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The synthesis of nitroaniline monomers and polymers as non-linear optical ferroelectric liquid crystals

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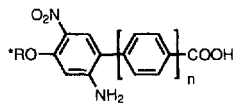
Chiral 2-amino-4-alkoxy-5-nitrobenzoate and 5-amino-4-alkoxy-2-nitrobenzoate derivatives as well as the corresponding biphenyl derivatives were synthesized. Some of them were also derivatised to the corresponding acrylates and polyacrylates. Many of the new substances exhibit a large spontaneous polarization and large second order NLO coefficients. In addition some of them show a broad range S_C^* phase. All these properties depend strongly on small changes in the molecular structures. Here we present the synthesis of these novel NLO FLC materials and discuss some of their properties.

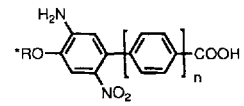
1. Introduction

Nitroanilines are among the most efficient organic substances exhibiting non-linear optical (NLO) activity [1]. If such molecules, possessing a large hyperpolarizability, are brought to a non-centrosymmetric orientation, second harmonic generation (SHG) is possible. The methods used to orient molecules are usually to grow single crystals (organic and inorganic materials), to produce Langmuir–Blodgett (LB) films or to pole the molecules by strong electric fields. These methods however have some disadvantages such as the difficult growth of single crystals, limited LB layers or too high electric fields for poling. More recently ferroelectric liquid crystals (FLC) were also considered as interesting candidates as NLO active substances [2, 3]. FLC materials are characterized by a non-centrosymmetric orientation and a sometimes strong spontaneous polarization which could result in a large deformation of the molecular orbitals, which in turn could lead to a strong optical non-linearity. However the NLO coefficients of the FLC materials published so far are still much smaller than those of other known materials like $LiNbO_3$ [3]. Relatively weak NLO chromophores and their low concentration in the liquid crystal host mixture are the main reasons for these unsatisfactory results.

Very recently we have presented new FLC materials which exhibit NLO coefficients comparable to the currently best inorganic NLO substances [4]. The basic idea in our materials was to incorporate the nitroaniline chromophore into the rigid core of chiral FLC molecules. The integration of the NLO chromophore has to be such that the acceptor–donor axis in the molecule is approximately perpendicular to the axis of the molecule and as close as possible to the chiral centre. Such a design requires the synthesis of compounds incorporating a phenyl ring with four different and specifically located substituents. Four different building blocks (see the figure) were considered as promising candidates to fulfil the above requirements. The carboxylic group would allow these units to be linked easily to diverse phenolic intermediates suitable for LC formation. To our knowledge the synthesis of type **3** and **4** molecules has not been described in the literature. Of type **1** and **2**, only one derivative corresponding to target **1** has been reported, namely 2-amino-4-methoxy-5-nitrobenzoic acid [5]. Its synthesis included as the final step the nucleophilic substitution of the 4-nitro group by a



1 : n = 0
2 : n = 1



3 : n = 0
4 : n = 1

R* = optically active alkyl

Figure 1. Two pairs of isomeric nitroaniline intermediates as synthetic targets.

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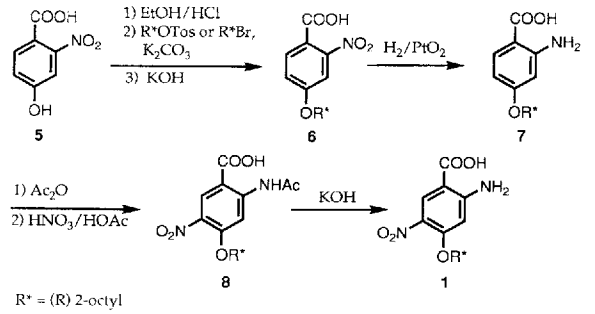
methoxy group in 2-amino-4,5-dinitrobenzoic acid using strongly alkaline methanolic solution. These conditions seemed rather unpromising for the introduction of a secondary chiral alkoxy group. Therefore a new general synthetic concept was required.

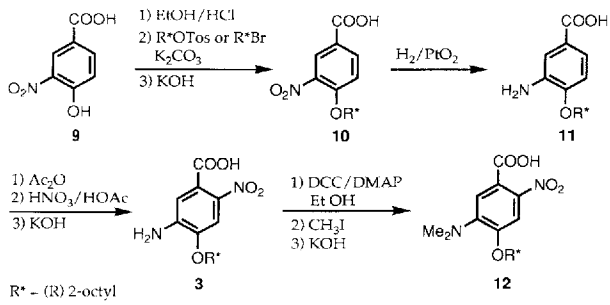
2. Synthesis

For the synthesis of 4-alkoxy-2-amino-5-nitrobenzoic acids (for example, **1**, scheme 1), 4-hydroxy-2-nitrobenzoic acid **5** was synthesized from *p*-toluidine in five steps according to the literature [6]. In absolute ethanol, compound **5** was then esterified by passing HCl gas through the reaction solution to give the corresponding ethyl benzoate. In the next step the side chain was introduced by alkylation of the phenolic function with alkyl bromide or the *p*-tosylate in 2-butanone at 85°C. Saponification in the third step gave the chiral acid **6**. The reduction of the nitro to the amino group was then carried out by hydrogenation in ethanol using PtO_2 as catalyst to give **7**. This compound was subsequently protected by acetylation of the amino group. The nitration of the resulting acetamide to yield **8** is a key step. Here a 1:1 mixture of fuming nitric acid and glacial acetic acid was employed. Alkaline cleavage of the *N*-acetate finally gave the title compound **1**.

For the synthesis of 4-alkoxy-5-amino-2-nitrobenzoic acids (for example, **3**, scheme 2), commercially available



Scheme 1. Synthesis of optically active 4-alkoxy-2-amino-5-nitrobenzoic acids (for example, **1**).

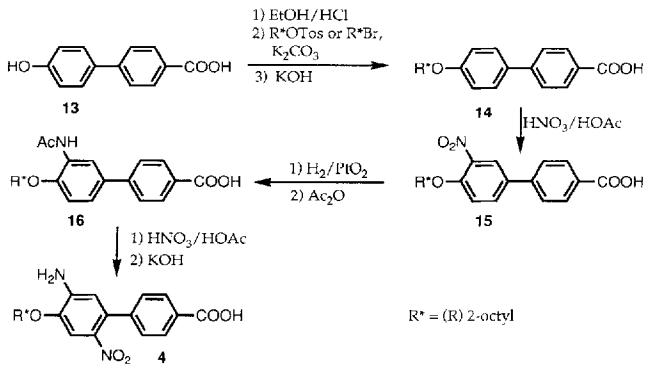


Scheme 2. Synthesis of optically active 4-alkoxy-5-amino-2-nitrobenzoic acids (for example, **3**) and the corresponding *N*,*N*-dimethylamino derivative (**12**).

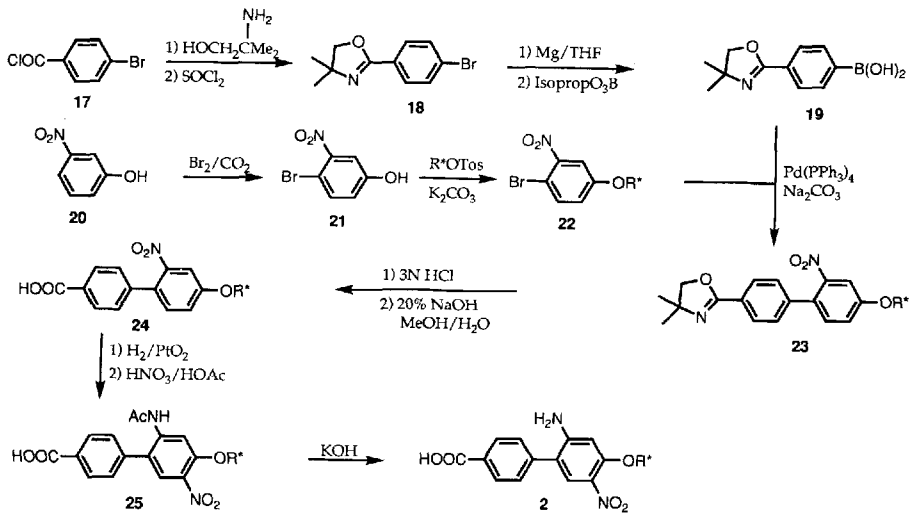
4-hydroxy-3-nitrobenzoic acid (**9**) served as starting material. The title compounds were obtained by analogous synthetic steps to those described for isomer **1**. The nitration of the *N*-acetyl derivative of **11**, however, was carried out in a 4:3 mixture of fuming nitric acid and glacial acetic acid. To obtain 5-dimethylamino-2-nitro-4-(2-octyloxy)benzoic acid (**12**) the ethyl ester of **3** was treated with methyl iodide/$NaHCO_3$ to give a mixture of the *N*-methyl- and *N*,*N*-dimethyl derivatives which had to be separated by column chromatography. Alkaline cleavage of the ester finally gave **12**.

The synthesis of the bicyclic (*R*)-4-[5-amino-2-nitro-4-(2-octyloxy)phenyl]benzoic acid (**4**) with the substitution pattern analogous to **3** started from 4-hydroxybiphenyl-4′-carboxylic acid (**13**), scheme 3). After esterification, alkylation and saponification of the ester group, the chiral alkoxy acid **14** was obtained. This was subsequently nitrated on an analogous manner to that described by Gray *et al.*, for other biphenyl derivatives [7]. The remaining steps were performed according to the methods for the monocyclic compounds, except that the nitration of the amide **16** was performed with HNO_3/HOAc (2:5) at 0°C. Under these relatively mild conditions, the ring bearing the activating substituents (alkoxy and acetamide) was nitrated exclusively and only *para* to the amide group.

