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Highly conjugated 4-ring nematic liquid crystals with a lateral alkoxy branch

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Three types of liquid crystalline compound containing a 4-ring mesogenic core with a lateral alkoxy chain on one of the inner rings were synthesized, and their mesogenic properties studied. The 4-ring core of these compounds bears an electron-accepting nitro group at one end and an electron-donating alkylamino moiety at or near the other end. Therefore, they are highly coloured and have $\lambda_{max} \geqslant 473$ nm. One of these three types of compound has a wide enantiotropic nematic range. Twelve homologous analogues in this series with different lengths for the terminal alkyl chain and the lateral alkoxy chain were synthesized and compared.

1. Introduction

Most rod-like liquid crystals have a rigid core composed of two or more aromatic and/or aliphatic rings and one or two flexible alkyl/alkoxy chains [1, 2]. In general, the introduction of a rigid lateral substituent in the mesogenic core perturbs the ordering in liquid crystalline phases, leading to a depression in the clearing point, a reduction of the liquid crystalline range, and a destabilization of smectic phases in favour of the nematic phase [3–5]. If the lateral substituent is large in comparison with the length of the mesogenic core, the liquid crystalline phase may become monotropic or even vanish [4]. However, for a flexible lateral substituent such as an alkyl or alkoxy chain, as the chain length increases, the effect of additional perturbation diminishes [6–9]. This is because the lateral alkyl or alkoxy chain tends to orient along the molecular axis [10].

In spite of the seemingly deleterious effect of lateral substitution, it can be used advantageously to impart desirable properties on special types of liquid crystal, such as those with lateral fluorine atoms or electron 'push–pull' groups. In other cases, when it is necessary to increase the length of the mesogenic core, the introduction of a lateral alkyl or alkoxy chain helps to lower the melting points of the mesogenic compounds. Compounds containing a 4-ring core with a lateral alkoxy branch have been known to possess large nematic ranges with low melting points [10–12].

Liquid crystalline materials containing a 4-nitrophenyl-4′-phenyldiazene unit have attracted some attention recently due to their large second-order molecular hyperpolarizability [13, 14]. The introduction of an alkylamino moiety at the opposite end (with respect to the nitro group) of a conjugated system leads to a large molecular dipole moment, which is favourable for nonlinear optics applications [15, 16]. Liquid crystals containing these electron 'push–pull' groups possess large dielectric anisotropy and high birefringence in the visible and infrared ranges [17, 18], and are good candidates for guest–host displays in the visible region and for IR and millimetre wave modulators. These desirable properties can be enhanced by lengthening the conjugated mesogenic core. However, the melting point also increases when the core is extended. Fortunately, this problem can be ameliorated by introducing a lateral alkyl or alkoxy chain, which also suppresses the smectic phase to yield desirable nematic compounds with useful mesomorphic ranges.

In this paper, we present the synthesis and mesomorphic properties of some new liquid crystalline compounds containing a 4-ring mesogenic core having a lateral alkoxy chain in one of the inner rings. The 4-ring core of these compounds bears an electron-accepting nitro group at one end and an electron-donating group, in the form of an amino-methylene linkage or a piperazine ring, at or near the other end.

2. Results and discussion

Three types of mesogenic compound have been synthesized and studied in this work. The compounds are: 4-(4-nitrophenylazo)-3-pentyloxy-1-[4-(4-hexyloxybenzyl)aminophenylazo]benzene (**I**), 4-[4-(4-pentyl-

