1,
D-06108 Halle (Saale), Germany

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The synthesis of unsymmetrically disubstituted mesogens bearing a cyclic unit within the bulky lateral branch is described. The three-ring basic mesogenic unit of the laterally 4-nitrobenzyloxycarbonyl substituted molecules has been additionally provided with chlorine atoms in one or two positions, thus influencing the stability of the smectic A phases.

The crystal and molecular structure of the smectogenic 4-nitrobenzyl 2-(3-chloro-4-*n*-octyloxybenzoyloxy)-5-(4-*n*-octyloxybenzoyloxy)benzoate (NCOOB) has been determined by X-ray analysis. NCOOB crystallizes in the triclinic space group $P\bar{1}$ with 4 molecules per unit cell and the following lattice parameters: $a = 13{\cdot}201(2)$ Å, $b = 16{\cdot}473(3)$ Å, $c = 19{\cdot}746(3)$ Å, $\alpha = 96{\cdot}11(2)^\circ$, $\beta = 95{\cdot}34(2)^\circ$, $\gamma = 99{\cdot}92(1)^\circ$, $V = 4178{\cdot}4(1)$ Å^3.

The phenylene bis(*n*-octyloxybenzoate) mesogenic basic fragment of the NCOOB molecule has a non-planar, but optimally stretched shape, with a perfect all-*trans*-conformation of the alkyloxy chains and the lateral benzene ring-containing branch is oriented parallel to it. The molecules are arranged in lamellar sheets which are characterized by a parallel molecular alignment with an interlocking of neighbouring molecules by their bulky branches and intercalation of the alkyl chains.

1. Introduction

Contrary to formerly prevailing opinion, laterally substituted three-ring compounds can exhibit liquid crystalline properties at relatively high temperatures [1–4]. Mesogens of this type contain one cyclic unit within the lateral segment, e.g. a phenyl or heterocyclic ring, which can itself be substituted. It is advantageous to connect the cyclic unit to the basic molecule by means of an odd-numbered flexible spacer. The molecular shape of such laterally aryl-substituted mesogens strongly deviates from the classical rod-like shape but also from a disc-like shape [5]. X-ray investigations have shown that the smectic A phases of 4-nitrobenzyl 2,5-bis(4-*n*-alkyloxybenzoyloxy)benzoates are characterized by an antiparallel packing of the molecules, a partial intercalation of the terminal alkyl chains, and an unusual behaviour in mixtures with rod-like molecules [6–8]. Therefore, the endeavour of such molecules to achieve a high packing density could be one decisive reason for the anisotropic characteristics of the corresponding liquid crystalline, as well as the solid crystalline state. For this reason, investigations of the relationships between the physical behaviour and the chemical constitution, as well as of the molecular and crystal structure, are of great interest in order to obtain new information which adds to a better understanding of the mesophase behaviour of laterally aryl-substituted mesogens.

In this paper, we report the variation of the chemical consitution of 4-nitrobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate **3a** [9] by chloro substituents attached to the three-ring basic molecule. A new reaction pathway to the unsymmetrically substituted compounds has been used. One of the new substances, **3c**, could be recrystallized to give single crystals suitable for X-ray analysis.

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* Author for correspondence.

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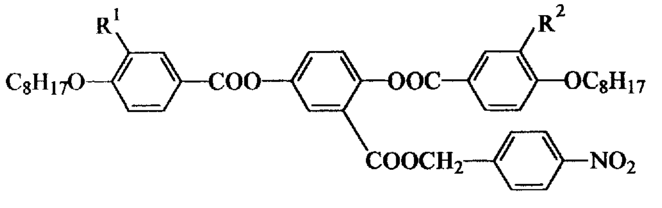
Table 1. Phase transition behaviour of laterally 4-nitrobenzyloxycarbonyl substituted phenylene bisbenzoates **3a–d** (transition temperatures in °C).



3a-d

No.	R^1	R^2	Cr		S_A		I
3a[9]	H	H	●	96	●	163	●
3b	Cl	H	●	90	●	155	●
3c	H	Cl	●	83	●	150	●
3d	Cl	Cl	●	120	●	139	●

2. Results and discussion

2.1. *Synthesis and liquid crystalline properties*

The chemical constitution and the melting behaviour of the laterally aryl-substituted mesogens **3a–d** are given in table 1.

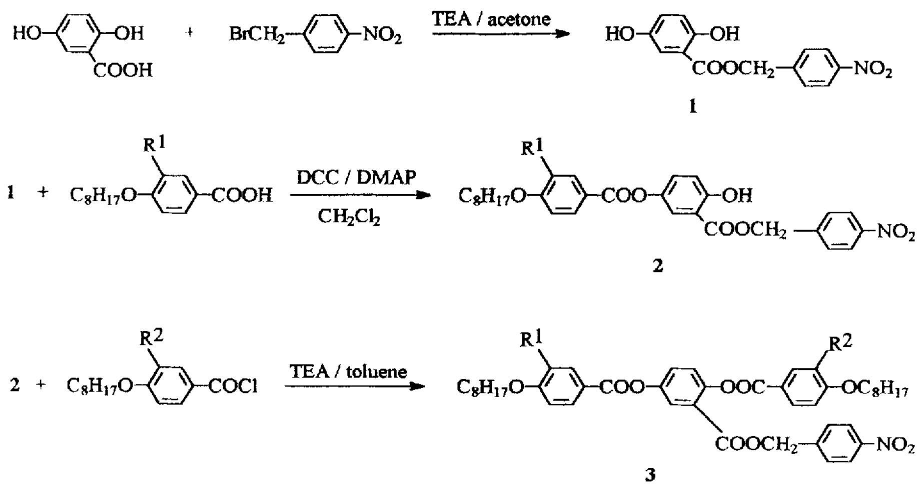
In previous papers, the synthesis preferentially of symmetrically substituted 1,4-phenylene bisbenzoates bearing bulky lateral groups has been described, and regioselective acylation of 2,5-dihydroxybenzoate esters was reported to give liquid crystalline gentisic acid derivatives [10, 11]. For the synthesis of compounds **3b** and **3c** a new reaction pathway was used; it is given in scheme 1.

