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Novel Mesogenic Benzoic Acids with Large Branches I. Synthesis, Liquid Crystalline Properties and Crystal Structure Analyses of 3-(4- Subst.-benzyloxycarbonyl)-4-(4-n- octyloxybenzoyloxy) benzoic Acids

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Novel Mesogenic Benzoic Acids with Large Branches I. Synthesis, Liquid Crystalline Properties and Crystal Structure Analyses of 3-(4-Subst.-benzyloxycarbonyl)-4-(4-*n*-octyloxybenzoyloxy)benzoic Acids

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New benzoyloxybenzoic acids bearing both terminal and lateral groups have been synthesized. Substituted aryl rings are laterally attached to the basic mesogens by means of an odd-numbered spacer. Therefore, liquid crystalline behaviour can be observed at high temperatures.

The crystal and molecular structure of 3-(4-cyano-benzyloxycarbonyl)-4-(4-*n*-octyloxybenzoyloxy)benzoic acid **3b** has been determined by X-ray analysis. **3b** crystallizes in space group $P2_1/n$ with four molecules in a unit cell of the following dimensions: $a = 15.682(2)$, $b = 7.701(1)$, $c = 23.107(3)$ Å, $\beta = 97.69(1)^\circ$. The structure was solved by direct methods and refined to an R value of 0.057 for 3684 observed reflections.

The molecules of **3b** are associated to dimers with a shape unusual for mesogens exhibiting nematic and smectic phases. In the crystal the dimers are closely packed to ribbons which on their part are connected to lamellar sheets. The nitro-substituted homologue **3c** was proved to be isostructural with **3b**.

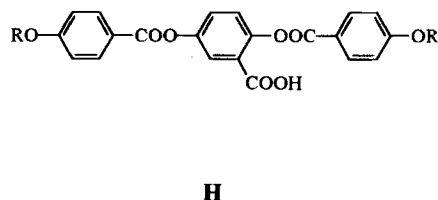
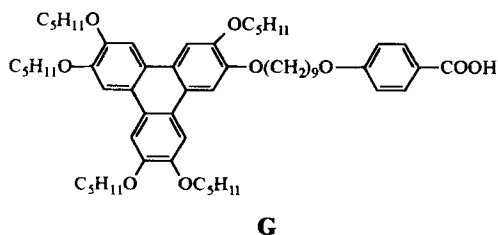
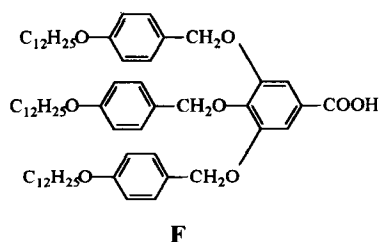
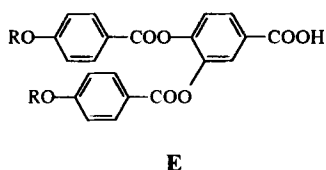
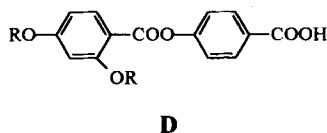
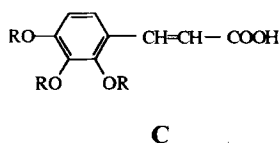
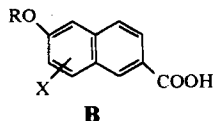
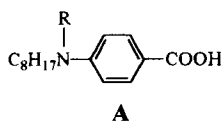
Keywords: Liquid crystalline benzoic acids, bulky branched mesogens, molecular structure, crystal structure, hydrogen-bonded dimers

1. INTRODUCTION

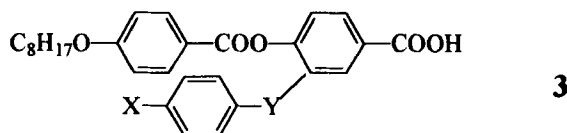
A great number of 4-substituted benzoic acids exhibit liquid crystalline behaviour because of their association to dimers with a high length-to-breadth ratio.¹ However, already small branches within the long-chain substituents can destroy the anisotropic order. For example, 4-*n*-octylaminobenzoic acid **A** ($R=H$) shows a nematic phase between 118–127°C but a mesophase cannot be detected in the branched 4-(*N*-methyl-

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N-*n*-octyl)benzoic acid **A** ($R=CH_3$).² Fundamental investigations on the influence of lateral substituents on the mesophase behaviour of 6-alkyloxynaphthoic acids **B** and of 4'-alkyloxy-biphenylcarboxylic acids were performed sometime ago by Gray.³ According to these previous results, laterally attached greater and bulky substituents prevent the formation of mesophases. But the situation is clearly changed if more than one long alkyl chain exists in the molecule. 2,3,4-trialkyloxycinnamic acids **C** show nematic phases⁴ whereas anisotropic behaviour has not been described for dialkyloxy- and trialkyloxybenzoic acids.⁵⁻⁷ Two-ring 4-alkyloxybenzoyloxybenzoic acids can be substituted by different groups, e.g., by two long chains like in formula **D**, without loss of the liquid crystalline properties.⁸ 3,4-Bis(4-alkyloxybenzoyloxy)benzoic acids **E** exhibit nematic phases on supercooling,⁹ these phase transitions will be discussed below in connection with the new compounds described in this paper. Three-fold substitution of benzoic acid by 4-*n*-dodecyloxybenzoyloxy groups in the 3,4,5-positions (formula **F**) gives discotic mesogens exhibiting one columnar phase.¹⁰ Connection of a disc-like triphenylene mesogen with one benzoic acid group by means of an alkylene, as shown in formula **G**, yields a substance having a liquid crystalline phase on supercooling.¹¹ The dimer of **G** represents a combination of two discotic with one calamitic structural element within a mesogen. In all examples discussed as yet, the carboxylic group is attached in a terminal position of the molecule. Lateral substitution of three-ring mesogens by a COOH group, as sketched in **H**¹², prevents the existence of mesophases, although many liquid crystalline 2-substituted *p*-phenylene bisbenzoates, bearing a small or bulky group in the same position, have been described.^{1,13-16}



In 1988, we found a new concept for the synthesis of bulky branched mesogens¹² while systematic investigations on the relationships between the chemical structure of the molecules and their liquid crystalline behaviour were being carried out. According to them, the lateral substitution of three-ring compounds with bulky aryl groups by means of an odd-numbered spacer results in mesogens with unexpectedly high transition temperatures. Now, this concept could be applied to two-ring benzoic acids. We would like to report on the synthesis and characterization of laterally bulky substituted two-ring benzoic acids of the general formula 3.