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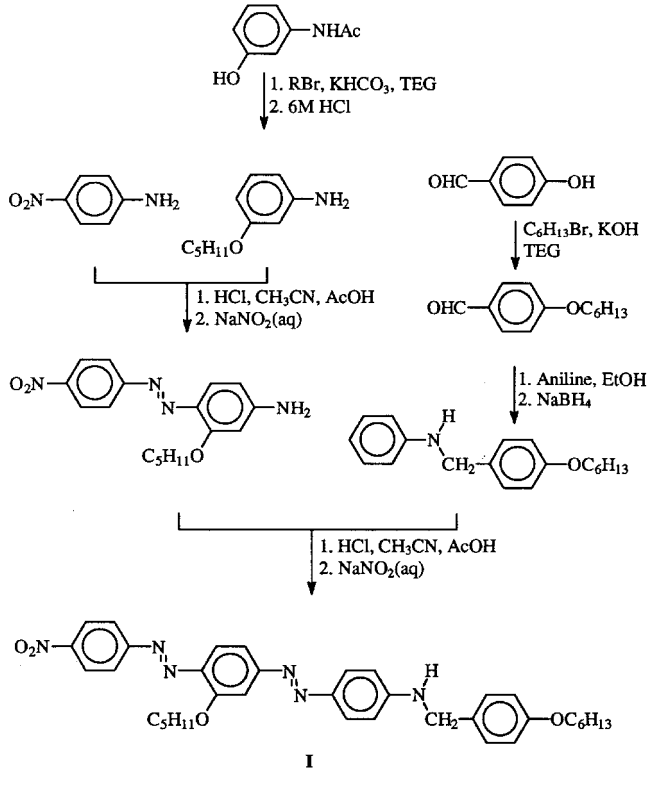
phenyl)piperazinyl]-2-pentyloxy-1-(4-nitrophenylazo) benzene (**II**), and 4-(4-nitrophenylazo)-3-alkoxy-1-[4-(4-alkylpiperazinyl)phenylazo]benzene (**III**). For **III**, 12 homologous compounds with systematic variations in the lengths of the terminal and lateral chains were synthesized. The synthetic schemes 1–3 are given in the following, and the details of the syntheses are described in the next section.

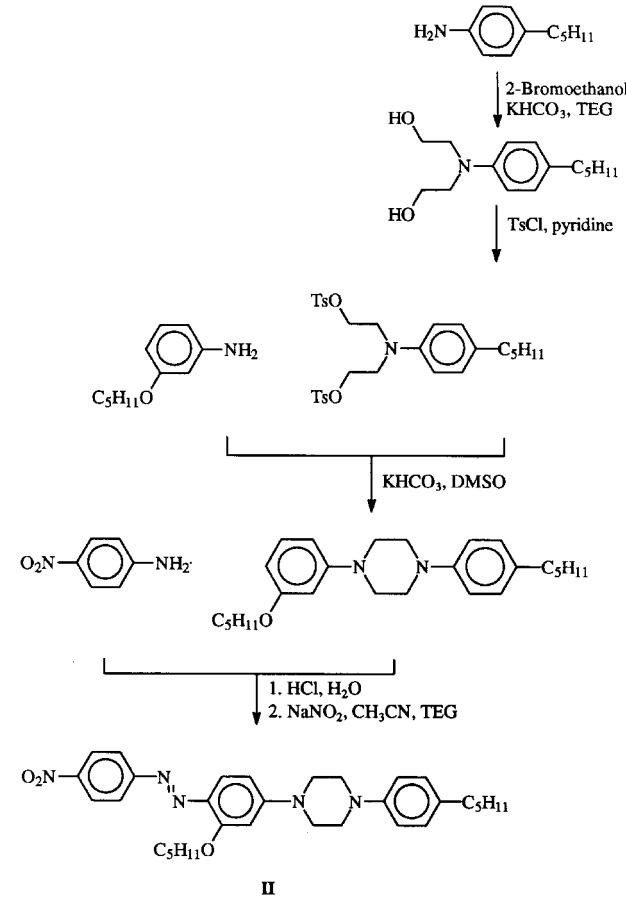
Compounds **I**, **II** and all members of the homologous series **III** are nematogenic. Therefore, it appears that the presence of the lateral alkoxy chain has effectively perturbed the molecular packing and does not allow the more ordered smectic phase to occur. Compounds **I** and **II** exhibit only a monotropic nematic phase; for this reason, other homologues were not synthesized. The monotropic range of **I** is from 124°C down to about 53°C, and that of **II** is from 133°C down to about 125°C. In contrast, all members of the homologous series **III** synthesized exhibit an enantiotropic nematic phase with a wide nematic range. The phase transition temperatures are listed in the table. The dependence of the transition temperatures on the number of carbon atoms in the lateral and terminal chains for series **III** is shown in the figure.