Due to the opposite substitution pattern of nitro and amino groups, it was difficult to design a synthesis of (*R*)-4-[2-amino-5-nitro-4-(2-octyloxy)phenyl]benzoic acid (**2**) starting directly from a biphenyl derivative. Therefore it seemed advisable to synthesize the biphenyl moiety by an aromatic coupling of suitably substituted phenyl derivatives (scheme 4). A powerful method for the coupling of unlike aromatic compounds is the Pd(0)-catalysed cross coupling of functionalized aryl boronic acids with aryl bromides [8,9]. As appropriate intermediates for this step a protected 4-carboxyphenylboronic acid and 4-alkoxy-2-nitro bromobenzene were chosen.



Scheme 3. Synthesis of optically active 4-[4-alkoxy-5-amino-2-nitrophenyl]benzoic acids (for example **4**).

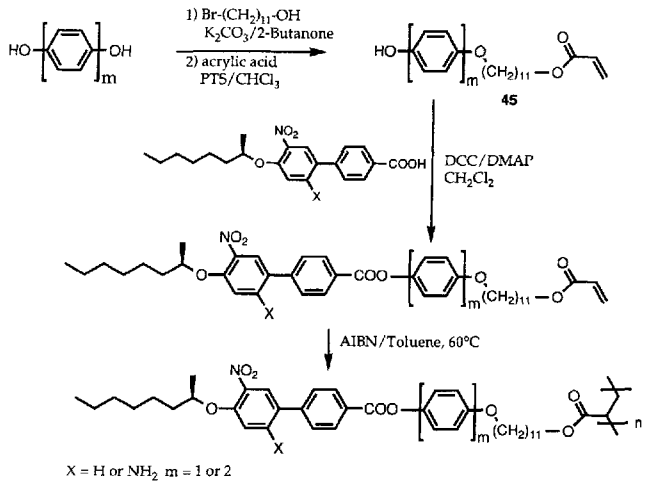


Scheme 4. Synthesis of optically active 4-[4-alkoxy-2-amino-5-nitrophenyl]benzoic acids (for example **2**).

The synthesis of the protected 4-carboxy phenyl boronic acid **19** started from 4-bromobenzoyl chloride (**17**), which reacted with 2-amino-2-methyl-1-propanol in two steps to give 2-(*p*-bromphenyl)-4,4-dimethyl-4,5-dihydro-oxazole (**18**). After formation of the Grignard reagent, tri-isopropyl borate was used at −70°C to give the di-isopropylboronate which after acid hydrolysis yielded the phenylboronic acid **19**. To synthesize 4-alkoxy-2-nitrobromobenzene **22**, 3-nitrophenol (**20**) was brominated at 130–140°C by passing a stream of Br_2/CO_2 through the reaction mixture, followed by alkylation of the phenol **21** with 2-octyl tosylate. The aryl–aryl cross coupling between **19** and **22**, catalysed by tetrakis(triphenylphosphine)palladium(0), occurred smoothly in aqueous Na_2CO_3 and toluene to give the asymmetrical biphenyl derivative **23** in more than 80 per cent yield. To liberate the carboxylic acid group, **23** was in turn hydrolysed first by 3 M HCl and then by 20 per cent NaOH. The final synthetic steps from **24** over **25** to **2** are analogous to those in the synthesis of the above 4-alkoxy-2-amino-5-nitrobenzoates (for example, **1**).

The monocyclic and bicyclic carboxylic acids **1**–**4** obtained according to the above procedures were finally esterified with suitably substituted phenol derivatives by a combination of dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP). The phenolic components chosen are well-known intermediates usually employed for the synthesis of liquid crystal materials.

For the synthesis of the monomeric acrylates and the corresponding polyacrylates, in principle the same route was followed as described above. The polymerizable acrylate units as well as the required spacers were attached to the phenolic part as described in scheme 5. Polymerizations were performed according to standard



Scheme 5. Synthesis of acrylates and polyacrylates from optically active 4-[4-alkoxy-2-amino-5-nitrophenyl]benzoic acids and 4-[4-alkoxy-5-nitrophenyl]-benzoic acids.

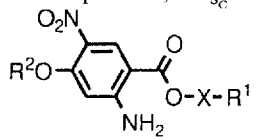
radical polymerization methods, for example, [10] using α,α′-azo-isobutyronitrile (AIBN).

3. Results and discussion

3.1. *Nitroaniline esters*

A variety of 1,4-nitroaniline esters formed from **1** or **3** and some of their physical properties are shown in table 1 and 2, respectively. None of them exhibits a mesophase except compound **30**, where a metastable monotropic phase was observed for a very short time on cooling from the isotropic phase. The relatively large nitro and amino groups obviously disturb the rod-like molecular structure which normally is necessary for mesophase formation. In compound **32**, which differs

Table 1. Melting points, spontaneous polarizations (P_s) and intensities (qualitative) of second harmonic generation (SHG) of chiral 2-amino-5-nitrobenzoates; P_s was measured in SMK-1796 (concentration = 7 per cent, $\Delta T_{S_C^*} = 15°C$, extrapolated to 100 per cent).



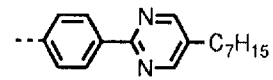
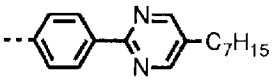
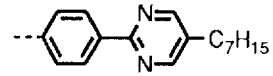
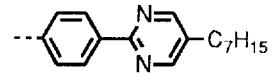
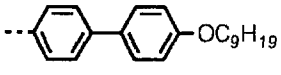
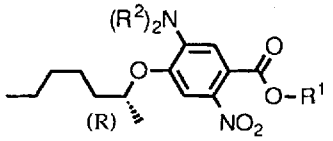
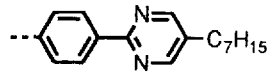
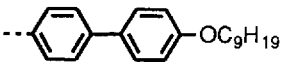
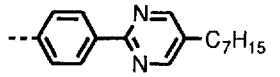
No.	R^1	X	R^2	m.p./°C	P_s/nC^{-1} cm^{-2}	SHG
26		—C*H(CH)$_3$COO—	—CH$_3$	148	0	–
27		—	—CH$_3$	206	0	–
28		—	(*S*)—CH$_2$C*H(CH$_3$)C$_2$H$_5$	150	5	–
29		—	(*R*)—C*H(CH$_3$)C$_6$H$_{13}$	92·4	38	+
30		—	(*R*)—C*H(CH$_3$)C$_6$H$_{13}$	132·3–134·3	58	+

Table 2. Melting points, spontaneous polarizations (P_s) and intensities (qualitative) of second harmonic generation (SHG) of chiral 2-nitro-5-aminobenzoates; P_s was measured in SC9-1219 (1) or SC0-0702 (2) (concentration = 7 per cent, $\Delta T_{S_C^*} = 15°C$, extrapolated to 100 per cent).



No.	R^1	R^2	m.p./°C	P_s nC$^+$ cm^{-2}	SHG
31		H	105	8[1]	+
32		H	140·5–142	131[1]	+
33		$-CH_3$	59·5–62·4	5[2]	+

from its isomer **30** only by change in the positions of nitro and amino groups, the metastable monotropic phase is not present. The bulkier nitro group is closer to the centre of the molecule in **32** than in **30** and therefore disturbs the rod-like molecular shape to a higher extent.

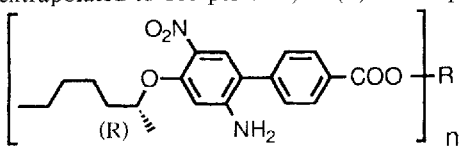
The magnitude of the spontaneous polarization, measured in a S_C host 15°C below the transition temperature of S_C^*/S_A, is strongly dependent on the nature and position of the chiral side chain, the substitution pattern of the nitroaniline ring and the nature of the additional aromatic rings. As expected, higher values were measured for those compounds which have the centre of chirality closest to the rigid core (cf. **28** and **29**). The chiral lactate used as a linking unit in **26** exhibits too low a P_s to be measured. Comparison of compound **30** with **32** leads to the conclusion that the position of the amino group *ortho* to the chiral centre is more favourable for a higher P_s than the opposite pattern. That this is not generally true is obvious from comparison of **29** and **31**. Unexpectedly, the vary large dimethylamino group in the neighbourhood of the chiral centre of **33** and its increased polarizability has no effect in increasing the spontaneous polarization as compared with **31**. Macroscopically, the smaller measured P_s of **33** is possibly due to poor molecular orientation. Comparison of **29**, **30** and **31**, **32** shows that the alkoxybiphenyl substructure leads to substantially higher P_s values than the alkylphenylpyrimidine moiety. This might be at least partly due to very different switching angles.