In the present paper the synthesis and investigation of the 3-(4-subst.-benzyloxycarbonyl)-4-(4-*n*-octyloxybenzoyloxy)benzoic acids **3a–c** are described. Compound **3d** bearing a longer spacer *Y* is listed in Table I only in order to compare the liquid crystalline properties, but details of such mesogens like **3d** will be given elsewhere.¹⁷

Of substances **3b** and **3c** single crystals suitable for X-ray investigations could be prepared. Therefore, their crystal structure determinations have been performed with the aim to obtain exact knowledge of both the molecular structure (including conformational behaviour) and the three-dimensional molecular packing of these very branched mesogens in the solid state.

2. RESULTS AND DISCUSSION

2.1 Liquid crystalline properties

Table I shows the transition temperatures of derivatives **3a–d**. Not only the substituent *X* in the 4-position but the length of the odd-numbered spacer *Y* has also been varied. Liquid crystalline behaviour could be detected for all four compounds. Strongly electron-withdrawing substituents like the cyano- or nitro-group cause the existence of smectic A structures which exhibit a clear tendency to form homeotropic orientation between glass plates. For compound **3d**, in which a long-chain substituted phenyl ring is attached by a five-numbered spacer at the lateral position of the basic mesogen, the nematic phase exists in the metastable state only. The melting points of all investigated

TABLE I
Phase transition behaviour of the laterally branched 4-(4'-*n*-octyloxybenzoyloxy)benzoic acids **3a–d**

no.	Y	X	cr	S _A	N	is
3a	–COOCH ₂ –	–H	• 151	–	(• 130.5)	•
3b	–COOCH ₂ –	–CN	• 147	(• 145)	• 156	•
3c	–COOCH ₂ –	–NO ₂	• 172	(• 160)	• 161.5)	•
3d	–COOCH ₂ CH ₂ O–	–COC ₈ H ₁₇	• 162	–	(• 131)	•

substances are comparatively high. One reason for that is the existence of hydrogen bonds forming dimers. Knowledge of the molecular packing of such mesogens in the different liquid crystalline phases as well as in the solid state is of great interest to understand the relationships between molecular structure and mesophase behaviour.

For the lateral substituted benzoic acids **3a–d** the trend to form mesophases depending on the length of the spacer Y and the substituent X is comparable to that observed for three-ring mesogens bearing the same bulky substituents in lateral position.¹² The clearing temperatures of the derivatives **3a–d** are generally higher than those of the 3,4-bis(4-*n*-alkyloxybenzoyloxy)benzoic acids illustrated by formula E.⁹ This is, in our opinion, a consequence of the odd-numbered spacer Y in **3a–d** compared with the even-numbered carboxylic group serving as a spacer in the acids E.

It should be mentioned that the benzoic acids **3a–d** show a very strong tendency to associate with proton acceptors, like pyridines, to form new hydrogen bonded mesogens.¹⁸

2.2 Synthesis

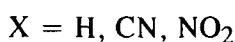
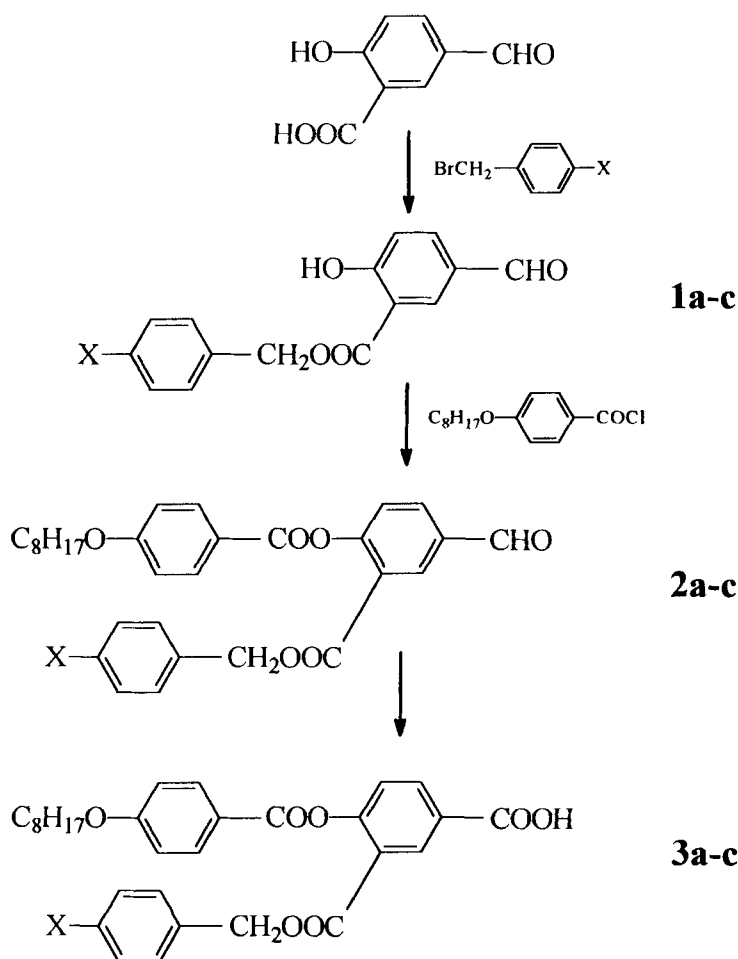
Substances **3a–c** have been prepared according to the reaction pathway shown in scheme 1. 5-Formylsalicylic acid was converted into the benzyl esters **1a–c** by means of two different methods usable in dependence of the substituent X. The activated benzyl bromides bearing the cyano- or nitro-group, respectively, react easily with the carboxylic group in the presence of triethylamine to form the esters **1b–c** according to a known procedure.¹⁹ The unsubstituted benzyl ester **1a** was prepared by a heterogenous solid state reaction in analogy to the method given by Barry *et al.*²⁰ Esterification of the intermediates **1a–c** with 4-*n*-octyloxybenzoyl chloride yielding **2a–c** was performed in toluene with triethylamine to trap the hydrogen chloride. Subsequent oxidation of the formyl group of the aldehydes **2a–c** was successful with chromium trioxide in acetic acid to give the substituted benzoic acids **3a–c**.