The lower mesomorphic stability of compounds **I** and **II** is most likely due to the presence of more flexible core components in these compounds, i.e. the flexible amino-methylene linkage in compound **I** and the inner piperazine ring in compound **II**. When the piperazine unit is incorporated as the outer ring and an additional rigid diazo linkage is introduced, as in the homologous series **III**, the mesophase becomes enantiotropic. Liquid crystalline compounds containing a piperazine ring as part of the rigid core often exhibit smectic phases [19, 20], but the presence of the lateral alkoxy chain suppresses the smectic behaviour, so that all compounds in series **III** exhibit a nematic phase. The figure shows that the clearing temperature, T_{NI}, exhibits a slight alternating odd–even behaviour for both the terminal and the lateral chains, but the melting point exhibits no such behaviour for either chain. The clearing temperature decreases slowly with the increase of the terminal chain length, and decreases much faster with increasing length of the lateral alkoxy chain. This is probably due to a larger perturbation of the molecular packing order in the nematic phase by the lateral chain, which leads to a larger impact on the mesomorphic stability.

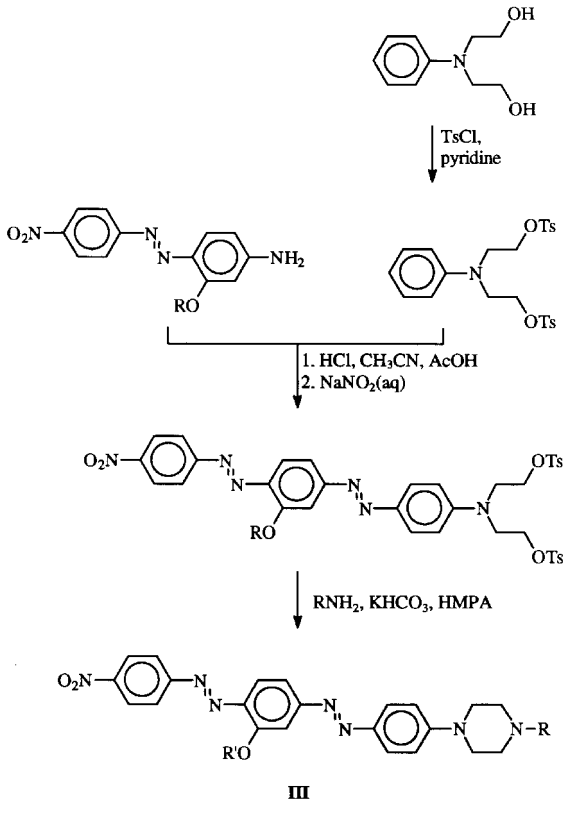
The UV–visible spectra of compounds **I**–**III** were measured in acetonitrile solutions, and the λ_{max} values are 494, 473 and 485 nm, respectively. Compound **II** has



Scheme 1



Scheme 2



Scheme 3

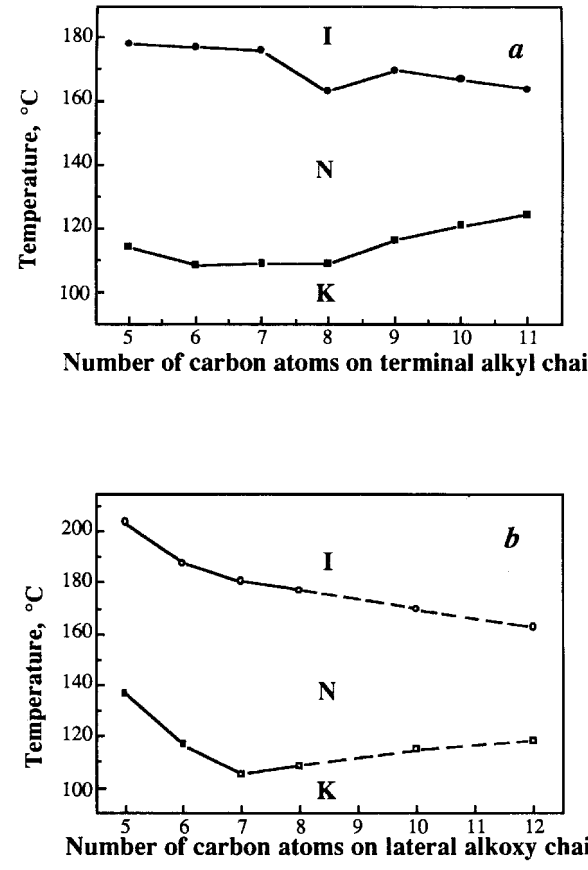


Figure. Phase behaviour for the homologous series **III** with (*a*) lateral alkoxy chain, $R' = C_8H_{17}$; (*b*) terminal alkyl chain, $R = C_6H_{13}$. The transition temperatures (heating) were obtained from DSC measurements.

the smallest λ_{max} because of a shorter conjugated system. An extension of the conjugation leads to a red shift; therefore, **III** has a longer λ_{max} than **II**. Compound **I** has the longest λ_{max} because its flexible amino-methylene linkage can easily adopt a planar conformation, whereas the piperazine ring in **III** has an inherent steric constraint rendering the planar conformation less favourable for the nitrogen moiety, making it less effective as an electron donor. On the other hand, the flexibility of the amino-methylene linkage reduces mesogenic tendency, so that **I** is only monotropic, whereas all homologous compounds in **III** have an enantiotropic nematic phase.