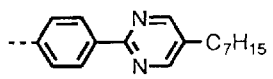
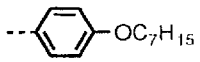
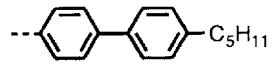
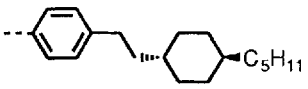
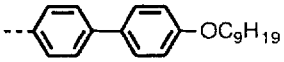
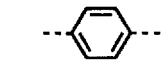
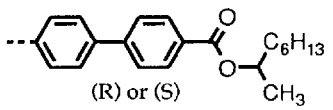
The investigation of the non-linear optical properties of these compounds was concentrated on the second harmonic generation (SHG) using the 1064 nm light of a pulsed Nd:YAG laser (Spectra Physics DCR-11). The results are included in tables 1 and 2 in a qualitative manner. The relative intensities of the SHG signals were measured using pure powders or dopants in a S_C host and are represented by '−' or '+'. The detailed measurement method and related set up have been previously reported [4]. Like the spontaneous polarizations, the SHG signals are strongly dependent on the nature of the chiral unit, but almost unchanged by the presence of a phenyl instead of a pyrimidine ring. Thus the SHG signals of **31** and **32** are of similar magnitude despite the considerably higher P_s of the latter. A large spontaneous polarization normally means good molecular orientation and a large dipole moment coupled with the centre of chirality. This should also lead to large nonlinearity. The inconsistency observed here might be caused by the S_C host.

3.2. *Phenyl substituted nitroanilines*

In comparison to the nitroanilines discussed above, the compounds now considered are characterized by an additional phenyl group directly linked to the nitroaniline moiety (see table 3 and 4). In the series with the nitro group *ortho* to the chiral side chain (see table 3), enantiotropic mesophases are frequently observed in contrast to the compounds possessing the opposite substitution pattern (see table 4), where only **42** exhibits a monotropic mesophase. This difference between both groups is in accordance with the findings already discussed for the nitroaniline series. Generally four ring systems (**36**–**38**) possess more thermally stable mesophases than three ring systems (**35**). However, when the 2-amino-5-nitro substituted biphenyl system is combined with

Table 3. Phase transitions, spontaneous polarizations (P_s) and relative intensities (qualitative) of second harmonic generations (SHG) of chiral 2′-amino-5′-nitrobiphenyl-4-carboxylic esters; P_s was measured in (1) SMK 1796 (concentration = 7 per cent, $\Delta T_{S_C^*} = 15°C$, extrapolated to 100 per cent) or (2) on the pure substance.



No.	*n*	*R*	Cr	S_C^*	S_A	N*	I	P_s/nC^{-1} cm^{-2}	SHG
34	1		• 176				•	141[1]	+
35	1		• 91		(• 74)		•	208[1]	+ + +
36	1		• 142		• 160·8	• 168·1	•	207[1]	+ +
37	1		• 110	(• 62)	• 132	• 139	•	179[2]	+ + +
38	1		• 80	• 132	• 186		•	306[2]	+ + +
39	2		• 175		• 186	• 201	•	139[1]	+
40	1		• 145 (*R*)				•		+
a/b			135(*S*)						

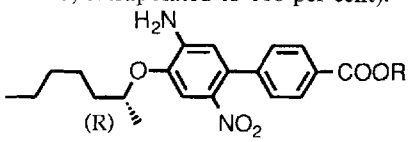
4-(heptyl-2-pyrimidinyl)phenol, usually considered as an efficient building block for smectic phases (compound **34**), no mesomorphic behaviour could be observed. The ease of crystallization, probably caused by intermolecular hydrogen bridge formation of the amino group with one of the pyrimidinyl nitrogen atoms, possibly prevents observation of an LC phase. Comparison of the three ring compound **35** with the three membered nitroaniline **30** of table 1 indicates that the biphenyl structure of **35** stabilises the mesophase more efficiently than its isomer **30**. The 2-amino-5-nitrobiphenyl substructure consequently leads to a better compensation for the lateral extension than the corresponding phenyl benzoate.

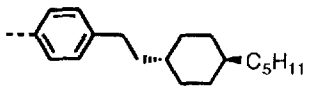
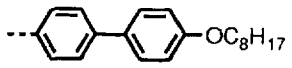
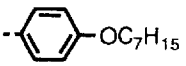
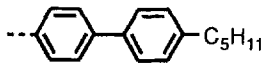
Compounds **37** and **38** exhibit chiral smectic C phases, in which a large spontaneous polarization can be measured directly. The maximum P_s measured for **38** is more than 750 nC cm^{-2}. More detailed phase assignments and deeper investigations of the ferroelectric properties of these compounds are to be found in our earlier report [4].

Introduction of a second chiral centre to give the five ring compound **39** or the epimers **40 a** and **40 b** does not increase, but rather decreases the spontaneous polarization. With **40 a** and **40 b**, obviously a compensation of P_s from both chiral centres occurs. Its independence of the combination of *R,R* or *R,S* chirality is difficult to understand.

The investigations of the non-linear optical properties reveal that the derivatives where the nitro group is *ortho* to the chiral side chain give very strong NLO effects. In table 3 the relative intensities of the SHG signals are collated. The strongest SHG signals were observed for compounds **35**, **37**, and **38** (represented by '+ + +'). For compound **38** and for a 1:1 mixture of compounds **37** and **38**, the non-linear coefficients d_{22} were quantitatively determined. This was done using thin homeotrop-

Table 4. Phase transitions, spontaneous polarizations (P_s) and relatives intensities (qualitative) of second harmonic generation (SHG) of chiral 2′-nitro-5′-aminobiphenyl-4-carboxylic esters; P_s was measured in SMK 1796 (concentration = 7 per cent, $\Delta T_{S_C^*}$ = 15°C, extrapolated to 100 per cent).



No.	R	Cr	N*	I	P_s/nC^{-1} cm^{-2}	SHG
41		• 166·5–167·6		•	153	+
42		• 177·8–180·5	(• 150)	•		
43		• 136·5–138·9		•		
44		• 187·2–188·3		•		

ically aligned cells in the unwound helical configuration. Comparison with the quartz standard gave d_{22} = 5 pm V^{-1} for compound **38** and d_{22} = 2·1 pm V^{-1} for the mixture **37**/**38**. These second order NLO responses are the largest observed so far in ferroelectric liquid crystals [4] and comparable to that of inorganic NLO single crystals like $LiNbO_3$.

3.3. *Monomeric and polymeric acrylates*

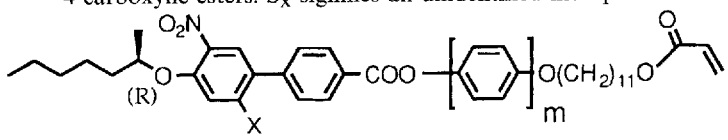
From the nitroanilines described, the successful structural principles of compounds **35** and **38** were selected for use in acrylate and polyacrylate formation. In addition, the corresponding nitrobiphenyl derivatives (without the amino group) were synthesized. The phase transitions of the monomers are listed in table 5. Acrylate **46**, containing four aromatic rings exhibits a relatively broad mesophase range, including a monotropic chiral smectic C phase. With the three ring acrylate **47**, only two crystalline states were observed. Compared to **46**, nitro derivative **48** exhibits a broader mesophase range. However, the smectic A phase disappears and an unidentified, highly ordered smectic phase (S_X) emerges between the crystalline and chiral smectic C phases. A short range monotropic S_A phase is observed however for compound **49**.

As expected, all the corresponding side chain polymers show broad range liquid crystal phases (see table 6). Compared to the monomers, some changes in mesophase types occur after polymerization. The cholesteric phases of the monomers **46** and **48** are no longer observed in the corresponding polymers. Some phase structures emerging in the polymers, such as in compound **50**, are still not clear. Chiral S_C phases were observed for compounds **51** and **53**. It is interesting to note that the influence of the amino group on the mesophase range of the polymers seems to be suppressed, as seen by comparing the clearing points of the nitroanilines **50** and **51** with those of the nitro compounds **52** and **53**, respectively. The polymers with four ring cores in the side chains (**50** and **52**) reach clearing points up to 270°C, while those with three ring cores are still around 132–139°C. The glass transitions of polymers **50**, **51** and **53** have not been exactly determined due to the small ΔCp on freezing highly ordered smectic phases, combined with the broad molecular weight distribution of the polymers. Studies of the exact phase assignments and detailed investigations of the mesomorphic and non-linear optical properties are in progress.

4. Conclusions

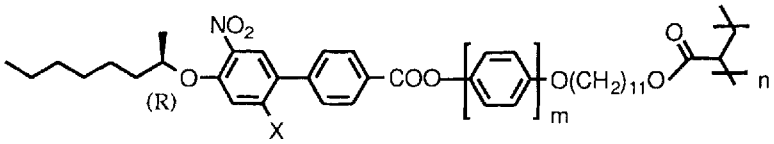
The incorporation of the nitroaniline substructure into rod-like molecules gives rise to a large non-linearity if the dipole moment of the chromophore is coupled with the chiral centre. The intensity of SHG strongly depends on the ability for mesophase formation. By far the best compounds in this respect are the *para*-nitroaminobiphenyls. Of the two possible isomers incorporating amino and nitro groups in the *para*-position, those with the nitro group *ortho* to the chiral side chain form more stable mesophases and consequently exhibit stronger SHG efficiency.

Table 5. Phase transitions of monomeric acrylates incorporating 3′-nitrobiphenyl-4-carboxylic esters or 2′-amino-5′-nitrobiphenyl-4-carboxylic esters. S_X signifies an unidentified mesophase.



No.	*X*	*m*	Phase transitions °C
46	NH_2	2	$Cr \xrightarrow[84{\cdot}5]{110} S_C^* \xrightarrow[134]{136} S_A \xrightarrow[136]{137} Ch \longrightarrow I$
47	NH_2	1	$Cr1 \xrightarrow{56{\cdot}6-58} Cr2 \xrightarrow{68} I$
48	H	2	$Cr \xrightarrow{90} S_X \xrightarrow{96{\cdot}5} S_C^* \xrightarrow{126} Ch \xrightarrow{149} I$
49	H	1	$Cr \xrightarrow[32]{65{\cdot}7-68} S_A \xrightarrow[41]{} I$

Table 6. Phase transitions of polyacrylates incorporating 3′-nitrobiphenyl-4-carboxylic esters or 2′-amino-5′-nitrobiphenyl-4-carboxylic esters as side chains. S_X signifies an unidentified mesophase.