2.3 Crystal structure determination

As already mentioned above, compounds **3b** and **3c** proved to be isomorphous crystallizing in the same space group with nearly identical unit cell dimensions and exhibiting in principle the same molecular structure and packing. Therefore, the following discussion is focussed on the structure of **3b** because of its higher precision and that of **3c** will only be used for comparison in special cases. For both structures a consistent numbering scheme has been adopted.

2.3.1 Molecular structure Figure 1 shows the molecular structure of **3b** in the form of a thermal motion plot.²¹ Relevant parameters of the molecular geometry are summarized for **3b** and **3c** in Tables II and III.

The most striking feature of the molecular structure is the extended shape of the mesogenic core (with the exception of the end atoms of the octyl chain) and the orientation of the large lateral substituent parallel to it. The molecule as a whole is not



SCHEME I Reaction pathway to synthesize the laterally branched acids **3a-c**.

planar but has some structural fragments of (near or exact) planarity. Benzene rings A (C9..C14) and C (C25..C30) show no significant deviation from planarity whereas ring B (C16..C21) has, besides other small distortions of regularity (see below), three significant deviations of 0.015(2), 0.010(2) and 0.012(2) Å for atoms C16, C17 and C19, respectively. Also strict planarity is observed for the C—CO₂O fragments (= carboxyl groups including the carbon atom of the benzene ring to which they are attached) with a maximum deviation of 0.009(2) Å for O4.

Recently, we performed an X-ray analysis of crystalline 4-nitrobenzyl 2,5-bis(4-ethoxybenzoyloxy)benzoate NEBB.²² It revealed that the phenylene bis(benzoate) mesogenic core of NEBB has a non-planar but optimally stretched shape and the large

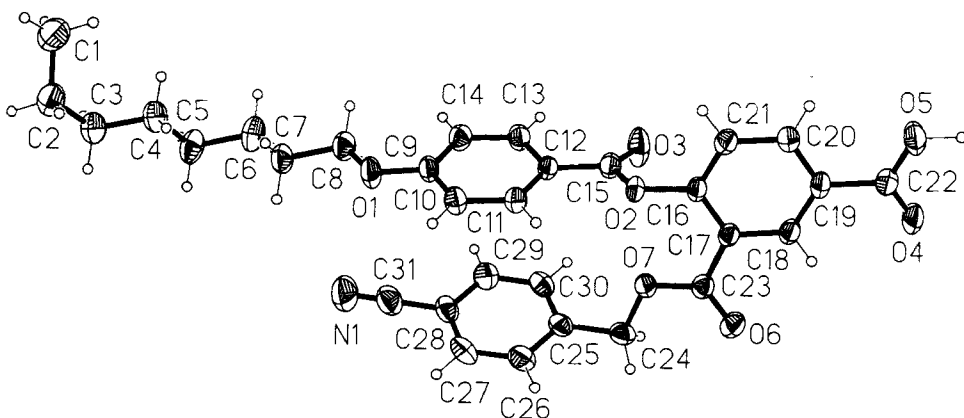


FIGURE 1 Molecular structure of **3b** with atom numbering. The displacement ellipsoids are drawn at the 50% probability level.

TABLE II

Selected bond lengths and angles for non-hydrogen atoms in **3b** and **3c** (esd's in parentheses)

Atoms	Distance (Å)		Atoms	Angle (°)	
	3b	3c		3b	3c
Carboxyl group I					
C15–O2	1.369(3)	1.365(5)	C12–C15–O2	112.0(2)	112.2(3)
C15–O3	1.179(3)	1.198(6)	C12–C15–O3	126.2(2)	126.4(4)
C15–C12	1.467(3)	1.460(6)	O2–C15–O3	121.8(2)	121.4(3)
O2–C16	1.392(3)	1.395(5)	C15–O2–C16	115.2(2)	115.4(3)
Carboxyl group II					
C22–O4	1.247(3)	1.256(6)	O4–C22–O5	123.6(2)	124.0(4)
C22–O5	1.283(3)	1.269(6)	O4–C22–C19	119.9(2)	118.7(4)
C22–C19	1.483(3)	1.485(6)	O5–C22–C19	116.4(2)	117.3(4)
Carboxyl group III					
C23–O6	1.202(3)	1.201(5)	C17–C23–O6	122.1(2)	122.3(3)
C23–O7	1.331(3)	1.330(5)	C17–C23–O7	114.5(2)	114.6(3)
C23–C17	1.494(3)	1.496(6)	O6–C23–O7	123.4(2)	123.1(3)
O7–C24	1.460(3)	1.455(5)	C23–O7–C24	114.4(2)	114.4(3)
Cyano group/Nitro group					
C28–C31	1.444(4)	–	C28–C31–N1	179.5(3)	–
C31–N1	1.139(4)	–			
C28–N1	–	1.473(6)	C28–N1–O8	–	118.3(4)
N1–O8	–	1.219(6)	C28–N1–O9	–	119.1(4)
N1–O9	–	1.209(6)	O8–N1–O9	–	122.6(4)
Mean values for benzene rings					
		Ring A (C9..C14)			
C—C	1.384(5)	1.378(7)	C—C—C	120.0(7)	120.0(6)
		Ring B (C16..C21)			
C—C	1.388(6)	1.383(7)	C—C—C	120.0(1.5)	120.0(1.6)
		Ring C (C25..C30)			
C—C	1.384(6)	1.371(6)	C—C—C	120.0(8)	120.0(1.9)