4-Nitrobenzyl 2,5-dihydroxybenzoate **1** is obtained by reaction of gentisic acid with 4-nitrobenzyl bromide in the presence of triethylamine (TEA) in acetone [12, 13]. The different reactivity of the two hydroxyl groups of the hydroquinone derivative **1** enables regioselective esterification step by step under suitable reaction conditions. Esterification of the hydroxyl group in the 5-position with 4-*n*-octyloxybenzoic or 3-chloro-4-*n*-octyloxybenzoic acid, respectively, is performed by means of *N,N'*-dicyclohexylcarbodiimide (DCC)/4-dimethylaminopyridine (DMAP) in dichloromethane to give the intermediates **2** (with R^1 = H or Cl). Acylation of the hydroxyl group in the 2-position of **2a,b** by the corresponding substituted benzoyl chlorides (R^2 = H or Cl) in toluene with triethylamine to remove the hydrogen chloride yields the substances **3b–c**.

All substances prepared exhibit enantiotropic smectic A phases. Compared with the laterally unsubstituted rod-like, basic mesogen *p*-phenylene bis(4-*n*-octyloxybenzoate) (Cr 123°C S_C 129°C N 195°C I) [14] the clearing temperatures of the derivatives **3a–d** are unexpectedly high. Substitution(s) of hydrogen in the compound **3a** by chlorine causes a decrease in the smectic–isotropic transition temperature. Surprisingly, the dependence of the clearing temperature on the site of the chloro substituent (R^1 or R^2) within the bulky branched, wedge-shaped molecule is rather low. To make a comparison, branching of the octyloxy chain in the *ortho*-position to R^2 giving the 1-methylheptyloxy isomer of **3a** produces a depression of the mesophase stability by 50°C [15].

2.2. *Molecular structure*

Apart from some small differences in their conformations, the two crystallographically independent molecules α and β in the crystal structure of NCOOB† have practically the same geometry. Therefore, only molecule



Scheme 1. Reaction pathway to unsymmetrically 2,5-disubstituted 4-nitrobenzyl benzoates **3b** and **3c**.

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† NCOOB is identical with **3c**, but this code name, derived from the chemical constitution of **3c** will be preferred in the structural discussion.

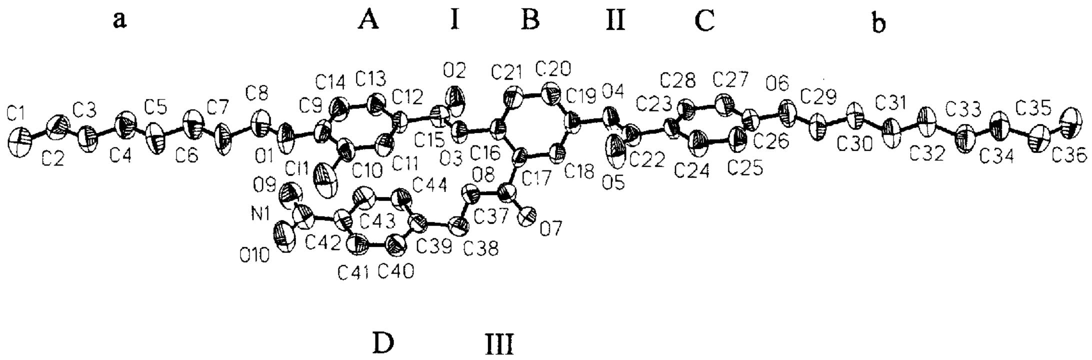

Figure 1. Molecular structure of NCOOB with atom numbering. The displacement ellipsoids are drawn at the 50 per cent probability level; H atoms are omitted.

α is illustrated by a thermal motion plot [16] in figure 1. Essential parameters of the molecular geometry are summarized in tables 2 and 3, whereas it can be seen there is full agreement within the 3σ criterion concerning bond lengths and angles and there are only a few significant differences in torsion angles between molecules α and β. Numerical values used in the following discussion are those of molecule α; the corresponding values for β are given in square brackets.