No.	*X*	*m*	Phase transitions °C
50	NH_2	2	$G \xrightarrow{?} LC \xrightarrow{270} I$
51	NH_2	1	$G \xrightarrow[118]{?} S_C^* \xrightarrow[127]{132} S_A \longrightarrow I$
52	H	2	$G \xrightarrow{90} S_X \xrightarrow{110} S_A \xrightarrow{260} I$
53	H	1	$G \xrightarrow[?]{?} S_C^* \xrightarrow[134]{139} S_A \longrightarrow I$

5. Experimental

^1H NMR spectra were recorded at 250 MHz with a Bruker HX-250 spectrometer, and mass spectra with a MS9 (AEZ, Manchester) spectrometer. IR spectra were measured with solid samples in KBr and with liquid films for liquid samples. A polarization microscope, Leitz Ortholux II POL BK, in conjunction with a Mettler FP 82 heating stage and a FP 80 control unit, was used for the measurement of melting points and the observation of phase transitions. The purity of the compounds was determined by thin layer chromatography (TLC); 4 × 8 cm precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0·25 mm (Macherey–Nagel) were utilized. Colum chromatography was carried out using silica-gel 60 (230–400 mesh ASTM).

5.1. *General synthetic procedures*

5.1.1. *Ethyl esters of benzoic acids*

The hydroxy–benzoic acid (0·05 mol) was dissolved in 370 ml of absolute alcohol and dry hydrogen chloride gas was passed through with stirring. The temperature rose to about 65°C and then fell to 35°C. After 5 h, the reaction mixture was poured into 1300 ml of ice water. The solid was separated and washed with 50 per cent alcohol. After recrystallization from diluted alcohol and drying the pure ethyl esters were obtained in yields of about 70 per cent.

5.1.2. *Alkylation of phenols*

19 mmol of the phenol, 19 mmol of 2-methylbutyl bromide or of optically active 2-octyl tosylate, 45 mmol of powdered K_2CO_3 and 110 ml of 2-butanone were heated to reflux at about 87°C for 25 h. Then the reaction mixture was cooled and the solid filtered off. The filtrate was evaporated to dryness, and the residue purified by silica gel column chromatography, providing the pure product in about 90 per cent yield.

5.1.3. *Reduction of nitro groups*

5·35 mol of the nitro-derivative, 0·1 g PtO_2 and 50 ml of absolute ethanol were mixed together and degassed under vacuum. Then hydrogen (produced by an electrical hydrogen generator) was passed into the mixture at room temperature until the absorption of H_2 ceased. Thereafter, the catalyst was filtered off and the solvent evaporated. The residue was purified by column chromatography using silica gel with CH_2Cl_2 as eluent. The yield generally was higher than 95 per cent.

5.1.4. *Acetylation of amino groups*

5 mmol of the amino-derivative was dissolved in 12 ml of acetic anhydride. The solution was stirred at 90°C for 1 h, cooled and poured slowly into 200 ml of ice cold water. Upon cooling a white solid separated. This was collected, dried and recrystallized from ether/ethyl acetate. The yield of the pure amide was generally about 90 per cent.

5.1.5. *Nitration of 2-acetylamino-4-(2-octyloxy)benzoic acid*

To a solution of fuming HNO_3 and glacial acetic acid (0·5 ml/0·5 ml), which was cooled in an ice/water bath, 0·1 g of 2-acetylamino-4-(2-octyloxy)benzoic acid was added in portions with stirring. Then the reaction mixture was warmed to room temperature and stirred for 1·5 h. Thereafter the reaction mixture was poured onto 5 g of cracked ice. The precipitated yellow solid was separated and dissolved in dilute aqueous Na_2CO_3 solution at 65°C. Insoluble material was filtered off and the filtrate neutralized with HCl. On cooling, the crude product was precipitated, filtered and used directly for the next reaction step.

5.1.6. *Deprotection of amino groups*

1 mmol of the acetylamino benzoic acid was dissolved in 10 ml of 10 per cent aqueous KOH and heated under reflux for 2 h. Then the cooled reaction solution was neutralized with acetic acid. The yellow precipitate was separated and recrystallized from 50 per cent alcohol to give the free amine in yields of 75 per cent.

5.1.7. *Esterification of benzoic acids with phenols*

0·19 mmol of the benzoic acid, 0·25 mmol of the phenol, 0·22 mmol of DCC, 0·01 mmol of DMAP and 10 ml of CH_2Cl_2 were mixed and stirred at room temperature under N_2 for 2 d. Then the precipitated solid was filtered off through celite and the filtrate evaporated to dryness. The residue was purified by silica gel column chromatography and the pure product obtained in yields generally $>80\%$.

5.2. *Amino-nitrobenzoic acids and esters*

The synthesis of 4-hydroxy-2-nitrobenzoic acid was carried out according to the literature [3]. For the other steps, the above described general procedures were used. The compounds exhibited the following spectral data:

4-Hydroxy-2-nitrobenzoic acid (**5**): ^{1}H NMR (DMSO) ppm: 7·07/7·16/7·77 ($J=8·5+2·5$, 3 H), 11·2 (s, 1 H), 13·4 (s, 1 H). MS *m/e* (per cent): 183 (M^+, 100), 166 (M-OH, 12), 137 (M-NO_2, 35). IR cm^{-1}: 3365 (OH), 2672, 2542 (COOH), 1695, 1292 (C=O), 1610, 1458 (aromat. C=C), 1551, 1380 (NO_2).

(R)-2-Nitro-4-(2-octyloxy)benzoic acid (**6**): ^{1}H NMR ($CDCl_3$) ppm: 0·880 (t, $J=6·9$, 3 H), 1·29–1·80 (m, 10 H), 1·31 (d, $J=6$, 3 H), 4·46 (m, 1 H), 7·01/7·14/7·84 ($J=8·75+2·5$, 3 H). IR cm^{-1}: 2678, 2558 (COOH), 1708, 1247 (COO), 1612 (aromat. C=C), 1541, 1322 (NO_2).

(R)-2-Amino-4-(2-octyloxy)benzoic acid (**7**): ^{1}H NMR (DMSO) ppm: 0·87 (t, $J=6·9$, 3 H), 1·26 (d, $J=6$ Hz, 3 H), 1·29–1·75 (m, 10 H), 4·43 (m, 1 H), 4·48 (s, 2 H), 6·13/6·21/7·71 ($J=8·75+2·5$, 3 H). MS *m/e* (per cent): 265 (M^+, 18), 180 (M-C_6H_{13}, 1), 153 (M-C_8H_{16}, 96), 125 (M-H_2O/C_8H_{16}, 100).

(R)-2-Amino-5-nitro-4-(2-octyloxy)benzoic acid (**1**): ^{1}H NMR (DMSO) ppm: 0·849 (t, 3 H), 1·31 (d, $J=6·25$, 3 H), 1·21–1·71 (m, 10 H), 4·50 (m, 1 H), 6·48 (s, 1 H), 7·18 (s, 2 H), 8·43 (s, 1 H), 13·0 (s, 1 H). MS *m/e* (per cent): 311 ($M^+ + H$, 25), 295 (M-NH, 12), 199 (M-C_8H_{16}, 100), 181 (M-C_8H_{16}/H_2O, 55). IR cm^{-1}: 3468, 3345 (−NH_2), 3073, 2646, 2571 (−COOH), 1672,

1253 (−COO−), 1620, 1525 (−C=C−), 1545, 1351 ($-NO_2$), 1273 (aryl-ether).

(R)-Ethyl 3-nitro-4-(2-octyloxy)benzoate: ^{1}H NMR ($CDCl_3$) ppm: 0·850 (t, J = 6·25, 3 H), 1·27 (d, J = 6·25, 3 H), 1·16–1·75 (m, 13 H), 4·38 (q, J = 7·25, 2 H), 4·61 (m, 1 H), 7·13/8·16/8·43 (J = 9 + 2·5, 3 H).

(R)-3-Amino-4-(2-octyloxy)benzoic acid (**11**): ^{1}H NMR: (DMSO) ppm: 0·850 (t, J = 7·5, 3 H), 1·25 (d, J = 6·25, 3 H), 1·29–1·80 (m, 10 H), 4·50 (m, 1 H), 4·78 (s, 2 H), 6·83/7·14/7·24 (J = 8·5 + 2·5, 3 H), 12·45 (s, 1 H). MS *m/e* (per cent): 266 (M + H, 22), 153 (M-C_8H_{16}, 100), 136 (M-C_8H_{16}/HO, 40). IR cm^{-1}: 3483, 3384 (−NH), 2659–2523 (−COOH), 1680, 1294 (−C=O), 1593, 1514 (−C=C−), 1148 (aryl-ether).