TABLE III
Selected torsion angles in **3b** and **3c**

Atoms	Angle (°)		Atoms	Angle (°)	
	3b	3c		3b	3c
Octyloxy group					
C1–C2–C3–C4	60.4(3)	79(1)	C5–C6–C7–C8	177.6(3)	177.9(9)
C2–C3–C4–C5	178.0(3)	179(1)	C6–C7–C8–O1	–179.0(2)	170.8(7)
C3–C4–C5–C6	177.7(3)	166(1)	C7–C8–O1–C9	176.8(2)	179.2(5)
C4–C5–C6–C7	70.9(3)	84(1)	C8–O1–C9–C10	–174.4(2)	–177.7(5)
Carboxyl groups					
C11–C12–C15–O2	–12.1(2)	–9.4(4)	C16–C17–C23–O6	–172.9(2)	–173.8(4)
C11–C12–C15–O3	167.6(3)	170.1(5)	C16–C17–C23–O7	6.4(3)	5.9(5)
C12–C15–O2–C16	179.5(2)	178.0(4)	C17–C23–O7–C24	178.5(2)	178.1(4)
C15–O2–C16–C17	–88.5(2)	–90.3(4)	C23–O7–C24–C25	–176.7(2)	176.6(4)
O3–C15–O2–C16	–0.2(3)	–1.5(4)	O6–C23–O7–C24	–2.2(2)	–2.2(4)
C18–C19–C22–O4	7.1(3)	178.2(5)	C18–C19–C22–O5	–174.6(3)	–0.4(5)

benzene ring-containing substituent is ordered parallel to it. Apart from the carboxylic group, the six terminal C-atoms of the octyl chain and the cyano (nitro) substituent the remaining fragment of **3b** (**3c**) can be considered as a constituent of compound NEBB. In fact, the molecular configuration of **3b** (and also **3c**, of course) agrees to a very large extent with this relation. This statement is valid not only for the parallel orientation of the lateral substituent but also for other details of molecular conformation. That can be described by the torsion angles given in Table III but is also illustrated by the dihedral angles between the planar fragments. Benzene rings A and C are approximately coplanar and perpendicular to ring B, the corresponding dihedral angles amount to A/C 7.43(8), A/B 80.76(8) and B/C 73.38(7)°. The orientation of the carboxyl group I (for denotation see Table II) with respect to the O- and C-bonded adjacent benzene rings is characterized by the dihedral angles A/I 12.20(9) and B/I 87.05(9)° in full agreement with the results of our previous investigations of mesogenic phenyl benzoates.²³ The nitro-group in **3c** is slightly twisted about the bond C28–N1 and inclined to the benzene ring C by 10.2(2)°.

Surprisingly, the octyloxy chains in both **3b** and **3c** are not fully staggered but include two *gauche* conformations between C2–C3 and C5–C6 (cf. Table III). In this way, the terminal alkyl chain is not optimally extended but considerably bent (cf. Fig. 1). In **3c** this effect, which can be explained by packing considerations (see below), is accompanied by a structural disorder indicated by very strange values for the C–C bond lengths within the octyl chain as well as the unrealistically high displacement parameters. This effect has been observed in several other cases and interpreted as a partial melting of the alkyl chain. In **3b** for which the structure was investigated at low temperature (200 K) such disorders were not be observed.

All other bond lengths and angles are as expected and agree well with appropriate standard values²⁴ except those for benzene ring B. Apparently as a consequence of its asymmetric substitution ring B is slightly deformed. This finds expression by the high

standard deviation of the mean bond angle $\overline{\text{C—C—C}}$ ($\sigma = 1.5^\circ$) as well as the individual bond angles $\text{C16—C17—C18} = 117.4(2)$, $\text{C17—C16—C21} = 121.8(2)$ and $\text{C17—C18—C19} = 121.4(2)^\circ$. Such benzene ring deformations are well known from the literature and have been discussed as substituent effects in detail by several authors, e.g., recently by Domenicano.²⁵

The molecules occur in the crystal as hydrogen-bonded dimers. Such a dimer has an exact centre of symmetry coincident with the space group inversion centre at 0, 0, 0.5 or 0.5, 0.5, 0, respectively (see Fig. 3). The two C—O bond lengths of the carboxylic group are significantly different [C22—O4 1.247(3), C22—O5 1.283(3) Å] but the difference is less than expected. Allen *et al.*⁴ give mean values of 1.226(20) and 1.305(20) Å, respectively, for such bonds in benzoic acids. An interpretation of our result in terms of a disorder of the two C—O bond types by 180° rotation about C19—C22 as given by Bryan and Hartley²⁶ is not justified because of the presence of only one peak corresponding to the carboxylic hydrogen atom in the difference electron density map. The O—H...O hydrogen bond has the following parameters: O5—H5 1.02(5) Å, H5...O4^i 1.60(5) Å, O5...O4^i 2.629(2) Å, O5—H5...O4^i $178(4)^\circ$ (symmetry code of O4^i : $1 - x, 1 - y, -z$).

2.3.2 Crystal packing One of the main results of the two performed X-ray analyses is the determination of molecular organization in the solid phase. The molecular packing of **3b** within the crystal is illustrated by Figures 2 to 4. It can be described in the following way.