The NCOOB molecules as a whole are not planar, but consist of structural fragments with more or less perfect planarity. As expected and known for other related compounds [17, 18], the phenylene bis(benzoate) three-ring skeleton has an optimally extended shape. Both terminal octyloxy chains are in the all-*trans*-conformation and only slightly inclined to the benzene rings to which they are bonded. The corresponding dihedral angles amount to *A*/*a* 3·0° [4·1°] and *C*/*b* 4·1° [3·9°] (for denotation of the structural fragments as benzene rings, carboxyl groups and alkyloxy chains see figure 1 and table 2). All four benzene rings are planar within 0·008 Å (= $1{\cdot}4\sigma$) and the C–CO·O fragments (= carboxyl groups including the carbon atom of the C-bonded benzene ring) also show no significant deviation from planarity. Benzene rings A and C are approximately coplanar, but perpendicular to ring B; the corresponding dihedral angles are A/C 8·5 [8·9], A/B 76·4 [82·0] and B/C 84·4° [89·7°]. The orientations of carboxyl groups I and II with respect to the O- and C-bonded adjacent benzene rings are described by the dihedral angles A/I 8·4 [6·1], B/I 84·7 [87·6], C/II 0·8 [3·3], and B/II 84·9° [86·5°]. This conformation of the phenylene bis(benzoate) mesogenic core can be described in an equivalent manner by the appropriate torsion angles given in table 3. Another characteristic feature of the molecular structure of NCOOB is the orientation of the bulky lateral substituent. It is largely parallel to the long axis of the three-ring basic moiety. The $-CH_2-O-C(O)-$ spacer is approximately parallel to ring B, but perpendicular to ring D; the corresponding dihedral angles are 4·9° [6·1°] and 73·0° [81·4°], respectively. Benzene ring D, as a component of the lateral branch, is almost parallel (4·7° [3·4°]) to the next neighbouring ring A of the mesogenic core. There is also a more (molecule α) or less (molecule β) marked coplanarity of ring D with the terminal nitro group (dihedral angle: 1·0° [6·4]).

The molecular length defined as the maximum distance between the centres of the terminal hydrogen atoms at C1 and C36, plus twice the van der Waals radius of hydrogen, given as 1·20 Å by Bondi [19], amounts to 41·6 Å [40·9 Å].

NCOOB is closely related to the mesogenic compound 4-nitrobenzyl 2,5-bis(4-ethoxybenzoyloxy)benzoate (NEBB), the crystal structure of which has been recently investigated by us [18]. The only, but striking constitutional differences between these two mesogens are the lengths of the terminal alkyl chains (octyl or ethyl) and (less important) the substituent at C10 in benzene ring A (chlorine or hydrogen). This variation results in significant differences both in the molecular structure and the crystal packing. In NEBB, a rather surprising mutual orientation of the two carboxyl groups attached at the 1,4-positions of benzene ring B was observed: their planes are, as expected, nearly perpendicular to the ring plane, but they are oriented towards the same side of it, and not towards opposite sides as is normally the case. This unusual conformational behaviour (illustrated in figure 2 (*a*) and (*b*)) can be described by a 'transannular torsion angle' O2–C15...C22–O5 of 12·5°, whereas in NCOOB the normal '*trans*'-conformation is proved by a 'torsion angle' of − 179·3° [− 178·1°]. All other molecular geometric parameters in NCOOB and NEBB are very similar, from which it can be concluded that the laterally bonded chlorine does not have a noticeable influence upon the molecular structure.

All the observed bond lengths and angles of NCOOB are normal within experimental error and hence, do not warrant further comment.

Table 2. Selected bond lengths and angles (esd's in parentheses).

	Distance/Å			Angle/°	
Atoms	Molecule α	Molecule β	Atoms	Molecule α	Molecule β
C10–C11	1·732(6)	1·712(6)			
Carboxyl group I					
C15–O2	1·199(6)	1·180(6)	C12–C15–O2	127·5(6)	126·5(6)
C15–O3	1·376(7)	1·370(6)	C12–C15–O3	112·2(5)	111·3(5)
C15–C12	1·460(7)	1·479(7)	O2–C15–O3	120·3(5)	122·2(5)
O3–C16	1·408(6)	1·399(6)	C15–O3–C16	117·4(4)	117·3(4)
Carboxyl group II					
C22–O5	1·194(6)	1·185(6)	C23–C22–O5	127·2(6)	126·4(6)
C22–O4	1·368(6)	1·345(7)	C23–C22–O4	112·0(6)	113·0(5)
C22–C23	1·454(7)	1·453(7)	O4–C22–O5	120·7(5)	120·6(5)
O4–C19	1·408(6)	1·406(6)	C22–O4–C19	117·1(4)	117·2(4)
Carboxyl group III					
C37–O7	1·195(6)	1·201(7)	C17–C37–O7	122·7(6)	123·0(6)
C37–O8	1·337(6)	1·337(6)	C17–C37–O8	112·1(6)	112·5(6)
C37–C17	1·517(8)	1·504(8)	O7–C37–O8	125·1(6)	124·5(6)
O8–C38	1·463(6)	1·456(6)	C37–O8–C38	113·1(5)	113·8(5)
C38–C39	1·505(7)	1·490(7)	O8–C38–C39	106·0(5)	105·8(5)
Nitro group					
N1–O9	1·228(6)	1·205(6)	O9–N1–O10	121·8(6)	120·2(6)
N1–O10	1·212(6)	1·188(7)	O9–N1–C42	119·7(6)	121·4(6)
N1–C42	1·456(7)	1·449(7)	O10–N1–C42	118·5(6)	118·4(7)
Mean values for benzene rings					
Ring A (C9...C14)					
C–C	1·379(15)	1·378(11)	C–C–C	120·0(1·3)	120·0(1·1)
Ring B (C16...C21)					
C–C	1·378(12)	1·379(12)	C–C–C	120·0(1·8)	120·0(1·4)
Ring C (C23...C28)					
C–C	1·378(15)	1·382(7)	C–C–C	120·0(1·9)	120·0(1·8)
Ring D (C39...C44)					
C–C	1·375(6)	1·368(16)	C–C–C	120·0(1·9)	120·0(1·3)
Mean values for alkyl chains					
Chain a (C1...C8)					
C–C	1·511(22)	1·512(19)	C–C–C	113·4(1·0)	113·8(8)
Chain b (C29...C36)					
C–C	1·510(21)	1·511(17)	C–C–C	113·6(1·8)	113·6(1·5)