Table. Transition temperatures (°C) for compounds in series **III**.

			T_m		T_{NI}	
Compound	R'	R	Microscope	DSC	Microscope	DSC
IIIa	C_8H_{17}	C_5H_{11}	114·0	114·1	179·1	178·1
IIIb	C_8H_{17}	C_6H_{13}	107·5	108·4	172·8	177·2
IIIc	C_8H_{17}	C_7H_{15}	108·0	108·6	172·9	176·0
IIId	C_8H_{17}	C_8H_{17}	106·3	108·8	165·2	163·2
IIIe	C_8H_{17}	C_9H_{19}	114·0	116·2	165·2	169·8
IIIf	C_8H_{17}	$C_{10}H_{21}$	118·2	120·8	161·2	167·0
IIIg	C_8H_{17}	$C_{11}H_{23}$	123·2	124·3	162·7	164·0
IIIh	C_5H_{11}	C_6H_{13}	138·2	136·6	205·0	203·7[a]
IIIi	C_6H_{13}	C_6H_{13}	118·4	116·8	189·1	187·5[a]
IIIj	C_7H_{15}	C_6H_{13}	110·3	105·3	187·9	180·6[a]
IIIk	$C_{10}H_{21}$	C_6H_{13}	113·7	114·6	165·3	169·7
IIIl	$C_{12}H_{25}$	C_6H_{13}	120·3	118·6	164·4	162·8

[a] With decomposition.

Although all the compounds in the homologous series **III** have melting points slightly higher than 100°C, proper formulation of eutectic mixtures, especially with the addition of other low-melting nematic liquid crystals, would make them suitable for room temperature operations. Furthermore, because the lateral chain acts to reduce intermolecular interactions, these compounds appear to have rather low viscosities in the nematic phase, although quantitative determinations have yet to be carried out. Considering these factors and their favourable optical and dielectric properties, series **III** and similar compounds may be good candidates for colour liquid crystal displays and light modulators operating in the infrared and microwave regions.

3. Experimental

The starting materials for synthesis were purchased from Aldrich Chemical Company, Inc., and were used without further purification. Column chromatography was performed on silica gel (Aldrich Chemical Company, Inc., 70–230 mesh, 6 nm). 1H NMR spectra were recorded on a Varian XL-300 spectrometer equipped with a VXR-4000 data station or a VXR-500S spectrometer, and processed on a Sun Sparc5 data station. UV–visible absorption spectra were recorded on a Shimadzu UV-160 UV–vis recording spectrophotometer. The transition temperatures of the final products were obtained by the use of an Olympus BH-2 polarizing microscope equipped with a Linkham PR 600 heating stage and a Perkin Elmer DSC 7 differential scanning calorimeter with a scanning rate of 10°C min^{-1}.

3.1. *N-(4-Hexyloxybenzyl)aniline*

A solution of 4-hydroxybenzaldehyde (12·5 g, 0·102 mol), 1-bromohexane (16·5 g, 0·100 mol), potassium hydroxide (7·0 g, 0·12 mol) and triethylene glycol (30 ml) was heated at 80°C with stirring for 6 h. The mixture was cooled and extracted with diethyl ether (3 × 30 ml). The combined ether extract was then washed with water, dried with anhydrous magnesium sulphate and evaporated under reduced pressure; 17·2 g (83·3%) of crude 4-hexyloxybenzaldehyde was obtained. The crude product was used in the next step without further purification. A solution of 4-hexyloxybenzaldehyde (4·0 g, 0·019 mol), aniline (1·9 g, 0·020 mol) and ethanol (20 ml) was heated under reflux for 30 min. The solution was cooled to room temperature, and sodium borohydride (0·60 g, 15 mmol) added in small portions. The mixture was allowed to stir at room temperature for another 30 min. The solid formed was filtered, washed with cold methanol, and air dried. Yield 3·0 g (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) = 0·91 (t, J = 7·0 Hz, 3H); 1·32–1·40 (m, 4H); 1·42–1·48 (m, 2H); 1·75–1·79 (m, 2H); 3·94 (t, J = 6·6 Hz, 2H); 4·00 (sbr, 1H); 4·24 (s, 2H); 6·64 (d, J = 7·3 Hz, 2H); 6·71 (t, J = 7·3 Hz, 1H); 6·87 (t, J = 8·8 Hz, 2H); 7·16–7·19 (m, 2H); 7·27 (d, J = 8·8 Hz, 2H).