By translation of the hydrogen-bonded dimers in y -direction ribbons are built. A realistic picture of the arrangement within a ribbon can be visualized by the space-filling model²¹ of Figure 2 using van der Waals radii given by Bondi²⁷ for plotting the atom contours. It demonstrates that the already above-mentioned strong bent of the alkyl chain can be considered as a packing phenomenon enabling a high packing density. By action of the twofold screw axes parallel b in $x = 1/4, z = 1/4$ and $x = 3/4, z = 3/4$, respectively, ribbons are connected to lamellar sheets oriented parallel (104). In Figure 3 the view is parallel to the sheets. The long axes of molecules in neighboured ribbons of the same sheet are inclined by 148.6° . The sheets on their part are stacked one upon another by action of the inversion centres at 0, 0, 0 and $1/2, 1/2, 1/2$, respectively, as well as the screw axes parallel b in $x = 3/4, z = 1/4$ and $x = 1/4, z = 3/4$, respectively. Two such related parallel sheets are shown in Figure 4. The resulting packing sequence of the sheets can be seen in Figure 3.

3. EXPERIMENTAL

3.1 Preparation

3.1.1 Benzyl 2-hydroxy-5-formylbenzoate 1a 6.00 g (0.03 mol) potassium 2-hydroxy-5-formylbenzoate (prepared by dissolving of 5-formylsalicylic acid in the stoichiometric amount of potassium hydroxide solution, evaporating water and drying over phosphorus pentoxide), 6.12 g (0.036 mol) benzyl bromide and 1.04 g (3.6 mmol)

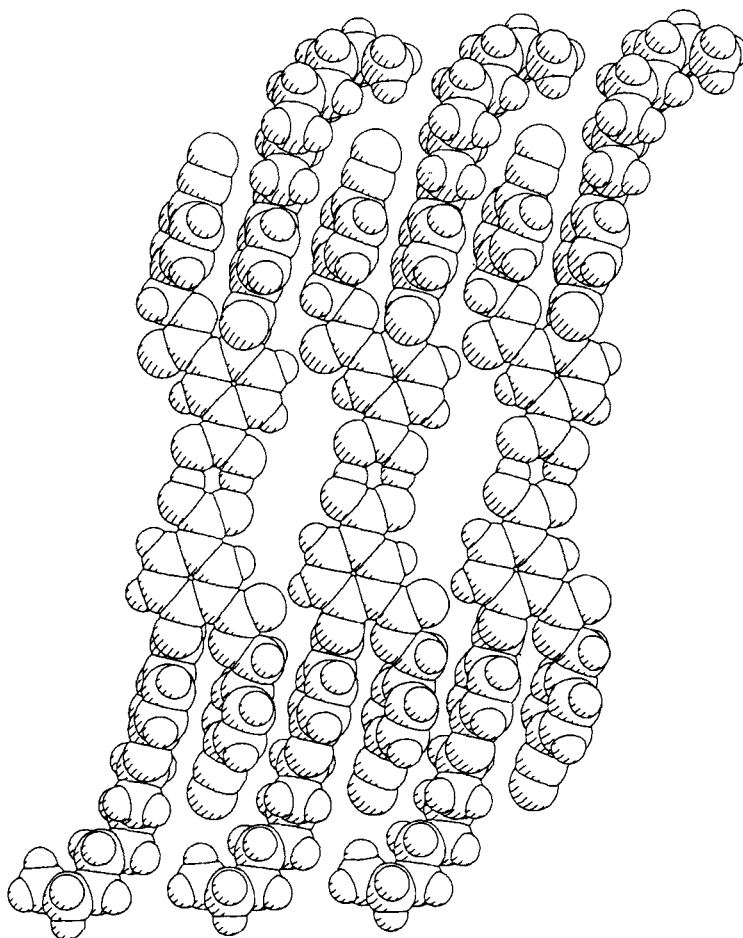
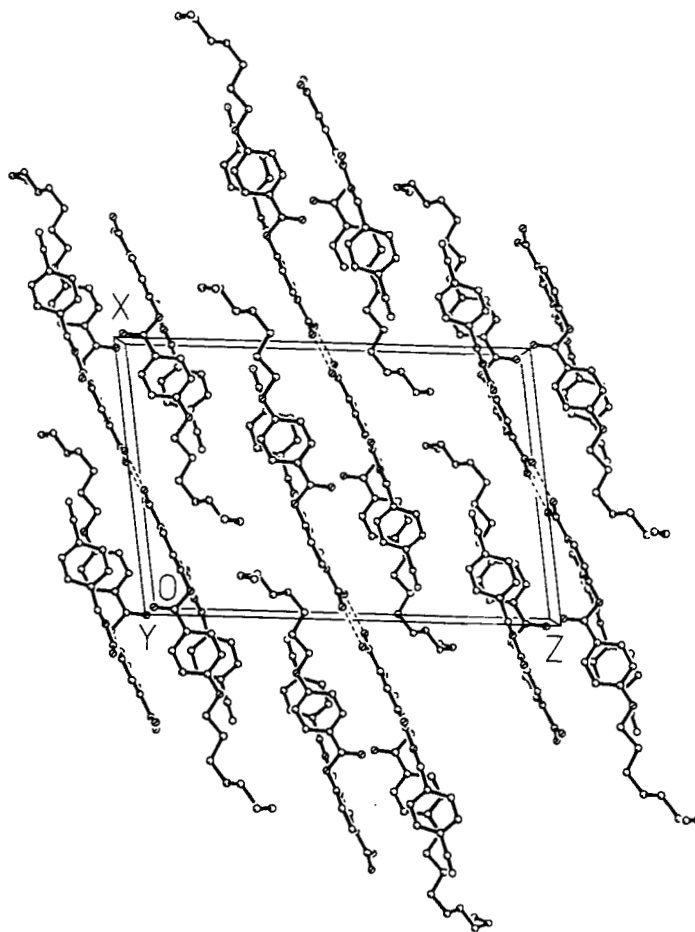


FIGURE 2 Packing of molecules of **3b** in a ribbon illustrated by a space filling model.

tetrabutylammonium bromide are heated at 88°C for 3 weeks. After this time the mixture is extracted with ethyl acetate, the solvent is evaporated and the crude product is purified by chromatography on silica gel with ethyl acetate/heptane (1:1) as eluent. Pure benzyl ester is obtained by recrystallization from toluene/heptane.

no.	X	m.p.(°C)	yield (%)
1a	H	64–68	20

3.1.2 4-Subst.-benzyl 2-hydroxy-5-formylbenzoates 1b–c 10,00 g (0.06 mol) 5-formylsalicylic acid and 9 ml (0.065 mol) triethylamine are dissolved in dry acetone.