2.3. *Molecular packing*

The complete content of a unit cell consisting of four molecules is illustrated in figure 3. The two symmetrically independent molecules α and β on the left in the figure have a nearly perfect parallel alignment; the angle between the molecular long axes amounts to only 3·0(2)°. By translation in the x and y directions, four types of sheets are built up by molecules α and β in their initial and inverted orientation, respectively. The resulting stacking sequence of the sheets in the z direction is $\alpha\beta\beta'\alpha'\alpha'\ldots$ and can be imagined by looking at figure 3. Sheets α and β are, as said before, not related by symmetry, but have the same packing mode which is illustrated in figure 4. The gap between two molecules, following one after the other in the direction of their long axes and so being members of a molecular row, is filled by the bulky lateral branch of a molecule belonging to the neighbouring row. In this way, the rows are interlocked and the principle of high economy of space is fulfilled. This fact can be clearly realized by the space-filling plot of a lamellar sheet of α molecules shown in figure 5. Another striking feature of the crystal structure is the strong intercalation of the molecules within the sheets by their alkyl chains. This can be seen in figure 3, which also demonstrates that two different regions can

Table 3. Selected torsion angles.

	Torsion angle/°	
Atoms	Molecule α	Molecule β
C11–C12–C15–O2	171·3(7)	175·5(7)
C11–C12–C15–O3	− 7·2(6)	− 4·8(6)
C12–C15–O3–C16	177·9(6)	179·1(6)
O2–C15–O3–C16	− 0·8(7)	− 1·2(7)
C15–O3–C16–C17	− 98·2(6)	− 94·7(6)
C28–C23–C22–O5	− 178·2(7)	176·1(7)
C28–C23–C22–O4	− 0·6(6)	− 3·7(6)
C23–C22–O4–C19	− 179·0(6)	− 179·7(6)
O5–C22–O4–C19	− 11·2(7)	0·4(7)
C22–O4–C19–C18	− 85·8(6)	− 88·2(6)
C16–C17–C37–O7	− 174·0(6)	− 173·6(6)
C16–C17–C37–O8	4·6(5)	5·8(5)
C17–C37–O8–C38	176·7(5)	− 179·9(4)
O7–C37–O8–C38	− 4·8(6)	− 0·5(6)
C37–O8–C38–C39	179·0(5)	179·6(5)
C41–C42–N1–O9	− 179·6(7)	173·3(7)
C41–C42–N1–O10	0·4(7)	− 6·4(8)

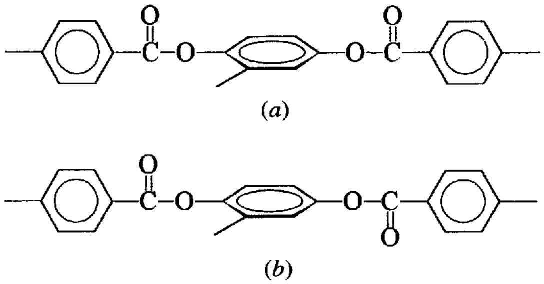

Figure 2. Schematic representation of the conformational behaviour of the carboxylic groups within the three-ring fragment of (*a*) NEBB [18] and (*b*) NCOOB.

be clearly discerned in the crystal: one extends from about y/b = 0·2 to 0·8 and comprises the benzene rings and polar components (carboxyl groups and nitro subsituents), whereas the other one is located around $y/b = 0$ and contains the non-polar hydrocarbon chains.

The stacking of the sheets results in an overall molecular arrangement which can be interpreted as a layered structure (similar to the model of smectic liquid crystalline phases) with strongly tilted molecules and an intercalation of the layers by the alkyl chains.

As a consequence of the parallel orientation of the molecules, the dipole moments of one kind (e.g. of the C–Cl or CO bonds) are not compensated within each sheet, but the inversion symmetry of the crystal structure avoids macroscopic polarization and ferroelectric properties of the substance.

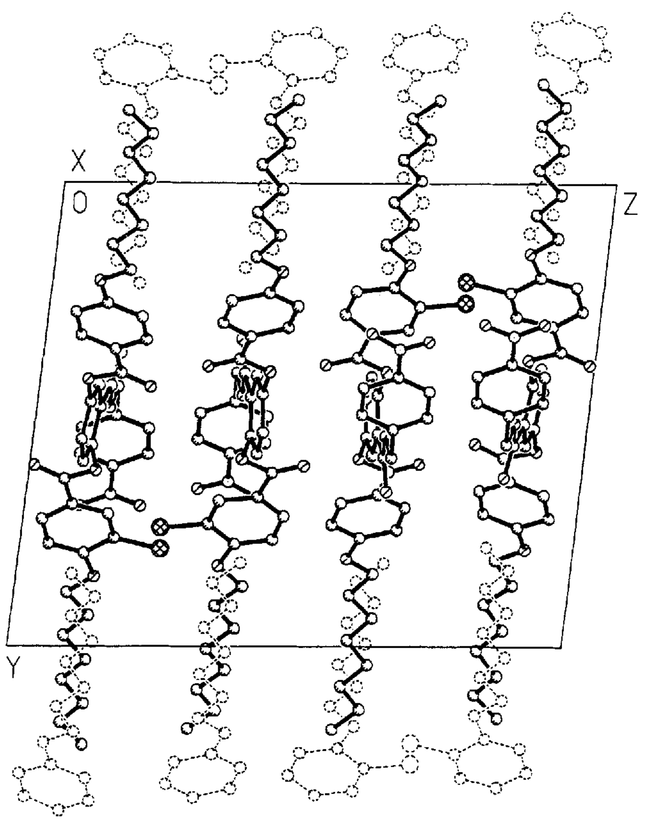

Figure 3. Crystal packing of NCOOB viewed along the *a*-axis.

