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Synthesis of highly chiral multisubstituted binaphthyl compounds as potential new biaxial nematic and NLO materials

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Synthesis of highly chiral multisubstituted binaphthyl compounds as potential new biaxial nematic and NLO materials

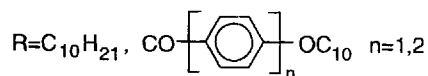
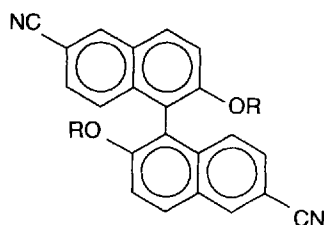
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A number of multi substituted binaphthalene compounds were synthesized in an attempt to obtain a highly chiral biaxial nematic (N_b) phase or a good NLO material. Introduction of two pairs of substituents into the binaphthalene molecule



with one of these being a nitrile group and $R = C_{10}$ was successful but neither this compound nor the above esters showed any mesophases. Introduction of additional pairs of substituents proved to be difficult. Friedel-Crafts acylation to add a third pair through a ketone gave complicated mixtures of products obtained by cleavage of the ether followed by acylation. Bromination, which could lead to either the necessary nitrile substituent or esters via the acid obtained from the nitrile generally gave mixtures of bromides as expected. Some of these could be separated by chromatography and successfully converted to the nitrile. However, attempts to hydrolyze these nitrile groups usually gave mixtures of various products of incomplete hydrolysis producing compounds that did not have the appropriate substituents for observing mesophases. No mesophases were observed in any of the binaphthalene compounds prepared. The (*R*)-(+) optical isomer of the above nitrile with $R = C_{10}$ was also prepared to study its potential use as a chiral dopant. This isomer had a melting temperature below that of the racemic material indicating that the latter is a racemic compound. A few mixture studies using primarily the racemic dopant with known liquid crystals indicated that low percentages (< 10 per cent) of this dopant gave good mixtures. The best mixtures were obtained using a cyanobiphenyl (8OCB) host which showed an enhanced nematic phase. Mixtures of a small amount of the chiral dopant in room temperature nematics gave highly coloured cholesteric (twisted nematic) phases.

1. Introduction

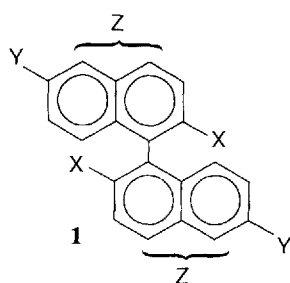
Nonlinear optical materials are of interest for use in a variety of interesting photonics applications [1, 2]. Chiral liquid crystals having a large second-order nonlinear

optical susceptibility have the potential for increasing switching times in liquid crystalline displays [3]. Such materials must be centro-symmetric. Thus, a chiral isotropic phase is inconsistent with second-harmonic generation. One approach towards achieving a good second-order NLO material is to prepare a chiral liquid crystalline material with electronic structures delocalized in three directions giving a large electrical dipole and

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optical asymmetry [4]. Most materials with a chiral centre in the aliphatic chain exhibit second-order NLO effects too small to be of any practical significance [5]. A similar electro-optical effect is the nematic electroclinic effect (CR) which is small in ordinary chiral nematics but expected to be larger in molecules with strong coupling between the chiral and optical portions. Liquid crystalline materials with a chiral centre in the core of the molecule such as in the central group or lateral substituents are known but the chirality and NLO effects are small. A better approach would be to incorporate the chirality into the entire molecule such as can be found in fused ring systems with restricted rotation due to steric hindrance. Such compounds have a much larger chirality and larger NLO effects. Liquid crystalline properties have already been reported in chiral biphenanthryl compounds [6, 7], despite the fact that the core of these molecules are quite twisted and bulky having no resemblance to the flat cores of rigid rod or nearly flat disk-like shapes usually required for observing mesophases. Thus, it seemed reasonable that a highly substituted binaphthyl ring compound **1**



with the substituents in the appropriate position would also exhibit mesophases. These should be easier to synthesize than the biphenanthryl analogues and a chiral starting material, the 2,2-diol ($X = OH$), is commercially available. Conceivably, cyano groups could be incorporated into the best positions to give the strong dipole needed to obtain good NLO materials as well as nematic phases (X or $Y = CN$). Long aliphatic chains or a combination of aliphatic chains on aromatic rings could be added via alkylation or esterification of the hydroxy or acid groups respectively (X or $Y = OR, CO_2R$ or Ar). Additional long chains elsewhere in the core (Z) would be more favourable for obtaining mesophases.