3.2. *3-Pentyloxyaniline*

3-Acetamidophenol (10 g, 0·066 mol), sodium hydroxide (3·2 g, 0·080 mol) and sodium iodide (10 g) were added to 2-butanone (200 ml). The mixture was heated to reflux temperature and 1-bromopentane (9·0 ml, 0·073 mol added); the resulting mixture was heated under reflux for 24 h. After cooling to room temperature, the mixture was extracted with 0·5M aqueous potassium hydroxide (2 × 100 ml). The organic layer was washed with water (100 ml) and the solvent was evaporated off under reduced pressure; 6M hydrochloric acid (80 ml) was added to the residue and the resulting mixture heated under reflux for 4 h. After the mixture had cooled to room temperature, it was neutralized with aqueous ammonia; the resulting mixture was extracted with diethyl ether (2 × 100 ml) and the combined organic extracts were washed with water (50 ml). They were then dried with anhydrous magnesium sulphate and filtered; the solvent was evaporated off under reduced pressure. The residue was purified by column chromatography—eluent: ethyl acetate/hexane (1:2)—and recrystallization from absolute ethanol. Yield 10·5 g (88%). Mass spectrum: m/e = 179 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0·91 (t, J = 6·9 Hz, 3H); 1·67–1·42 (m, 4H); 1·72–1·77 (m, 2H); 3·62 (sbr, 2H); 3·89 (t, J = 6·8 Hz, 2H); 6·22–6·32 (m, 3H); 7·00–7·06 (m, 1H).

3.3. *4-(4-Nitrophenylazo)-3-pentyloxyaniline*

A mixture of 4-nitroaniline (6·2 g, 0·045 mol) with 6M hydrochloric acid (33 ml) was warmed until the solid dissolved; the solution was cooled rapidly in an ice bath with vigorous stirring to precipitate out fine nitroaniline hydrochloride crystals, and the resulting mixture was stirred at 0°C for another 15 min. A solution (17 ml) of sodium nitrite (3·4 g, 0·049 mol) was added dropwise, and the resulting diazonium solution was added to a pre-cooled solution of 3-pentyloxyaniline (8·0 g, 0·045 mol) in 30% (v/v) aqueous acetic acid (600 ml) with vigorous stirring. The resulting suspension was stirred at 0°C for 1 h and then at room temperature for another 2 h. The solid was removed by suction filtration and recrystallized twice from ethyl acetate/hexane (1:3). Yield 9·4 g (64%). Mass spectrum: m/e = 328 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0·94 (t, J = 7·1 Hz, 3H); 1·41–1·56 (m, 4H); 1·89–1·94 (m, 2H); 4·12 (t, J = 6·6 Hz, 2H); 4·23 (sbr, 2H); 6·25–6·28 (m, 2H); 7·75 (d, J = 9·5 Hz, 1H); 7·90 (d, J = 8·9 Hz, 2H); 8·30 (d, J = 8·9 Hz, 2H).

3.4. *4-(4-Nitrophenylazo)-3-pentyloxy-1-[4-(4-hexyloxybenzyl)aminophenylazol]benzene* (**I**)