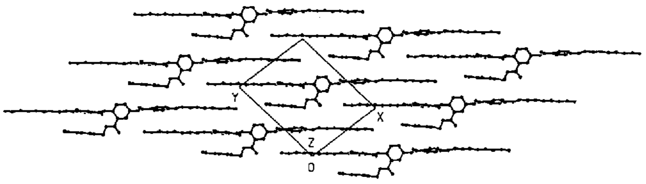

Figure 4. Lamellar sheet consisting of α molecules within the crystal structure of NCOOB.

It should be noted that for the above-mentioned homologous compound NEBB, not only another conformation, but also a quite different molecular packing from that of NCOOB has been found [18]. It is also characterized by the formation of sheets and layers. But both the building up of the sheets and their stacking into a layered structure follow other principles and no intercalation of the molecules by their short ethyl groups is observed.

Recently, we reported on the crystal structure determination of 2-*n*-nonyl-1,4-phenylene bis(*n*-octyloxybenzoate) (NPOB) as another laterally branched mesogen [17]. Considerating their consitution, NCOOB and NPOB are only differentiated from each other by the lateral branch and the substituent at C10. But great differences between their molecular structures, as well as their crystal packing were observed. The nonyl chain in NPOB is in the all-*trans*-conformation and strongly inclined at 53·8° to the three-ring core. Both fully staggered octyl chains are attached through an oxygen atom to the benzene rings by a *gauche*-conformation at the C7–C8 and C29–C30 bonds,

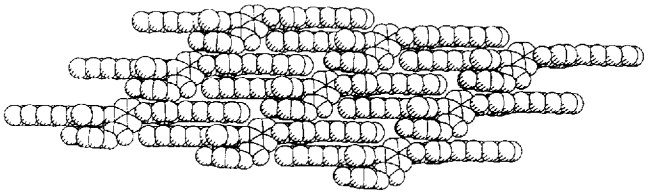

Figure 5. Space filling packing model of α molecules of NCOOB forming a lamellar sheet.

respectively, thus enabling their approximatley parallel (C1...C8) and antiparallel orientation (C29...C36) with respect to the nonyl chain. The molecules are arranged one after another in rows, and each row is interlocked through its three alkyl chains with two neighbouring rows in a double comb-like manner.

It should be mentioned here, that earlier, in 1986, nearly the same compound as NCOOB, containing a hydrogen atom instead of the chlorine substituent in benzene ring A (= **3a**) was investigated in its liquid crystalline state by Diele *et al.* [9]. As a result of X-ray measurements, they established a structural model for the smectic A phase of that compound. Essentially, a layer structure with intercalating molecules was postulated and the intercalation of the alkyl chains considered to be a consequence of the stiff and bulky lateral branches. Because of the missing positional long range order in the S_A phase, this packing model is valid only on a local scale, of course. But it is in very good agreement with our above results obtained for the molecular arrangement in the crystalline phase of NCOOB.

Judging from the observed non-hydrogen intermolecular atomic distances, there is no indication of other than normal van der Waals forces within the crystal lattice of NCOOB.

3. Conclusions

Since the classical paper of Bernal and Crowfoot [20] published in 1933, many attempts have been made to find correlations between the supermolecular arrangement of the molecules within the liquid crystalline phase(s) and, on the other hand, the molecular structure and packing within the crystal of a given mesogenic compound. Recently, a concise review of the present state in this field and of the difficulties connected with this problem was given by Thyen *et al.* [21]. In our opinion, there are good chances of success for such investigations for mesogens (i) exhibiting highly ordered smectic phases, (ii) with specific intermolecular interactions, e.g. hydrogen bonds, or (iii) showing structural peculiarities which demand special steric requirements in order to reach a high packing density, e.g. mesogens with bulky lateral substituents. According to this conception, we have lately been engaged in systematic X-ray investigations of mesogens belonging to the last-mentioned group of compounds [17, 18, 22]. As a typical example, NCOOB has indeed met our expectations. As has been described in detail in this paper, its observed crystal structure is in good agreement with the packing model established on the base of X-ray investigations for the smectic A phase [9]. This result confirms the conception of strong correlations between the crystal and the mesophase structure under certain conditions and gives reason to continue our investigations in this field.

4. Experimental

4.1. *Synthesis*

4.1.1. *4-Nitrobenzyl 2,5-dihydroxybenzoate* 1

0·1 mol (14·2 ml) of triethylamine dissolved in 250 ml of dried acetone was neutralized with 0·1 mol (7·1 g) of gentisic acid and 0·1 mol (28·9 g) of 4-nitrobenzyl bromide and catalytic amounts of sodium iodide were added. The mixture was stirred at room temperature. After a certain time a precipitate of triethylammonium bromide was produced. To complete the reaction, the mixture was

Table 4. Crystal data and details of intensity measurements and stucture refinements.