FIGURE 3 Crystal packing of **3b** viewed along the *b*-axis.

0.06 mol of the appropriate benzyl bromide and some potassium iodide are added. The mixture is heated under reflux for 6 h. After cooling water is added to precipitate the product. Recrystallization from *n*-pentanol gives the pure compound.

no.	X	m.p.(°C)	yield (%)
1b	CN	145–146.5	57.8
1c	NO ₂	148–149.5	58.2

3.1.3 4-Subst.-benzyl 2-(4-*n*-octyloxybenzoyloxy)-5-formylbenzoates 2a–c 0.01 mol of **1a–c** are dissolved in 350 ml toluene (for **1b,c** heating is necessary). 2.68 g (0.01 mol) 4-*n*-octyloxybenzoyl chloride and 2.1 ml (0.015 mol) triethylamine are added slowly under stirring at about 5–10°C. The solution is stirred overnight at room

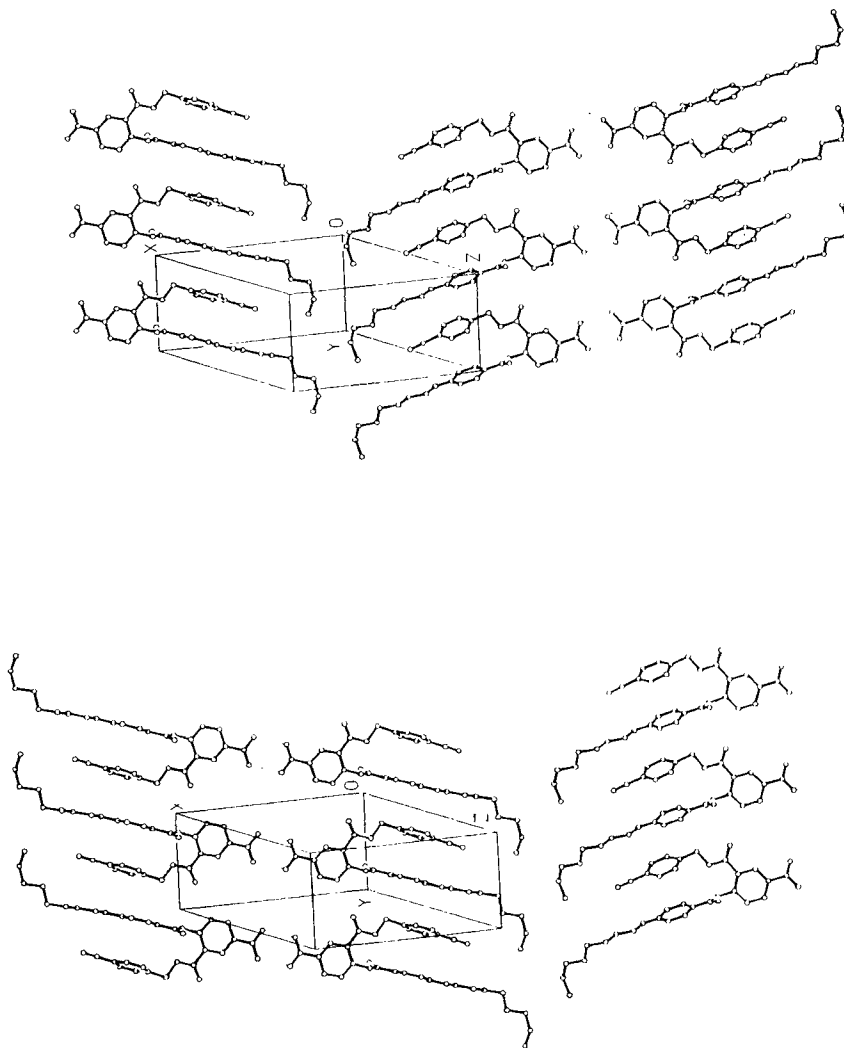


FIGURE 4 Two sheets of molecules parallel (104) following one on top of the other in the stacking direction in the crystal of **3b** but separately plotted for the sake of clarity.

TABLE IV
Crystal data and details of intensity measurements and structure refinements of **3b** and **3c**