4-(4-Nitrophenylazo)-3-pentyloxyaniline (0·33 g, 1·0 mmol) was first dissolved in a 1:1 mixture of triethyleneglycol (TEG) and acetonitrile (8 ml). The solution was cooled to 0°C, and sodium tetrafluoroborate (0·12 g, 1·1 mmol) added. Concentrated hydrochloric acid (0·2 ml) was added to the mixture followed by a solution of sodium nitrite (0·076 g, 1·1 mmol) in water (0·8 ml); the resulting solution was stirred at 0°C for 30 min. A solution of *N*-(4-hexyloxybenzyl)aniline (0·29 g, 1·0 mmol) in a 1:1 mixture of TEG and acetonitrile (4 ml) was added, and the resulting mixture stirred for 3 h. It was diluted to 40 ml with water and then neutralized with potassium bicarbonate. The mixture was extracted with diethyl ether (4 × 20 ml), and the combined organic extracts were washed with water. The organic layer was dried with anhydrous magnesium sulphate, and the solvent evaporated off under reduced pressure. The residue was purified by column chromatography—eluent: ethyl acetate/hexane (1:4). Yield 0·12 g (19%), m.p. 127·6–131·3°C. λ_{max} (nm)=494, log ε=4·60. Mass spectrum: *m/e*=621 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)=0·90 (t, *J*=7·0 Hz, 3H); 0·96 (t, *J*=7·3 Hz, 3H); 1·32–1·34 (m, 4H); 1·34–1·46 (m, 4H); 1·47–1·56 (m, 2H); 1·75–1·79 (m, 2H); 1·95–1·99 (m, 2H); 3·94 (t, *J*=6·6 Hz, 2H); 4·30 (t, *J*=6·6 Hz, 2H); 4·41 (s, 2H); 6·76–6·82 (m, 2H); 6·89 (d, *J*=8·8 Hz, 2H); 7·28 (d, *J*=8·1 Hz, 2H); 7·54–7·56 (m, 1H); 7·63–7·64 (m, 1H); 7·85 (d, *J*=8·1 Hz, 2H); 8·03 (d, *J*=8·8 Hz, 2H); 8·37 (d, *J*=9·5 Hz, 2H).

3.5. *N-4-Pentylphenyldiethanolamine*

4-Pentylaniline (1·5 ml, 8·4 mmol) and 2-bromoethanol (2·6 ml, 0·037 mmol) were dissolved in TEG (15 ml). Potassium hydroxide (1·04 g, 0·018 mmol) was added, and the resulting mixture was heated at 100°C for 16 h. It was then cooled to room temperature and diluted to 40 ml with water. The solution was extracted with diethyl ether (3 × 20 ml), and the combined ether extracts were washed with water (3 × 20 ml) and dried with anhydrous magnesium sulphate. The solvent was evaporated off, and the residue purified by column chromatography (eluent: ethyl acetate). Yield 0·36 g (20%). Mass spectrum: *m/e*=251 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=0·88 (t, *J*=6·9 Hz, 3H); 1·27–1·33 (m, 4H); 1·53–1·58 (m, 2H); 3·30 (sbr, 2H); 3·51 (t, *J*=4·9 Hz, 4H); 3·79 (t, *J*=4·9 Hz, 4H); 6·64 (d, *J*=8·6 Hz, 2H); 7·04 (d, *J*=8·6 Hz, 2H).

3.6. *N-(4-Pentylphenyl)diethanolamine di-p-toluenesulphonate*

N-(4-Pentylphenyl)diethanolamine (0·90 g, 4·1 mmol) was dissolved in pyridine (2·6 ml), and the resulting solution cooled to 0°C. *p*-Toluenesulphonyl chloride (1·9 g, 0·010 mol) was then added in small portions. The mixture was allowed to stir at 0°C for 3 h and was poured into a mixture of concentrated hydrochloric acid (5 ml) and ice (15 g). The resulting mixture was extracted with diethyl ether (2 × 20 ml). The ether extracts were washed with water (2 × 20 ml), dried with anhydrous magnesium sulphate, and the solvent evaporated off under reduced pressure. Yield of crude product 1·5 g (65%). Mass spectrum: *m/e*=559 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)=0·88 (t, *J*=6·8 Hz, 3H); 1·27–1·32 (m, 4H); 1·51–1·56 (m, 2H); 2·41 (s, 6H); 3·51 (t, *J*=6·1 Hz, 4H); 4·06 (t, *J*=6·1 Hz, 4H); 6·39 (d, *J*=8·6 Hz, 2H); 6·94 (d, *J*=8·6 Hz, 2H); 7·27 (d, *J*=8·2 Hz, 4H); 7·70 (d, *J*=8·2 Hz, 4H).