Compound	NCOOB
Empirical formula	$C_{44}H_{50}ClNO_{10}$
Molecular weight (g mol^{-1})	788·30
Crystal system	triclinic
Space group	$P\bar{1}$
Lattice parameters	
a (Å)	13·201(2)
b (Å)	16·473(3)
c (Å)	19·746(3)
α (°)	96·11(2)
β (°)	95·34(2)
γ (°)	99·92(1)
V (Å^3)	4178·4(12)
(*Z*)	4
F(0 0 0)	1672
D_{calc} (g cm^{-3})	1·253
$\mu(MoK_\alpha)$ (mm^{-1})	0·149
Crystal size (mm)	0·68 × 0·27 × 0·11
Check reflections	3
Range of measurement (°)	$1{\cdot}3 \leqslant \theta \leqslant 22{\cdot}5$
Min. *h k l*/max. *h k l*	$\bar{14}\ \bar{17}\ \bar{21}/14\ 17\ 21$
R_{int}	0·099
Measured reflections	21810
Observed reflections, $I > 2\sigma(I)$	4187
Reflections used in refinement	10907
Refined parameters	1014
Weighting scheme	
$w = 1/[\sigma^2(F_0^2) + (a \cdot P)^2, P = (F_0^2 + 2F_c^2)/3$	$a = 0{\cdot}0933$
Min./max. heights in the final	
$\Delta\rho$ map (e Å^{-3})	− 0·423/0·383
$R^1/wR^2/S$ (observed data)	0·073/0·147/1·246
$R^1/wR^2/S$ (all data)	0·208/0·200/0·970

Table 5. Final fractional coordinates and equivalent displacement parameters (Å^2) of NCOOB, $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