Conceivably, such materials which are neither solely rods or disks could also show biaxial nematic (N_b) phases. Since the discovery of a N_b phase in lyotropic systems [8] several attempts have been made to synthesize a compound having a disk-rod shape with hindered rotation along the molecular axis of the mesogenic group, features believed to be necessary to obtain a N_b phase [9, 10]. Although a number of thermotropic N_b phases in single compounds have been reported [11–16] further studies

have shown that these are not N_b phases [17, 18]. Thus, observance of a thermotropic N_b phase remains elusive and synthesis of a compound which would show such a phase still remains an interesting challenge in organic synthesis.

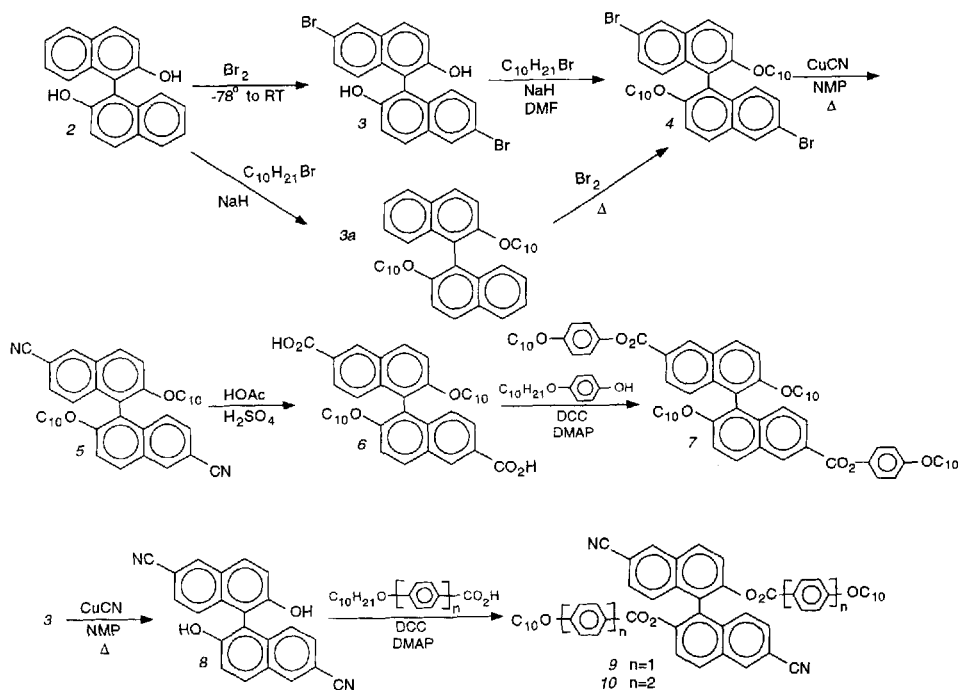
Mesophases occur in a compound when step-wise melting is possible. Usually, this is accomplished by balancing a rigid core with flexible substituents allowing for the retention of enough intermolecular forces to maintain a parallel alignment while others are broken, destroying the three-dimensional crystalline lattice and forming a mesophase. Since the binaphthalene core is quite rigid, it seemed reasonable that several pairs of flexible substituents would have to be incorporated into the structure to observe a mesophase. Flexible chains containing aromatic rings were needed to compensate for the twisted core.

Synthetically, the incorporation of at least two pairs of chains seemed reasonable. However, each chain added affects reactivity and orientation making it more difficult to incorporate additional chains. At the same time, it was necessary to include a pair of substituents such as a bromine atom which could eventually be converted to the cyano group. Such a group needs to be in the proper position in relationship to the binaphthalene ring, the other substituents and with the other member of the pair to obtain the dipoles with the preferred orientation (for example, $X = OR, Y = CN$ and $Z = OR$ or CO_2R) in order to obtain the desired properties. Thus, our initial goal was to determine what was feasible synthetically. Racemic starting materials were first used to determine the feasibility of these synthesis goals.

2. Synthesis

Several approaches were tried to introduce increasing numbers of long chains into the binaphthyl ring system while retaining a bromide pair which could eventually be converted to the desired dinitrile. A pair of long chains were successfully introduced using the binaphthol **2** (scheme 1) as the starting material. Bromination of this diol gave the previously reported dibromide **3** [19–21]. Alkylation of this dibromide to the diether **4** followed by treatment with $CuCN$ gave the dinitrile **5** with a pair of long alkyl chains.