(R)-3-Acetylamino-4-(2-octyloxy)benzoic acid: ^{1}H NMR (DMSO) ppm: 0·848 (t, J = 7, 3 H), 1·28 (d, J = 6·25, 3 H), 1·25–1·75 (m, 10 H), 2·10 (s, 3 H), 4·55 (m, 1 H), 7·12/7·68/8·53 (J = 8·5 + 2·5, 3 H), 8·85 (s, 1 H), 12·65 (s, 1 H). MS *m/e* (per cent): 307 (M^+, 4·2), 195 (M-C_8H_{16}, 11), 153 (M-C_8H_{16}/$COCH_2$, 100), 43 (CH_3CO^+, 40). IR cm^{-1}: 3330 (−NH), 2643–2548 (−COOH), 1690 (−C=O), 1670 (CONH), 1610, 1543 (−C=C−), 1268 (aryl-ether).

(R)-5-Acetylamino-2-nitro-4-(2-octyloxy)benzoic acid: ^{1}H NMR (DMSO) ppm: 0·894 (t, J = 7·0, 3 H), 1·40 (d, J = 6·25, 3 H), 1·29–1·80 (m, 10 H), 2·28 (s, 3 H), 4·61 (m, 1 H), 7·37 (s, 1 H), 7·92 (s, 1 H), 8·81 (s, 1 H). MS *m/e* (per cent): 352 (M^+, 2·2), 322 (M-NO, 1·7), 308 (M-CO_2, 0·45), 240 (M-C_8H_{16}, 16), 198 (M-C_8H_{16}/$COCH_2$, 58), 43 (CH_3CO^+, 100). IR cm^{-1}: 3255 (−NH), 2646–3088 (−COOH), 1690 (−C=O), 1479, 1248 ($-NO_2$).

(R)-5-Amino-2-nitro-4-(2-octyloxy)benzoic acid (**3**): ^{1}H NMR (DMSO) ppm: 0·897 (t, J = 7, 3 H), 1·33 (d, J = 6, 3 H), 1·30–1·82 (m, 10 H), 4·55 (m, 1 H), 6·67 (s, 1 H), 7·51 (s, 1 H).

(R)-Ethyl 5-N,N-dimethylamino-2-nitro-4-(2-octyloxy) benzoate: 30 mg (0·148 mmol) of (*R*)-ethyl 5-amino-2-nitro-4-(2-octyloxy)benzoate, 130 mg of powdered $NaHCO_3$ and 2·5 ml of MeI were mixed and heated under reflux for 75 h. Then the solution was evaporated to dryness under reduced pressure. The residue was mixed with 20 ml of water and shaken three times with ether. The organic phase was dried over $MgSO_4$ and evaporated. The crude product was purified by chromatography on silica gel with CH_2Cl_2 as eluent. Yield: 32 mg (60 per cent). ^{1}H NMR ($CDCl_3$) ppm: 0·886 (t, J = 7 Hz, 3 H), 1·25–1·85 (m, 13 H), 4·36 (q, J = 7·25 Hz, 2 H), 4·52 (m, 1 H), 4·65 (s, 2 H), 6·72 (s, 1 H), 7·48 (s, 1 H).

4-(5-Heptyl-2-pyrimidinyl)phenyl 2-amino-5-nitro-4-methoxybenzoate (**27**): ^{1}H NMR ($CDCl_3$) ppm: 0·89 (t, J = 7, 3 H), 0·98 (t, J = 7·4, 3 H), 1·11–1·67 (m, 10 H), 2·63 (t, J = 7·5, 2 H), 3·98 (s, 3 H), 6·19 (s, 1 H), 6·61 (s, 2 H), 7·31/8·51 (AA'MM', J = 8·75, 4 H), 8·63 (s, 1 H), 8·96 (s, 1 H). IR cm^{-1}: 3453, 3372 ($-NH_2$), 1743, 1256 (C=O), 1620 (−C=C−), −C=N−), 1508, 1350 ($-NO_2$), 1118, 1018 (aryl-ether).

(S)-4-(5-Heptyl-2-pyrimidinyl)phenyl 2-amino-5-nitro-4-(2-methylbutyloxy)benzoate (**28**): ^{1}H NMR ($CDCl_3$) ppm: 0·89 (t, J = 7, 3 H), 0·98 (t, J = 7·4, 3 H), 1·09 (d, J = 6·75, 3 H), 1·29–1·75 (m, 11 H), 1·65 (m, 4 H), 2·0 (m, 1 H), 2·63 (t, J = 7, 2 H), 3·93 (m, 2 H), 6·15 (s, 1 H), 6·43 (s, 2 H), 7·33/8·50 (A_2B_2, J = 9, 4 H), 8·62 (s, 2 H), 8·94 (s, 1 H). MS *m/e* (per cent): 520 (M^+, 5), 490 (M-NO, 1), 251 (M-$OC_6H_4C_4H_2N_2C_7H_{15}$, 67), 181 (M-$C_5H_{11}$/$OC_6H_4C_4H_2N_2C_7H_{15}$, 100). IR cm^{-1}: 3466, 3352 ($-NH_2$), 3083 (=C−H), 1696 (C=O), 1616, 1548 (−C=C−, −C=N−), 1524, 1300 (NO_2), 1247, 1046 (aryl-ether).

(R)-4-(5-Heptyl-2-pyrimidinyl)phenyl 2-amino-5-nitro-4-(2-octyloxy)benzoate (**29**): ^{1}H NMR ($CDCl_3$) ppm: 0·889 (t, J = 7, 6 H), 1·29–1·75 (m, 20 H), 1·40 (d, J = 6, 3 H), 2·75 (t, J = 6, 2 H), 4·50 (m, 1 H), 6·15 (s, 1 H), 6·35 (s, 2 H), 7·49/8·50 (J = 9, 4 H), 8·62 (s, 2 H), 8·90 (s, 1 H) MS *m/e* (per cent): 562 (M^+, 2·2), 532 (M-NO, 0·75), 450 (M-C_8H_{16}, 0·35), 293 (M-$OC_6H_4C_4H_2N_2C_7H_{15}$, 17). IR cm^{-1}: 3461, 3352 ($-NH_2$), 1710, 1246 (−COO−), 1625, 1483 (−C=C−), 1516, 1379 ($-NO_2$), 1159, 1033 (aryl-ether).

(R)-4-(4-Nonyloxyphenyl)phenyl 2-amino-5-nitro-4-(2-octyloxy)benzoate (**30**): ^{1}H NMR ($CDCl_3$) ppm: 0·889 (t, 6 H), 1·29–2·00 (m, 24 H), 1·40 (d, J = 6, 3 H), 4·50 (m, 1 H), 6·15 (s, 1 H), 6·35 (s, 2 H), 6·98/7·51 (J = 8·75, 4 H), 7·23/7·59 (J = 8·75, 4 H), 8·90 (s, 1 H). MS *m/e* (per cent): 603 (M-H, 78), 491 (M-C_8H_{17}, 40). IR cm^{-1}: 3474, 3354 ($-NH_2$), 1706, 1296 (−COO−), 1632, 1497 (−C=C−), 1547, 1296 ($-NO_2$), 1251 (aryl-ether).

(R)-4-(5-Heptyl-2-pyrimidinyl)phenyl 5-amino-2-nitro-4-(2-octyloxy)benzoate (**31**): ^{1}H NMR ($CDCl_3$) ppm: 0·89 (t, 6 H), 1·37 (d, J = 6, 3 H), 1·20–1·80 (m, 20 H), 2·65 (t, J = 8, 2 H), 4·61 (m, 1 H), 4·72 (s, 2 H), 6·89 (s, 1 H), 7·39/8·49 (J = 8·75, 4 H), 7·57 (s, 2 H), 8·62 (s, 1 H). MS *m/e* (per cent): 532 (M-NO, 0·78), 293 (M-$OC_6H_4C_4H_2N_2C_7H_{15}$, 94), 270 ($HOC_6H_4C_4H_2N_2C_7H_{15}$, 44), 185 ($HOC_6H_4C_4H_2N_2CH_2$, 100).

IR cm^{-1}: 3512, 3399 ($-NH_2$), 1757, 1249 (−COO−), 1619, 1500 (−C=C−), 1530, 1300 ($-NO_2$), 1240 (aryl-ether).

(R)-4-(4-Nonyloxyphenyl)phenyl 5-amino-2-nitro-4-(2-octyloxy)benzoate (**32**): ^{1}H NMR: ($CDCl_3$) ppm: 0·889 (t, $J=7$, 6H), 1·38 (d, $J=6$, 3H), 1·29–1·63 (m, 24H), 3·99 (t, 2H), 4·54 (m, 1H), 4·63 (s, 2H), 6·69 (s, 1H), 6·95/7·60 ($J=8·5$, 4H), 7·31/7·49 ($J=8·75$, 4H), 7·56 (s, 1H). MS *m/e* (per cent): 574 (M-NO, 0·14), 312 ($HOPhPhOC_9H_{19}$, 100), 293 ($M-HOPhPhOC_9H_{19}$, 55). IR cm^{-1}: 3504, 3363 ($-NH_2$), 1752, 1252 (−COO−), 1619, 1493 (−C=C−), 1526, 1299, ($-NO_2$).

(R)-4-(5-Heptyl-2-pyrimidinyl)phenyl 5-N,N-dimethylamino-2-nitro-4-(2-octyloxy)benzoate (**33**): ^{1}H NMR ($CDCl_3$) ppm: 0·89 (t, 6H), 1·39 (d, $J=6$, 3H), 1·20–1·85 (m, 20H), 2·65 (t, $J=8$, 2H), 3·03 (s, 6H), 4·53 (m, 1H), 7·00 (s, 1H), 7·42/8·50 ($J=8·75$, 4H), 7·56 (s, 1H), 8·62 (s, 2H). MS *m/e* (per cent): 321 ($M-HOC_6H_4C_4H_2N_2C_7H_{15}$, 100), 270 ($HOC_6H_4C_4H_2N_2C_7H_{15}$, 11), 209 ($M-HOC_6H_4C_4H_2N_2C_7H_{15}/C_8H_{16}$, 25), 185 ($HOC_6H_4C_4H_2N_2CH_2$, 23). IR cm^{-1}: 1752, 1252 (−COO−), 1570, 1498 (−C=C−), 1522, 1318 ($-NO_2$).