	Molecule α				Molecule β			
Atom	*x/a*	*y/b*	*z/c*	U_{eq}	*x/a*	*y/b*	*z/c*	U_{eq}
C1	−0·2385(6)	1·2143(5)	0·1575(4)	0·128(5)	0·7784(5)	−0·1793(4)	−0·3425(4)	0·105(4)
C2	−0·1818(6)	1·1653(5)	0·1113(4)	0·103(4)	0·7110(5)	−0·1398(4)	−0·3887(4)	0·081(3)
C3	−0·1035(5)	1·1248(4)	0·1501(4)	0·089(3)	0·6366(5)	−0·0948(4)	−0·3512(3)	0·072(3)
C4	−0·0452(5)	1·0731(4)	0·1053(4)	0·093(4)	0·5689(5)	−0·0514(4)	−0·3963(4)	0·080(3)
C5	0·0270(5)	1·0300(5)	0·1443(4)	0·097(4)	0·4981(5)	−0·0061(4)	−0·3581(3)	0·078(3)
C6	0·0847(6)	0·9770(5)	0·0987(4)	0·104(4)	0·4315(5)	−0·9610(4)	−0·4035(4)	0·086(3)
C7	0·1549(6)	0·9339(5)	0·1396(4)	0·106(4)	0·3659(5)	−0·9132(4)	−0·3639(4)	0·085(3)
C8	0·2181(5)	0·8840(4)	0·0945(4)	0·091(3)	0·2950(5)	−0·8704(4)	−0·4080(3)	0·080(3)
C9	0·3456(5)	0·7991(4)	0·1176(4)	0·067(3)	0·1744(5)	−0·7790(4)	−0·3845(4)	0·069(3)
C10	0·4015(5)	0·7665(4)	0·1688(3)	0·063(3)	0·1311(5)	−0·7363(4)	−0·3329(3)	0·077(3)
C11	0·4693(4)	0·7149(4)	0·1529(3)	0·057(3)	0·0617(4)	−0·6863(4)	−0·3485(3)	0·064(3)
C12	0·4821(4)	0·6942(3)	0·0853(3)	0·052(2)	0·0347(4)	−0·6772(4)	−0·4164(3)	0·051(3)
C13	0·4280(5)	0·7266(4)	0·0342(3)	0·066(3)	0·0769(4)	−0·7200(4)	−0·4668(3)	0·060(3)
C14	0·3618(5)	0·7784(4)	0·0506(4)	0·072(3)	0·1471(5)	−0·7696(4)	−0·4515(3)	0·064(3)
C15	0·5530(5)	0·6393(4)	0·0655(4)	0·061(3)	−0·0418(5)	−0·6255(4)	−0·4357(4)	0·056(3)
C16	0·6802(5)	0·5659(4)	0·1086(3)	0·049(3)	−0·1577(5)	−0·5449(4)	−0·3906(3)	0·048(3)
C17	0·6555(5)	0·4825(4)	0·1153(3)	0·046(2)	−0·1298(5)	−0·4594(4)	−0·3818(3)	0·048(3)
C18	0·7329(5)	0·4354(4)	0·1088(3)	0·051(3)	−0·2088(5)	−0·4131(4)	−0·3881(3)	0·053(3)
C19	0·8294(5)	0·4717(5)	0·0964(3)	0·055(3)	−0·3106(5)	−0·4531(5)	−0·4021(3)	0·053(3)
C20	0·8538(5)	0·5538(4)	0·0888(3)	0·066(3)	−0·3364(5)	−0·5376(4)	−0·4110(3)	0·061(3)
C21	0·7782(5)	0·6020(4)	0·0961(3)	0·066(3)	−0·2597(5)	−0·5841(4)	−0·4050(3)	0·064(3)
C22	0·9612(5)	0·4079(4)	0·1455(4)	0·059(3)	−0·4273(5)	−0·3774(4)	−0·3541(4)	0·063(3)
C23	1·0377(4)	0·3569(4)	0·1298(3)	0·052(3)	−0·5067(4)	−0·3284(4)	−0·3684(3)	0·051(2)
C24	1·1014(5)	0·3363(4)	0·1827(3)	0·071(3)	−0·5581(4)	−0·2994(4)	−0·3163(3)	0·060(3)
C25	1·1732(5)	0·2871(4)	0·1705(3)	0·070(3)	−0·6338(5)	−0·2514(4)	−0·3270(3)	0·064(3)
C26	1·1838(5)	0·2571(4)	0·1052(3)	0·062(3)	−0·6578(4)	−0·2339(4)	−0·3926(4)	0·061(3)
C27	1·1205(5)	0·2761(4)	0·0503(3)	0·069(3)	−0·6080(5)	−0·2626(4)	−0·4463(3)	0·067(3)
C28	1·0497(4)	0·3264(4)	0·0643(3)	0·064(3)	−0·5319(4)	−0·3091(4)	−0·4337(3)	0·064(3)
C29	1·3217(5)	0·1864(4)	0·1389(3)	0·081(3)	−0·7894(5)	−0·1567(4)	−0·3604(3)	0·071(3)
C30	1·3848(5)	0·1319(4)	0·1019(4)	0·087(3)	−0·8620(5)	−0·1104(4)	−0·3990(3)	0·080(3)
C31	1·4524(5)	0·0910(4)	0·1493(4)	0·088(3)	−0·9207(5)	−0·0613(4)	−0·3524(4)	0·083(3)
C32	1·5116(5)	0·0351(4)	0·1095(4)	0·089(3)	−0·9896(5)	−0·0132(4)	−0·3927(3)	0·080(3)
C33	1·5798(5)	−0·0089(4)	0·1528(4)	0·089(3)	−0·0475(5)	0·0400(4)	−0·3505(3)	0·082(3)
C34	1·6383(5)	−0·0643(4)	0·1097(4)	0·086(3)	−0·1143(5)	0·0866(4)	−0·3941(3)	0·076(3)
C35	1·7121(6)	−0·1050(5)	0·1477(4)	0·096(4)	−0·1783(5)	0·1369(4)	−0·3552(4)	0·087(3)
C36	1·7688(6)	−0·1553(4)	0·1002(4)	0·111(4)	−0·2431(5)	0·1801(4)	−0·4003(4)	0·107(4)
C37	0·5526(5)	0·4354(5)	0·1305(3)	0·055(3)	−0·0224(5)	−0·4086(5)	−0·3662(3)	0·056(3)
C38	0·3788(5)	0·4379(4)	0·1432(3)	0·063(3)	0·1557(4)	−0·4079(4)	−0·3521(3)	0·065(3)
C39	0·3084(4)	0·5007(4)	0·1453(3)	0·057(3)	0·2253(4)	−0·4701(4)	−0·3551(3)	0·055(3)
C40	0·2780(5)	0·5295(4)	0·2071(3)	0·070(3)	0·2643(5)	−0·4953(5)	−0·2953(3)	0·088(4)
C41	0·2110(5)	0·5855(4)	0·2108(3)	0·074(3)	0·3302(6)	−0·5522(5)	−0·2967(3)	0·090(4)
C42	0·1772(4)	0·6123(4)	0·1507(3)	0·058(3)	0·3554(5)	−0·5838(4)	−0·3570(3)	0·061(3)
C43	0·2055(5)	0·5843(4)	0·0887(3)	0·068(3)	0·3171(5)	−0·5602(4)	−0·4174(3)	0·071(3)
C44	0·2715(5)	0·5283(4)	0·0865(3)	0·064(3)	0·2528(5)	−0·5025(4)	−0·4152(3)	0·073(3)
N1	0·1082(4)	0·6730(4)	0·1531(4)	0·077(3)	0·4228(4)	−0·6446(4)	−0·3599(4)	0·084(3)
O1	0·2829(4)	0·8504(3)	0·1415(2)	0·094(2)	0·2417(4)	−0·8267(3)	−0·3608(2)	0·091(2)
O2	0·5625(4)	0·6100(3)	0·0087(2)	0·092(2)	−0·0656(4)	−0·6102(3)	−0·4914(2)	0·088(2)
O3	0·6113(3)	0·6208(2)	0·1212(2)	0·055(2)	−0·0848(3)	−0·5959(2)	−0·3797(2)	0·052(2)
O4	0·9048(3)	0·4218(3)	0·0876(2)	0·068(2)	−0·3878(3)	−0·4047(3)	−0·4107(2)	0·066(2)
O5	0·9473(4)	0·4382(3)	0·2008(2)	0·100(2)	−0·3972(4)	−0·3935(4)	−0·2996(2)	0·114(3)
O6	1·2525(3)	0·2092(3)	0·0866(2)	0·085(2)	−0·7315(3)	−0·1890(3)	−0·4115(2)	0·082(2)
O7	0·5402(3)	0·3644(3)	0·1408(2)	0·070(2)	−0·0056(3)	−0·3342(3)	−0·3536(2)	0·074(2)
O8	0·4804(3)	0·4832(2)	0·1325(2)	0·055(2)	0·0508(3)	−0·4554(2)	−0·3672(2)	0·055(2)
O9	0·0767(4)	0·6975(3)	0·0999(3)	0·091(2)	0·4388(4)	−0·6789(3)	−0·4138(3)	0·092(2)
O10	0·0839(4)	0·6978(4)	0·2082(3)	0·116(3)	0·4621(6)	−0·6604(5)	−0·3075(3)	0·180(4)
C11	0·3806(2)	0·7903(1)	0·2533(1)	0·111(1)	0·1681(2)	−0·7448(2)	−0·2489(1)	0·153(1)