Compound	3b	3c
Empirical formula	C ₃₁ H ₃₁ NO ₇	C ₃₀ H ₃₁ NO ₉
Molecular weight (g mol ⁻¹)	529.57	549.56
Measuring temperature (K)	200	295
Crystal size (mm)	0.07 × 0.10 × 0.41	0.10 × 0.13 × 0.31
Radiation	MoKα, λ = 0.7103 Å	
Collection method	ω/θ-scan	
μ(MoKα) (cm ⁻¹)	0.090	0.095
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	15.682(2)	15.575(2)
<i>b</i> (Å)	7.701(1)	7.699(1)
<i>c</i> (Å)	23.107(3)	23.847(3)
β (°)	97.69(1)	97.40(1)
Unit cell volume (Å ³)	2765.5(5)	2835.6(6)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.272	1.287
<i>F</i> (000)	1120	1160
Range of measurement (°)	1.5 ≤ θ ≤ 27.5	1.5 ≤ θ ≤ 25.0
<i>h, k, l</i> min./max.	20, 0, 0/20, 10, 29	18, 9, 28/18, 9, 28
<i>R</i> _{int}	—	0.049
No. of measured reflections	6316	9925
No. of independent reflections	6316	4969
No. of reflections used in refinement	6258	4949
No. of observed data (<i>I</i> > 2σ(<i>I</i>))	3684	2424
No. of refined parameters	356	361
Weighting scheme		
<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (<i>a</i> · <i>P</i>) ² + <i>b</i> · <i>P</i>],	<i>a</i> = 0.0341,	<i>a</i> = 0.0505,
<i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	<i>b</i> = 1.54	<i>b</i> = 3.00
Min./max. Δρ (e Å ⁻³)	−0.219/0.215	−0.213/0.289
<i>R</i> 1/ <i>wR</i> 2/ <i>S</i> (observed data)*	0.0567/0.1041/1.115	0.0705/0.1470/1.138
<i>R</i> 1/ <i>wR</i> 2/ <i>S</i> (all data)*	0.1252/0.1564/1.147	0.1561/0.2070/1.048

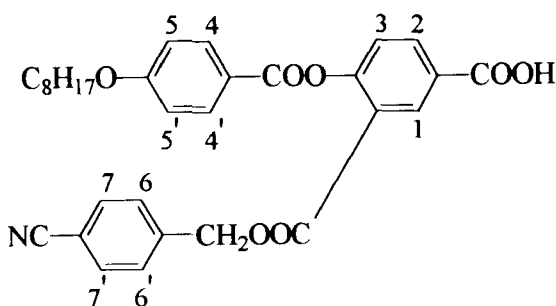
* Values of *R*1, *wR*2 and *S* are defined as $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

temperature and after that 3 h at 60°C. The mixture is filtered through a short column of silica gel, the toluene is evaporated and the products are recrystallized from cyclohexane (**2a, b**) or from ethanol (**2c**), respectively.

no.	X	m.p. (°C)	yield (%)
2a	H	82–84	73.8
2b	CN	89–91.5	57.3
2c	NO ₂	101–102.5	61.8

3.1.4 3-(4-Subst.-benzyloxycarbonyl)-4-(4-*n*-octyloxybenzoyloxy)benzoic acids **3a–c**

5.84 mmol of the formyl compounds **2a–c** and 200 ml acetic acid are heated at 50°C. 1.10 g (11.1 mmol) chromium trioxide, dissolved in 90% acetic acid, are added slowly. The mixture is stirred at 60°C for 12 h. The precipitate is filtered and recrystallized from toluene/heptane (yields: 47–66%). Acting for all substances **3** the analytical data for **3b** are given. $^1\text{H-NMR}$ (CDCl_3 , TMS), δ in ppm: 0.8–1.89 (*m*, 15H, C_7H_{15}); 4.04 (*t*, 2H, $\text{OCH}_2\text{C}_7\text{H}_{15}$); 5.24 (*s*, 2H, COOCH_2); 6.9 (*d*, 2H, $\text{H}_{5,5'}$); 7.3 (*d*, 2H, $\text{H}_{6,6'}$); 7.47 (*d*, 1H, H_3); 7.5 (*d*, 2H, $\text{H}_{7,7'}$); 7.94–8.0 (*q*, 2H, $\text{H}_{4,4'}$); 8.3–8.35 (*q*, 1H, H_2); 8.81 (*d*, 1H, H_1). Elemental analysis, calculated (found): C = 70.32% (70.06%), H = 5.86% (5.89%), N = 2.64% (2.73%).



3.2 X-ray investigations

Colorless needle-shaped crystals of **3b** and **3c**, obtained by recrystallization from an ethanol/cyclohexane mixture (**3b**) and pure ethanol (**3c**), respectively, were cut to give specimens suitable for X-ray diffraction measurements. A summary of crystal data and details of the structure determination are given in Table IV.

The intensity data were measured on a Stoe STADI4 diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation at low temperature ($T = 200\text{ K}$) in the case of **3b** but at room temperature for **3c**. Lattice parameters were derived by least-squares treatment of the setting angles for 72 (for **3b**) and 78 reflections (for **3c**), respectively. Lorentz and polarization corrections were applied during data reduction but absorption and extinction effects were neglected. Both structures were solved by direct methods²⁸ and defined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms.²⁹ The hydrogen atoms were placed at their geometrically calculated positions and refined isotropically using the riding model with the exception of the carboxylic H atoms in **3b**. Its position was derived from a difference Fourier map and refined independently.

Final atomic parameters of the non-hydrogen atoms are given in Table V. 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 numbers CSD-401081 (**3b**) and CSD-401080 (**3c**), the names of the authors, and the journal citation.