5.3. *Amino-nitrobiphenylcarboxylic acids and esters*

For the alkylation of phenol derivatives (**13**, step 2 in scheme 3 and **21**), esterification of hydroxy-substituted biphenyl carboxylic acid (**13**, step 1 in scheme 3), reduction of the nitro group (**15**, **24**), protection of the amino group (**15** and **24**, step 2 in scheme 4), nitration (**16** and **24**, step 3 in scheme 4), deprotection of amino group (**16**, step 2 in scheme 3 and **25**) and esterification of biphenyl carboxylic acid derivatives the above mentioned general procedures were applied. In addition the following specific reactions were performed:

(R)-4-[4-(2-Octyloxy)phenyl]benzoic acid (**14**): ^{1}H NMR (DMSO-d_6)) ppm: 0·852 (t, $J=7·5$, 3H), 1·25 (d, $J=6$, 3H), 1·21–1·75 (m, 10H), 4·5 (m, 1H), 7·02/7·66 ($J=8·75$, 4H), 7·74/8·00 ($J=8·5$, 4H), 12·85 (s, 1H). MS *m/e* (per cent): 326 (M^+, 5), 214 ($M-C_8H_{16}$, 100), 197 ($M-C_8H_{16}/OH$, 10). IR cm^{-1}: 2672, 2551, (−COOH), 1686, 1292 (−C=O), 1604, 1525 (−C=C−), 1248 (aryl-ether), 841 (*p*-disubst. benzene).

(R)-4-[3-Nitro-4-(2-octyloxy)phenyl]benzoic acid (**15**): ^{1}H NMR (DMSO-d_6) ppm: 0·850 (t, $J=7$, 3H), 1·29 (d, $J=6$, 3H), 1·21–1·75 (m, 10H), 4·78 (m, 1H), 7·49/8·02/8·20 ($J=10+2$, 3H), 7·84/8·01 ($J=8·5$, 4H), 13·10 (s, 1H). MS *m/e* (per cent): 371 (M^+, 1·5), 259 ($M-C_8H_{16}$, 100), 242 ($M-C_8H_{16}/OH$, 3), 213 ($M-C_8H_{16}/OH/NO$, 3·5). IR cm^{-1}: 2669, 2554 (−COOH), 1689, 1282 (−C=O), 1608, 1489 (−C=C−), 1535, 1351 ($-NO_2$).

(R)-4-[3-Acetylamino-4-(2-octyloxy)phenyl]benzoic acid (**16**): ^{1}H NMR (DMSO)-d_6) ppm: 0·865 (t, $J=7$, 3H), 1·28 (d, $J=6$, 3H), 1·21–1·71 (m, 10H), 2·12 (s, 2H), 4·53 (m, 1H), 7·16/7·44/8·34 ($J=8·8+2$, 3H), 7·69/8·00 ($J=8·5$, 4H), 12·91 (s, 1H). MS *m/e* (per cent): 383 (M^+, 7), 271 ($M-C_8H_{16}$, 10·5), 229 $M-C_8H_{16}/COCH_3$, 100). IR cm^{-1}: 3316 (NH), 2663, 2546 (−COOH), 1683, 1275 (−C=O), 1606, 1509 (−C=C−), 1541 (−CONH), 1179 (aryl-ether), 812 (*p*-disubst. benzene).

(R)-4-[5-Acetylamino-2-nitro-4-(2-octyloxy)phenyl]benzoic acid: ^{1}H NMR (DMSO-d_6) ppm: 0·861 (t, $J=7$, 3H), 1·33 (d, $J=6$, 3H), 1·25–1·78 (m, 10H), 2·18 (s, 3H), 4·70 (m, 1H), 7·40/7·99 ($J=8·25$, 4H), 7·73 (s, 1H), 8·26 (s, 1H), 9·33 (s, 1H), 13·07 (s, 1H). MS *m/e* (per cent): 428 (M^+, 1), 316 ($M-C_8H_{16}$, 4), 274 ($M-C_8H_{16}/COCH_2$, 12), 43 (MeC=O, 100). IR cm^{-1}: 3403 (NH), 3252, 3078 (−COOH), 1696, 1242 (−C=O), 1615, 1505 (−C=C−), 1520, 1350 ($-NO_2$), 1240 (aryl-ether), 808 (*p*-disubst. benzene).

(R)-4-[5-Amino-2-nitro-4-(2-octyloxy)phenyl]benzoic acid (**4**): ^{1}H NMR (DMSO-d_6) ppm: 0·865 (t, $J=7$, 3H), 1·29 (d, $J=6$, 3H), 1·21–1·78 (m, 10H), 4·61 (m, 1H), 6·26 (s, 1H), 6·49 (s, 1H), 7·37/7·94 ($J=8·25$, 4H), 7·56 (s, 1H), 13·15 (s, 1H). MS *m/e* (per cent): 387 (M + H, 100), 369 (M-OH, 9), 356 (M-NO, 7), 274 ($M-C_8H_{16}$, 30). IR cm^{-1}: 3498, 3350, 1621 ($-NH_2$), 2605, 2541 (−COOH), 1691, 1289 (−C=O), 1566, 1510 (−C=C−), 1528, 1289 ($-NO_2$), 1240 (aryl-ether), 801 (*p*-disubst. benzene).

4-Bromo-N-(2-hydroxy-1,1-dimethylethyl)benzamide: To a solution of 30g (0·34mol) of 2-amino-2-methyl-1-propanol in 75ml of CH_2Cl_2 cooled in ice water, 38g (0·14mol) of 4-bromobenzoyl chloride in 75ml of CH_2Cl_2 was added dropwise with stirring during 50min. Then the white suspension was stirred for 3h at room temperature and thereafter mixed with 300ml cold water. The organic phase was separated and the water solution shaken twice with CH_2Cl_2. The combined organic phases were washed twice with 1 M HCl and dried over Na_2SO_4. After evaporation of the solvent 44·5g (98·3 per cent) of the product was obtained as white crystals. m.p. 87·6–90·6°C.

2-(4-Bromophenyl)-4,4-dimethyl-4,5-dihydro-oxazole (**18**): Under N_2, 44·5g (0·127mol) of 4-bromo-*N*-(2-hydroxy-1,1-dimethylethyl)benzamide were dissolved in 350ml of acetonitrile. The solution was cooled to 0–5°C and then 20ml of thionyl chloride was added dropwise with stirring during 30min (initially a white creamy suspension formed which dissolved again after the addi-

tion). The reaction mixture was stirred at 0°C for 18 h and then poured into a solution of 115 g of K_2CO_3 in 1150 ml of ice water. After intense stirring for 1 min, the aqueous mixture was shaken three times with ether. The ether extracts were dried over Na_2SO_4 and the solvent evaporated. The crude product was distilled under reduced pressure and 35 g (90 per cent) of **18** were obtained, m.p. 35–37°C.

4-(4,4-Dimethyl-4,5-dihydro-oxazol-2-yl)phenylboronic acid (**19**): 2·7 g of magnesium were heated to 95°C for 15 min in an oil bath under vacuum and then cooled to 40°C. Then a very small crystal of iodine was added and the temperature maintained for 0·5 h. Then a solution of 25·4 g of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline in 100 ml of THF (water content less than 0·005 per cent) was added slowly. When the reaction started, the speed of addition was controlled to maintain gentle boiling. When the heat of formation ceased, the reaction mixture was boiled for additional 2 h and then cooled. A small sample was hydrolysed and by GLC analysis shown to be 95 per cent pure.

A solution of 10 ml of tri-isopropyl borate in 0·5 ml of dry THF was cooled to −70°C and then 20 ml of the Grignard reagent solution was added under N_2 with vigorous stirring. The speed of the addition was controlled to keep the reaction mixture at about −70°C. Then the reaction solution was warmed up to room temperature gradually and stirred at RT for another 10 min. Thereafter, the mixture was poured into 100 ml of 10 per cent hydrochloric acid. The acid solution was neutralized with solid Na_2CO_3 to pH = 9 and shaken with ethyl acetate three times. The extracts were washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue purified by chromatography on silica gel with ethyl acetate/alcohol (2:1) as eluent. Recrystallization from ethyl acetate/cyclohexane gave a white solid product. ^{1}H NMR ($CDCl_3$) ppm: 1·34 (s, 6 H), 4·12 (s, 2 H), 7·93/8·05 (dd, J = 8·1, 4 H). MS *m/e* (per cent): 220 (M + H, 100), 176 (M-$B(OH)_2$, 7). IR cm^{-1}: 3425, 2895 (OH), 1643 (C=N), 1600, 1511 (C=C), 1352, 1318 (B-O).