stirred overnight. The reaction mixture was poured into water to precipitate the ester **1** which was filtered off and washed with 5 per cent aqueous $NaHCO_3$ and water several times. The crude material was recrystallized from ethanol (yield 80 per cent); m.p. 172°C.

4.1.2. *4-Nitrobenzyl 2-hydroxy-5-(4-*n*-octyloxybenzoyloxy-3-substituted)benzoates* **2a, 2b**

0·025 mol (7·22 g) of compound **1**, 0·025 mol (6·25 g) of 4-*n*-octyloxybenzoic acid or 0·025 mol (7·1 g) of 3-chloro-4-*n*-octyloxybenzoic acid and 0·03 mol (6·18 g) of *N,N'*-dicyclohexylcarbodiimide and catalytic amounts of dimethylaminopyridine was stirred in 100 ml of dry dichloromethane with exclusion of moisture overnight. The solvent was removed and the crude product was recrystallized from ethanol.

no.	R^1	m.p. (°C)	yield (%)
2a	H	81–82	75
2b	Cl	62–64	68

4.1.3. *4-Nitrobenzyl 5-(3-chloro-4-*n*-octyloxybenzoyloxy)-2-(4-*n*-octyloxybenzoyloxy)benzoate* **3b**

5 mmol (2·60 g) of **2a** was dissolved in 50 ml of toluene and 5 mmol (1·51 g) of 3-chloro-4-*n*-octyloxybenzoyl chloride and 6 mmol (0·84 ml) of triethylamine were added slowly with agitation. The solution was stirred overnight at room temperature and after that for two hours at 60°C. The mixture was filtered through a short column of silica gel and the toluene evaporated from the filtrate. Recrystallization from a mixture of ethanol and a small amount of toluene gave the pure compound **3b**.

4.1.4. *4-Nitrobenzyl 2-(3-chloro-4-*n*-octyloxybenzoyloxy)-5-(4-*n*-octyloxybenzoyloxy)benzoate* **3c**

Reaction of 5 mmol (2·77 g) of **2b** and 5 mmol (1·42 g) of 4-*n*-octyloxybenzoyl chloride according to the procedure given for the preparation of derivative **3b** yielded compound **3c**.

4.1.5. *4-Nitrobenzyl 2,5-bis(3-chloro-4-*n*-octyloxybenzoyloxy)benzoate* **3d**

Compound **3d** was synthesized by acylation of 5 mmol (1·44 g) of 4-nitrobenzyl 2,5-dihydroxybenzoate **1** with 10 mmol (3·02 g) of 3-chloro-4-*n*-octyloxybenzoyl chloride in the presence of 12 mmol (1·68 ml) of triethylamine in 100 ml of dry toluene. Recrystallization of **3d** and **3c** was from pentan-1-ol or dimethylformamide. The melting behaviour is summarized in table 1.

The purity and constitution of all compounds have been checked by ^{1}H-NMR and elemental analysis. The analytical data for one selected derivative, **3c,** are given below: ^{1}H-NMR ($CDCl_3$, TMS) δ in ppm: δ 0·84–0·90 (t, 6H, $2\times CH_3$); 1·30–1·51 (m, 20H, $10\times CH_2$); 1·77–1·88 (m, 4H, $2\times CH_2CH_2O$); 4·00–4·09 (t, 4H, $2\times OCH_2$); 5·24 (s, 2H, $COOCH_2$); 6·82–8·14 (m, 14 arom. H). Elemental analysis; calculated (found): C = 67·06 per cent (67·21 per cent), H = 6·40 per cent (6·22 per cent), N = 1·78 per cent (1·75 per cent), Cl = 4·44 per cent (4·30 per cent).

4.2. *Crystal structure determination*

Optically clear, colourless crystals of NCOOB were obtained by recrystallization from a mixture of acetone and dichloroethane.

Relevant crystal data and details of the structure determination are given in table 4. The intensity data were measured on a Stoe STADI 4 diffractometer using graphite-monochromated MoK_α radiation at room temperature using the ω/θ-scan mode. Lattice parameters were derived by a least-squares treatment of the setting angles for 60 reflections. Data correction was carried out applying Lorentz and polarization corrections, but neglecting absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions and refined isotropically using the riding model. An empirical extinction correction was applied to F_c with $F_{c,corr} = kF_c[1 + \chi F_c^2\lambda^3/(\sin 2\Theta)]^{-0{\cdot}25}$, where k and χ were refined to 0·0585(1) and 0·031(4), respectively.

All calculations were done on an IBM RISC/6000-320 work station using the program packages SHELXS-86 [23], SHELXL-93 [24] and EDIT [25]. Figures of the molecular structure and packing were plotted using the program Siemens XP [16].

Final atomic parameters are given in table 5. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, Postfach 2465, D-76012 Karlsruhe, on quoting the depository number CSD-401935, the names of the authors, and the journal citation.

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