3.7. *4-(4-Pentylphenyl)-1-(3-pentyloxy)phenylpiperazine*

N-(4-Pentylphenyl)diethanolamine di-*p*-toluenesulphonate (1·48 g, 2·64 mmol) and 3-pentyloxyaniline (0·47 g, 2·6 mmol) were dissolved in dry DMSO (7 ml). Potassium bicarbonate (0·6 g, 6 mmol) was added, and the resulting mixture was heated at 100°C for 8 h; it was then cooled to room temperature and diluted to 40 ml with water. The solution was extracted with diethyl ether (3 × 10 ml), and the combined ether extracts were washed with water (2 × 10 ml), dried with anhydrous magnesium sulphate, and the solvent was evaporated off under reduced pressure. The residue was purified by column chromatography—eluent: ethyl acetate/hexane (1:6). Yield 0·37 g (36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=0·86–0·95 (m, 6H); 1·27–1·60 (m, 10H); 1·75–1·80 (m, 2H); 2·53 (t, *J*=7·8 Hz, 2H); 3·25–3·33 (m, 8H); 3·94 (t, *J*=6·6 Hz); 6·43 (dd, *J*=8·2, 2·3 Hz, 1H); 6·50–6·52 (m, 1H); 6·57 (dd, *J*=8·2, 2·1 Hz, 1H); 6·90 (d, *J*=8·6 Hz, 2H); 7·10 (d, *J*=8·6 Hz, 2H); 7·17 (dd, *J*=8·2, 8·2 Hz, 1H).

3.8. *4-[4-(4-Pentylphenyl)piperazinyl]-2-pentyloxy-1-(4-nitrophenylazo)benzene* (**II**)

4-Nitroaniline (0·07 g, 0·51 mmol) was dissolved in a 1:1 mixture of acetonitrile and TEG. Concentrated hydrochloric acid (0·1 ml) was added and the solution cooled to 0°C. A pre-cooled solution of sodium nitrite (0·039 g, 0·50 mmol) in water (0·5 ml) was added dropwise, and the resulting solution allowed to stir at 0°C for another 15 min. This was added to a solution of 4-(4-pentylphenyl)-1-(3-pentyloxy)phenylpiperazine (0·2 g, 0·5 mmol) in a 1:1 mixture of acetonitrile and TEG (2 ml). The resulting solution was stirred at 0°C for 2 h; it was diluted to 40 ml with water, and extracted with diethyl ether (3 × 20 ml). The combined ether extracts were washed with water (2 × 20 ml) and dried with anhydrous magnesium sulphate. The solvent was

evaporated off under reduced pressure. The residue was purified by column chromatography—eluent: ethyl acetate/hexane (1:4). Yield 0·08 g (30%), m.p. 137·2–139·2°C. λ_{max} (nm)=473, log ε=4·38. Mass spectrum: *m/e*=543 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=0·88 (t, *J*=6·8 Hz, 3H); 0·95 (t, *J*=7·1 Hz, 3H); 1·29–1·58 (m, 10H); 1·91–1·96 (m, 2H); 2·53 (t, *J*=7·7 Hz, 2H); 3·29–3·33 (m, 4H); 3·55–3·58 (m, 4H); 4·19 (t, *J*=6·6 Hz, 2H); 6·48 (d, *J*=2·5 Hz, 1H); 6·57 (dd, *J*=9·3, 2·5 Hz, 1H); 6·90 (d, *J*=8·5 Hz, 2H); 7·11 (d, *J*=8·5 Hz, 2H); 7·81 (d, *J*=9·3 Hz, 1H): 7·92 (d, *J*=9·0 Hz, 2H); 8·31 (d, *J*=9·0 Hz, 2H).

3.9. *N-Phenyldiethanolamine di-*p*-toluenesulphonates*

N-Phenyldiethanolamine (30 g, 0·17 mol) was dissolved in pyridine (88 ml) and the resulting solution cooled to 0°C. With stirring, *p*-toluenesulphonyl chloride (69·6 g, 0·36 mol) was added in small portions to the solution; after the addition was complete, the mixture was allowed to stir at 0°C for 30 min, and then at room temperature for another 30 min. It was then poured into a mixture of concentrated hydrochloric acid (185 ml) and ice (460 g). The resulting mixture was filtered with suction; the residue was washed with water, followed by a small amount of cold absolute ethanol, and was air dried. Yield 71·7 g (89%). Mass spectrum: *m/e*=489 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)=2·40 (s, 6H); 3·53 (t, *J*=6·1 Hz, 4H); 4·07 (t, *J*=6·1 Hz, 4H); 6·55 (d, *J*=8·5 Hz, 2H); 6·69 (t, *J*=7·2 Hz, 1H); 7·11 (dd, *J*=7·2, 8·5 Hz, 2H); 7·26 (d, *J*=8·0 Hz, 4H); 7·69 (d, *J*=8·0 Hz, 4H).