TABLE V

Final fractional atomic coordinates and equivalent displacement parameters (\AA^2) of **3b** and **3c**, $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Atom	3b				3c			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
C1	-0.6419(3)	1.6554(5)	0.2271(2)	0.063(1)	-0.6412(8)	1.659(1)	0.2275(4)	0.244(7)
C2	-0.6500(2)	1.4880(4)	0.2601(1)	0.056(1)	-0.6365(10)	1.503(2)	0.2525(5)	0.273(9)
C3	-0.6565(2)	1.3259(4)	0.2223(1)	0.051(1)	-0.6424(7)	1.343(2)	0.2203(4)	0.220(6)
C4	-0.5799(2)	1.2932(4)	0.1897(1)	0.047(1)	-0.5713(6)	1.283(2)	0.1966(4)	0.214(6)
C5	-0.5876(2)	1.1266(5)	0.1542(2)	0.055(1)	-0.5805(5)	1.119(1)	0.1659(4)	0.187(5)
C6	-0.5130(2)	1.0963(5)	0.1193(1)	0.055(1)	-0.5059(6)	1.088(1)	0.1298(4)	0.214(6)
C7	-0.4292(2)	1.0495(5)	0.1566(1)	0.046(1)	-0.4380(4)	1.023(1)	0.1534(4)	0.185(5)
C8	-0.3597(2)	1.0138(4)	0.1192(1)	0.045(1)	-0.3687(4)	-0.9913(9)	0.1108(3)	0.128(3)
C9	-0.2123(1)	0.9209(3)	0.1324(1)	0.0346(8)	-0.2202(3)	0.9061(6)	0.1249(2)	0.079(2)
C10	-0.1427(2)	0.8629(4)	0.1711(1)	0.0373(8)	-0.1502(3)	0.8560(6)	0.1626(2)	0.080(2)
C11	-0.0682(2)	0.8124(3)	0.1505(1)	0.0326(7)	-0.0739(3)	0.8118(6)	0.1440(2)	0.067(2)
C12	-0.0620(1)	0.8191(3)	0.0913(1)	0.0298(7)	-0.0659(3)	0.8156(5)	0.0869(2)	0.058(1)
C13	-0.1317(2)	0.8773(4)	0.0530(1)	0.0376(8)	-0.1358(3)	0.8675(6)	0.0491(2)	0.076(2)
C14	-0.2070(2)	0.9294(4)	0.0732(1)	0.0385(8)	-0.2132(3)	0.9128(7)	0.0679(2)	0.083(2)
C15	0.0159(2)	0.7663(3)	0.0670(1)	0.0344(8)	0.0138(3)	0.7667(6)	0.0647(2)	0.064(2)
C16	0.1607(1)	0.6929(3)	0.0900(1)	0.0297(7)	0.1590(3)	0.6911(6)	0.0886(2)	0.058(1)
C17	0.1802(1)	0.5176(3)	0.08328(9)	0.0284(7)	0.1794(2)	0.5174(5)	0.0839(2)	0.055(1)
C18	0.2580(1)	0.4783(4)	0.0636(1)	0.0327(8)	0.2584(3)	0.4777(6)	0.0654(2)	0.062(2)
C19	0.3145(1)	0.6075(3)	0.0519(1)	0.0319(7)	0.3146(3)	0.6055(6)	0.0527(2)	0.059(2)
C20	0.2947(2)	0.7807(3)	0.0607(1)	0.0349(8)	0.2936(3)	0.7788(6)	0.0597(2)	0.068(2)
C21	0.2174(2)	0.8232(3)	0.0798(1)	0.0347(8)	0.2158(3)	0.8205(6)	0.0778(2)	0.069(2)
C22	0.3955(2)	0.5603(4)	0.0292(1)	0.0366(8)	0.3967(3)	0.5607(7)	0.0306(2)	0.066(2)
C23	0.1261(2)	0.3665(3)	0.0963(1)	0.0317(7)	0.1252(3)	0.3662(6)	0.0972(2)	0.061(2)

TABLE V (Continued)

Atom	3b				3c			
	x/a	y/b	z/c	U _{eq}	x/a	y/b	z/c	U _{eq}
C24	-0.0045(2)	0.2611(4)	0.1217(1)	0.0375(8)	-0.0062(3)	0.2603(6)	0.1212(2)	0.074(2)
C25	-0.0895(2)	0.3309(3)	0.1334(1)	0.0339(8)	-0.0931(3)	0.3295(5)	0.1313(2)	0.063(2)
C26	-0.1137(2)	0.3212(4)	0.1887(1)	0.0434(9)	-0.1177(3)	0.3294(6)	0.1847(2)	0.076(2)
C27	-0.1927(2)	0.3819(4)	0.1997(1)	0.048(1)	-0.1975(3)	0.3916(7)	0.1944(2)	0.081(2)
C28	-0.2481(2)	0.4552(4)	0.1547(1)	0.0399(9)	-0.2522(3)	0.4510(6)	0.1491(2)	0.065(2)
C29	-0.2244(2)	0.4678(4)	0.0989(1)	0.0408(9)	-0.2301(3)	0.4526(6)	0.0956(2)	0.074(2)
C30	-0.1458(2)	0.4042(4)	0.0884(1)	0.0386(8)	-0.1502(3)	0.3917(6)	0.0872(2)	0.073(2)
C31	-0.3305(2)	0.5226(4)	0.1654(1)	0.053(1)	—	—	—	—
N1	-0.3958(2)	0.5747(4)	0.1737(1)	0.075(1)	-0.3378(3)	0.5179(6)	0.1585(2)	0.088(2)
O1	-0.2829(1)	0.9674(3)	0.15712(7)	0.0450(6)	-0.2936(2)	0.9452(5)	0.1475(2)	0.111(2)
O2	0.08452(9)	0.7445(2)	0.10968(7)	0.0307(5)	0.0813(2)	0.7438(4)	0.1066(1)	0.060(1)
O3	0.0218(1)	0.7428(3)	0.01652(7)	0.0606(8)	0.0225(2)	0.7461(6)	0.0160(1)	0.103(2)
O4	0.4083(1)	0.4068(3)	0.01535(8)	0.0487(7)	0.4450(2)	0.6816(5)	0.0182(2)	0.086(1)
O5	0.4482(1)	0.6845(3)	0.0237(1)	0.0551(7)	0.4128(2)	0.4007(4)	0.0244(1)	0.085(1)
O6	0.1510(1)	0.2193(2)	0.09460(8)	0.0446(6)	0.1506(2)	0.2190(4)	0.0963(2)	0.087(1)
O7	0.0492(1)	0.4091(2)	0.11047(7)	0.0349(5)	0.0473(2)	0.4082(4)	0.1102(1)	0.065(1)
O8	—	—	—	—	-0.3904(3)	0.5494(6)	0.1174(2)	0.116(2)
O9	—	—	—	—	-0.3530(3)	0.5405(6)	0.2065(2)	0.124(2)

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