4-Bromo-3-nitrophenol (**21**): A current of dry carbon dioxide was passed through bromine and then into 10·5 g of *m*-nitrophenol heated to 120–140°C. After 2 h the product was freed from excess of bromine by a rapid current of pure CO_2 gas and then dissolved in an excess of dilute NaOH. The mixture was then neutralized with dilute HCl (10 per cent) to give a partially oily precipitate. The oil solidified upon cooling in ice water. The crude product was then dissolved in dilute HCl and separated from some remaining oil. On slow cooling of the acid solution, 8 g (50 per cent) of **21** crystallized as yellow needles, m.p. 146–147·5°C. ^{1}H NMR ($CDCl_3$) ppm: 6·95/7·36/7·58 (J = 8·75 + 2·5, 3 H). MS *m/e* (per cent): 217 (M^+, 100), 171 (M^+-NO_2, 36). IR cm^{-1}: 3406 (−OH), 1609 (−C=C−), 1524, 1352 (−NO_2).

(R)-1-Bromo-2-nitro-4-(2-octyloxy)benzene (**22**): ^{1}H NMR ($CDCl_3$) ppm: 0·882 (t, 3 H), 1·31 (d, J = 5·8, 3 H), 1·17–1·72 (m, 10 H), 4·36 (m, 1 H), 6·94/7·34/7·57 (J = 8·75 + 2·9, 3 H). MS *m/e* (per cent): 329 (M^+, 14), 219 (M-C_8H_{16}, 92), 112 (C_8H_{16}, 73). IR cm^{-1}: 1601, 1475 (−C=C−), 1538, 1351 (−NO_2).

(R)-4,4-Dimethyl-2-[2'-nitro-4'-(2-octyloxy)biphenyl-4-yl]-4,5-dihydro-oxazole (**23**): To the mixture of 684 mg (2·28 mmol) of (*R*)-1-bromo-2-nitro-4-(2-octyloxy)-benzene (**22**), 80 mg (0·068 mmol) of $Pd(PPh_3)_4$ and 4·6 ml of toluene, 2·28 ml of a 2 M aqueous solution of Na_2CO_3 and 600 mg (2·73 mmol) of 4-(4,4-dimethyl-4,5-dihydro-oxazol-2-yl)phenylboronic acid (**19**) in 1·14 ml of methanol was added. The vigorously stirred mixture was warmed to 80°C for 48 h, cooled and partitioned between 20 ml of methylene chloride and 10 ml 2 M aqueous Na_2CO_3 containing 1 ml of concentrated $NH_3 \cdot H_2O$. The organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel with ethyl acetate/cyclohexane (2:3) as eluent. Thus 0·79 g (81 per cent) of pure product was obtained. ^{1}H NMR ($CDCl_3$) ppm: 0·89 (t, J = 7, 3 H), 1·26–1·80 (m, 10 H), 1·35 (d, J = 6, 3 H), 1·40 (s, 6 H), 4·12 (s, 2 H), 4·48 (m, 1 H), 7·13/7·32/7·37 (J = 8·1 + 2·5, 3 H), 7·40/7·94 (J = 8·05, 2 H). MS *m/e* (per cent): 424 (M^+, 8), 409 (M-CH_3, 11), 312 (M-C_8H_{16}, 7), 297 (M-C_8H_{16}/CH_3, 100). IR cm^{-1}: 1649 (−C=N−), 1618, 1488 (−C=C−), 1532, 1353 (−NO_2), 1226 (aryl-ether).

(R)-4-[4-(s-Octyloxy)-2-nitrophenyl]benzoic acid (**24**): 0·62 g of dihydro-oxazole derivative **9** was mixed with 15 ml of 3 M HCl. The resultant mixture was heated to about 95°C and stirred at this temperature until the amine hydrochloride deposited. Thereafter the reaction mixture was cooled and the supernatant solution decanted. The residue was washed with a small amount of water; then 15 ml of 20 per cent NaOH in MeOH/H_2O (1:1) were added and the mixture was heated to 70°C with vigorous stirring. After 40 min, the reaction mixture was cooled and neutralized with concentrated HCl. The solid was collected and dried under reduced pressure for 15 h to give 0·48 g (88·5 per cent) of **24**. ^{1}H NMR (DMSO-d_6) ppm: 0·858 (t, 3 H), 1·28 (d, J = 6·5, 3 H), 1·25–1·75 (m, 10 H), 4·61 (m, 1 H), 7·37/7·48/7·55 (J = 8·1 + 2·5, 3 H), 7·42/7·98 (J = 8·25, 2 H), 13·15 (s, 1 H). MS *m/e* (per cent): 371 (M^+, 12), 259 (M-C_8H_{16}, 59), 242 (M-C_8H_{16}/OH, 21), 231 (M-C_8H_{16}/CO, 35).

IR cm^{-1}: 2721, 2551 (−COOH), 1695, 1299 (−C=O); 1612, 1488 (−C=C−), 1534, 1348 ($-NO_2$), 1278 (aryl-ether).

(R)-4-[2-Acetylamino-4-(2-octyloxy)phenyl]benzoic acid: ^{1}H NMR (DMSO-d_6) ppm: 0·859 (t, $J=7$, 3 H), 1·25 (d, $J=6$, 3 H), 1·21–1·62 (m, 10 H), 1·69 (s, 3 H), 4·42 (m, 1 H), 6·89/7·05/7·19 ($J=8·1+2·5$, 3 H), 7·45/7·96 ($J=8·5$, 2 H), 9·28 (s, 1 H), 12·92 (s, 1 H). MS *m/e* (per cent): 383 (M^+, 8), 271 (M-C_8H_{16}, 46), 229 (M-C_8H_{16}/$COCH_2$, 100). IR cm^{-1}: 3297 (−NH), 2673, 2358 (−COOH), 1706, 1235 (−C=O), 1670 (−CONH), 1611, 1510 (−C=C−), 1233 (aryl-ether).

(R)-4-[2-Acetylamino-5-nitro-4-(2-octyloxy)phenyl] benzoic acid (**25**): ^{1}H NMR (DMSO-d_6) ppm: 0·857 (t, $J=7·2$, 3 H), 1·32 (d, $J=6$, 3 H), 1·21–1·71 (m, 10 H), 1·97 (s, 3 H), 4·60 (m, 1 H), 7·54/8·01 ($J=8·25$, 4 H), 7·73 (s, 1 H), 7·84 (s, 1 H), 9·58 (s, 1 H), 13·07 (s, 1 H). MS *m/e* (per cent): 428 (M^+, 2·5), 316 (M-C_8H_{16}, 43), 274 (M-C_8H_{16}/$COCH_2$, 100). IR cm^{-1}: 3328 (−NH), 2659–2547 (−COOH), 1720, 1237 (−COOH), 1692 (−CONH), 1624 (−C=C−), 1504, 1341 (NO_2), 867 (*p*= disubst. benzene).

(R)-4'-(5-Heptylpyrimidin-2-yl)phenyl 4-[2-amino-5-nitro-4-(2-octyloxy)phenyl]benzoate (**34**): ^{1}H NMR ($CDCl_3$) ppm: 0·891 (t, $J=7$, 6 H), 1·40 (d, $J=6$, 3 H), 1·29–1·75 (m, 20 H), 2·64 (t, $J=7·7$, 2 H), 4·40 (s, 2 H), 4·5 (m, 1 H), 6·30 (s, 1 H), 7·37/8·52 ($J=8·75$, 4 H), 7·94 (s, 1 H), 7·60/8·31 ($J=8·5$, 4 H), 8·64 (s, 2 H). MS *m/e* (per cent): 638 (M^+, 2·5), 608 (M-NO, 6·3), 526 (M-C_8H_{16}, 3·5), 496 (M-C_8H_{16}/NO, 7·5), 369 (M-$OC_6H_4C_4H_2N_2C_7H_{15}$, 10), 257 (M-$OC_6H_4C_4H_2N_2C_7H_{15}$/$C_8H_{16}$, 100). IR cm^{-1}: 3422, 3352 ($-NH_2$), 1727, 1299 (−C=O), 1613, 1523 (−C=C−), 1549, 1348 ($-NO_2$).

(R)-4'-Heptyloxyphenyl 4-[2-amino-4-(2-octyloxy)-5-nitrophenyl]benzoate (**35**): ^{1}H NMR ($CDCl_3$) ppm: 0·889 (t, 3 H), 0·902 (t, 3 H), 1·40 (d, $J=6$, 3 H), 1·29–1·71 (m, 20 H), 3·96 (t, $J=6·25$, 2 H), 4·36 (s, 1 H), 4·47 (m, 1 H), 6·94/7·13 (AA'BB', $J=8·5$, 4 H), 7·92 (s, 1 H). MS *m/e* (per cent): 576 (M^+, 3) 546 (M^+-NO, 1), 464 (M^+-C_8H_{16}, 4), 369 (M^+-$OPhOC_7H_{15}$, 26,5), 257 (M^+-C_8H_{16}/$OPhOC_7H_{15}$, 100). IR cm^{-1}: 3465, 3387 ($-NH_2$), 1732, 1290 (−C=O), 1617, 1506 (−C=C−), 1552, 1351 ($-NO_2$), 819 (*p*-disubst. benzene).

(R)-4'-(4-Pentylphenyl)phenyl 4-[2-amino-4-(2-octyloxy)-5-nitrophenyl]benzoate (**36**): ^{1}H NMR ($CDCl_3$) ppm: 0·892 (t, 3 H), 0·913 (t, 3 H), 1·40 (d, $J=6$, 3 H), 1·30–1·75 (m, 16 H), 2·65 (t, $J=8·1$, 2 H), 4·37 (s, 1 H), 4·48 (m, 1 H), 6·30 (s, 1 H), 7·27/7·52 (AA'BB', $J=8·2$, 4 H), 7·29/7·64 (AA'BB', $J=8·75$, 4 H), 7·59/8·31 (AA'BB', $J=8·5$, 2 H), 7·94 (s, 1 H).