3.10. *4-(4-Nitrophenylazo)-3-pentyloxy-1-[4-N,N-di-(2-*p*-toluenesulphonyloxyethyl)aminophenylazo]benzene*

4-(4-Nitrophenylazo)-3-pentyloxyaniline (4·2 g, 0·013 mol) was dissolved in a 2:1 mixture of acetic acid and acetonitrile (60 ml) with heating. Concentrated hydrochloric acid (2·2 ml) was added, and the resulting solution cooled to 0°C with vigorous stirring. A pre-cooled solution of sodium nitrite (0·93 g, 0·013 mol) in water (2 ml) was added dropwise, and the resulting solution allowed to stir at 0°C for 15 min. A pre-cooled solution of *N*-phenyldiethanolamine di-*p*-toluenesulphonate (6·0 g, 0·013 mol) in a 30% mixture (40 ml) of acetic acid in acetonitrile was added rapidly with vigorous stirring; the resulting mixture was stirred at 0°C for 2 h. It was diluted to 200 ml with water and filtered with suction. The residue was purified by column chromatography—eluent: ethyl acetate/hexane (1:2). Yield 6·6 g (61%). Mass spectrum: *m/e*=829 (M^++1). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)=0·97 (t, *J*=7·4 Hz, 3H); 1·45–1·50 (m, 4H); 1·96–2·04 (m, 2H); 2·39 (s, 6H); 3·69 (t, *J*=5·9 Hz, 4H); 4·17 (t, *J*=5·9 Hz, 4H); 4·32 (t, *J*=6·6 Hz, 2H); 6·54 (d, *J*=8·8 Hz, 2H); 7·27 (d, *J*=8·4 Hz, 4H); 7·55 (d, *J*=8·4 Hz, 1H); 7·62 (sbr, 1H); 7·70 (d, *J*=8·4 Hz, 4H); 7·84 (d, *J*=8·8 Hz, 2H); 7·87 (d, *J*=8·4 Hz, 1H); 8·05 (d, *J*=8·8 Hz, 2H); 8·38 (d, *J*=8·8 Hz, 2H).

3.11. *4-(4-Nitrophenylazo)-3-alkoxy-1-[4-(4-alkylpiperazinyl)phenylazo]benzene* (**III**)

4-(4-Nitrophenylazo)-3-pentyloxy-1-[4-*N*,*N*-di-(2-*p*-toluenesulphonyloxyethyl)aminophenylazo]benzene (3·1 g, 3·7 mmol) and potassium bicarbonate (0·77 g, 7·7 mmol) were dissolved in hexamethylphosphoramide (30 ml). Hexylamine (0·49 ml, 3·1 mmol) was added and the resulting solution heated at 100°C for 1 h. The resulting mixture was cooled to room temperature and diluted to 150 ml with diluted sodium chloride solution; it was filtered and the residue was washed with water. The residue was purified by column chromatography—eluent: ethyl acetate/hexane (1:2)—followed by recrystallization from a mixture of ethyl acetate and ethanol (1:2). Yield 1·3 g (61%), m.p. 137·2–139·2°C. λ_{max} (nm)=485, log ε=4·34. Mass spectrum: *m/e*=586 (M^++1). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)=0·90 (t, *J*=6·6 Hz, 3H); 0·961 (t, *J*=7·3 Hz, 3H); 1·25–1·60 (m, 12H); 1·94–2·00 (m, 2H); 2·41 (br, 2H); 2·62 (br, 4H); 3·45 (br, 4H); 4·31 (t, *J*=6·6 Hz, 2H); 6·99 (d, *J*=8·8 Hz, 2H); 7·54 (d, *J*=8·8 Hz, 1H); 7·59 (s, 1H); 7·86 (d, *J*=8·8 Hz, 1H); 7·92 (d, *J*=8·8 Hz, 2H); 8·19 (d, *J*=8·8 Hz, 2H); 8·38 (d, *J*=8·8 Hz, 2H). Elemental analysis: calcd for $C_{33}H_{43}N_7O_3$: C 67·62, H 7·39, N 16·80, O 8·19, found: C 67·67, H 7·37, N 16·75, O 8·33.

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