(R)-4'-[2-(trans-4-Pentylcyclohexyl)ethyl]phenyl 4-[2-amino-4-(2-octyloxy)-5-nitrophenyl]benzoate (**37**): ^{1}H NMR ($CDCl_3$) ppm: 0·886 (t, $J=7·5$, 6 H), 1·40 (d, $J=6$, 3 H), 1·25–1·75 (m, 29 H), 2·64, (t, $J=8·1$, 2 H), 4·41 (s, 2 H), 4·48 (m, 1 H), 6·29 (s, 1 H), 7·12/7·24 (AA'BB', $J=9$, 2 H), 7·57/8·29 (AA'BB', $J=8·5$, 2 H), 7·93 (s, 1 H).

(R)-4'-4(4-Nonyloxyphenyl)phenyl 4-[2-amino-4-(2-octyloxy)-5-nitrophenyl]benzoate (**38**): ^{1}H NMR ($CDCl_3$) ppm: 0·891 (t, $J=7·5$, 6 H), 1·40 (d, $J=6$ H), 1·30–1·75 (m, 24 H), 4·00 (t, $J=6$, 2 H), 4·30 (s, 2 H), 4·48 (m, 1 H), 6·30 (s, 1 H), 6·98/7·52 (AA'BB', $J=8·8$, 2 H), 7·28/7·61 (AA'BB', $J=8·8$, 2 H), 7·60/8·30 (AA'BB', $J=8·5$, 2 H), 7·94 (s, 1 H).

Phenyl 1,4-bis-(R)-4-[2-amino-4-(2-octyloxy)-5-nitrophenyl]benzoate (**39**): ^{1}H NMR ($CDCl_3$) ppm: 0·867 (t, $J=7$, 6 H), 1·34 (d, $J=6$, 6 H), 4·51 (m, 2 H), 6·31 (s, 4 H), 6·56 (s, 2 H), 7·43 (s, 4 H) 7·77 (s, 2 H), 7·68/8·23 (AA'BB', $J=8·5$, 4 H). MS *m/e* (per cent): 845 M-H, 52), 733 (M-C_8H_{17}, 9), 107 ($OC_6H_3O^+$, 100). IR cm^{-1}: 3460, 3361 ($-NH_2$), 1736, 1285 (−C=O), 1610, 1503 (−C=C−), 1550, 1349 ($-NO_2$), 1262 (aryl-ether).

4-(4-Methoxycarbonyloxyphenyl)benzoic acid: 0·5 g of 4-(4-Hydroxyphenyl)benzoic acid was dissolved in 40 ml of 4 per cent NaOH and the resulting solution cooled to 0–5°C; 1 ml of methyl chloroformate was added in three portions with constant stirring. After an additional 15 min, the solution was neutralized with 3 M HCl. The precipitate was filtered off, washed with water and then dried under reduced pressure. The pure product was obtained by recrystallization from alcohol, m.p. 260°C (decomp.).

(S)-2-Octyl 4-(4-methoxycarbonyloxyphenyl)benzoate: 0·45 g of 4-(4-Methoxycarbonyloxyphenyl)benzoic acid was dissolved in 10 ml of thionyl chloride and the resultant solution was heated under reflux at 50°C for 1 h. Then the excess of $SOCl_2$ was removed by destillation and the residue mixed with CH_2Cl_2 to form a solution to which 0·27 g of (*S*)-2-octanol and 0·21 g of triethylamine in 5 ml of CH_2Cl_2 were added slowly at room temperature. Then the reaction mixture was stirred at RT for 3 h and evaporated to a small volume. The product was purified by column chromatography with methylene chloride as eluent to give a colourless oil.

(S)-2-Octyl 4-(4-hydroxyphenyl)benzoate: 0·2 g of (*S*)-2-Octyl 4-(4-methoxycarbonyloxyphenyl)benzoate was dissolved in 3 ml of pyridine, 6 ml of acetone, 0·4 ml of

concentrated $NH_3 \cdot H_2O$ and 3 ml of water. The resulting solution was stirred at room temperature for 12 h and then evaporated to dryness. The residue was dissolved in ethyl acetate and washed twice with water. After drying and evaporation of the solvent, a crude product was obtained which was used for the esterification to give **40**.

(S)-4'-[4-(2-Octyloxycarbonyl)phenyl (R)-4-[2-amino-4-(2-octyloxy)-5-nitrophenyl]benzoate (**40**): ^{1}H NMR (DMSO-d_6) ppm: 0·86 (t, $J=7·5$, 6 H), 1·31 (d, $J=6$, 3 H), 1·33 (d, $J=6$, 3 H), 1·21–1·75 (m, 20 H), 4·48 (m, 1 H), 5·08 (m, 1 H), 6·32 (s, 2 H), 6·56 (s, 1 H), 7·45/7·76 ($J=8·75$, 4 H), 7·68/8·23 ($J=8·5$, 4 H), 7·87/8·05 ($J=8·5$, 4 H), 7·78 (s, 1 H). MS *m/e* (per cent): 694 (M^+, 1·35), 663 (M-NO/H, 3), 584 (M-C_8H_{16}, 1·5), 369 (M-OPhPhCO$_2$C$_8$H$_{17}$, 15), 257 (M-OPhPhCO$_2$-C$_8$H$_{17}$/C$_8$H$_{16}$, 100). IR cm^{-1}: 3466, 3372, 1636 (NH_2), 1730, 1273 (−C=O), 1702 (−C=O conj. ester), 1464, 1351 ($-NO_2$), 1182, 1029 (aryl-ether), 841 (*p*-disubst. benzene).

(R)-4'-[2-(trans-4-Pentylcyclohexyl)ethyl]phenyl 4-[5-amino-2-nitro-4-(2-octyloxy)phenyl]benzoate (**41**): ^{1}H NMR (DMSO-d_6) ppm: 0·865 (t, $J=7$, 6 H), 1·29 (d, $J=6$, 3 H), 1·21–1·78 (m, 28 H), 2·62 (t, $J=7·5$, 2 H), 4·56 (m, 1 H), 6·30 (s, 1 H), 6·51 (s, 1 H), 7·20/7·28 ($J=10$, 4 H), 7·46/8·14 ($J=9·5$, 4 H), 7·61, (s, 1 H). MS *m/e* (per cent): 642 (M^+, 4·4), 612 (M-NO, 3·4), 500 (M-C_8H_{16}/NO, 2·5), 369 (M-OPhC$_2$H$_4$C$_6$H$_{10}$C$_5$H$_{11}$, 100), 257 (M-OPhC$_2$H$_4$C$_6$H$_{10}$C$_5$H$_{11}$/C$_8$H$_{16}$, 78). IR cm^{-1}: 3501, 3360 ($-NH_2$), 1732, 1238 (−C=O), 1620, 1533 (−C=C−), 1507, 1325 ($-NO_2$).

(R)-4'-(4-Nonyloxyphenyl)phenyl 4-[5-amino-2-nitro-4-(2-octyloxy)phenyl]benzoate (**42**): ^{1}H NMR (DMSO-d_6) ppm: 0·87 (t, $J=7$, 6 H), 1·28 (d, $J=6$, 3 H), 1·21–1·75 (m, 22 H), 4·08 (t, $J=7$, 2 H), 4·58 (m, 1 H), 6·31 (s, 1 H), 6·54 (s, 1 H), 7·04/7·63 ($J=9$, 4 H), 7·38/7·73 ($J=8·9$, 4 H), 7·48/8·16 ($J=8·75$, 4 H), 7·61 (s, 1 H). MS *m/e* (per cent): 666 (M^+, 21), 636 (M-NO, 6), 554 (M-C_8H_{16}, 4), 369 (M-OPhPhOC$_8$H$_{17}$, 100), 257 (M-OPhPhOC$_8$H$_{17}$/C$_8$H$_{16}$, 40). IR cm^{-1}: 3502, 3359 ($-NH_2$), 1734, 1269 (C=O), 1515 (−C=C−), 1494, 1325 ($-NO_2$), 1170, 990 (aryl-ether), 842 (*p*-disubst. benzene).

(R)-4-Heptyloxyphenyl 4-[2-nitro-4-(2-octyloxy)-5-aminophenyl]benzoate (**43**): ^{1}H NMR (DMSO-d_6) ppm: 0·870 (t, $J=7$, 6 H), 1·28 (d, $J=6$, 3 H), 1·21–1·75 (m, 20 H), 3·96 (t, $J=6$, 2 H), 4·61 (m, 1 H), 6·21 (s, 2 H), 6·52 (s, 1 H), 7·01/7·19 (AA'BB', $J=9·5$, 4 H), 7·46/8·14 (AA'BB', $J=10$, 4 H), 7·5 (s, 1 H). MS *m/e* (per cent): 576 (M^+, 5), 546 (M^+-NO, 3), 434 (M^+-NO/C$_8$H$_{16}$, 2·5), 369 (M^+-OPhOC$_7$H$_{15}$, 100), 257 (M^+-C$_8$H$_{16}$/OPhOC$_7$H$_{15}$, 42).

5.4. *Acrylates and polyacrylates*

4-(11-Hydroxyundecanyloxy)phenylphenol m.p. 146·4–147·8°C and *4-(11-acryloyloxyundecanyloxy)phenylphenol* (**45**), m.p. 91·6–92·9°C, were prepared according to the literature [10]. For ester formation with the corresponding acids, the previously described esterification method was used. The polymerization of the monomeric ester using azoisobutyronitrile as initiator was performed according to standard procedures [10].

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