The optically active dinitrile **5** was also prepared from (*R*)-(+)-binaphthol using this method. However, the dibromodiols **3** was difficult to purify because of its poor solubility in organic solvents. The crude material was contaminated with a small amount of an impurity showing NMR peaks at δ 8.49, 7.45, 6.90, 5.08, and 4.96. This material was removed by converting the diol to a tetrabutylphenylsilyl ether, purifying by chromatography and then converting this back to the diol [22]. Synthesis of the dibromide **4** by first alkylating the diol **2**



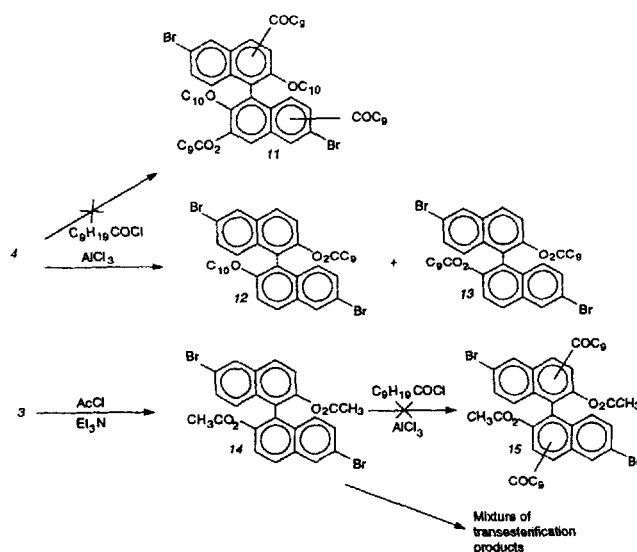
to the diether **3a** and then brominating avoided the solubility problem with the diol.

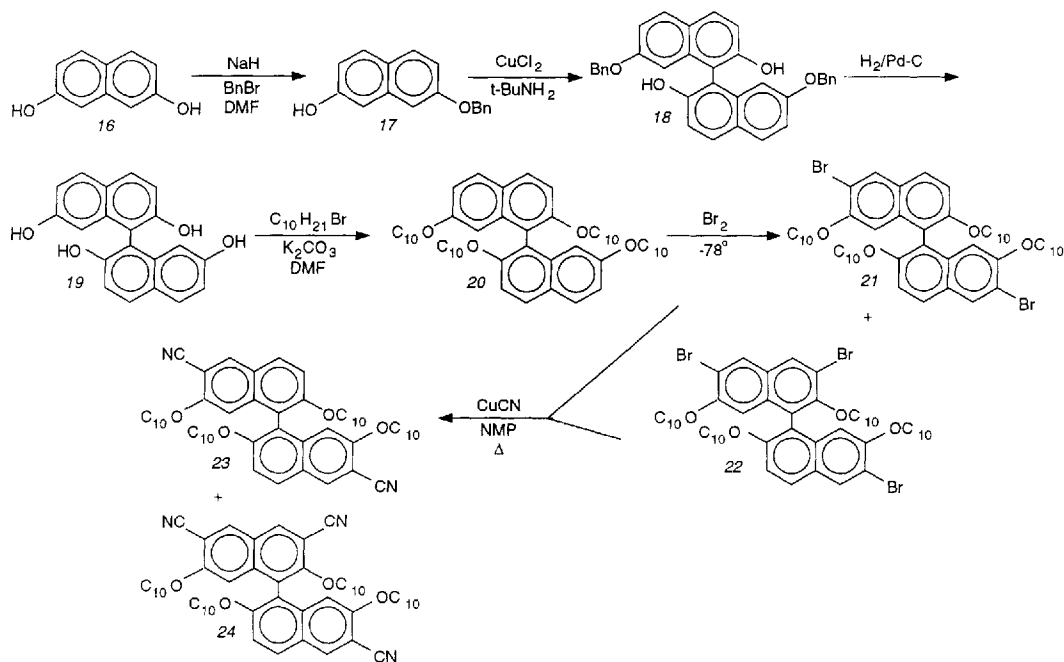
Hydrolysis of the nitrile to the acid **6** followed by esterification yielded a binaphthalene with two pairs of long chains, one being alkyl and the other an alkyl-aryl combination **7**. The dibromodiols **3** was also converted to the nitrile **8** and then esterified to give a new dinitrile **9** or an alkoxybiphenyl ester **10**. Yields of purified materials were reasonably high (50–90 per cent). Conversion of the dinitrile **8** to the alkylated dinitrile **5** was also achieved but the overall yield was lower (47.1 per cent) than that obtained via the dibromide **4** (67.9 per cent) because a higher yield was obtained in converting **4** to **5** than **3** to **8**.

Attempts to introduce a third set of long chains through Friedel–Crafts acylation of the dibromodiether **4** (see scheme 2) failed to give any of the desired ketone **11** after several attempts using varying conditions. A slight excess of the reagents in two different solvents, CH_2Cl_2 and CH_3NO_2 , gave no ketone when stirred up to 16 h at RT. Only starting material was isolated. Refluxing also gave no ketone. Instead, cleavage of the ether groups followed by esterification occurred as indicated by isolation of the esters **12** and **13**. Several attempts to circumvent this problem by protecting the phenol **3** through esterification with acetyl chloride to give the ester **14** and then treating this compound with the C_9 acid chloride also did not produce the ketone **15**. Instead, a complex mixture of transesterification products was isolated. The failure to isolate any ketone discouraged additional attempts,

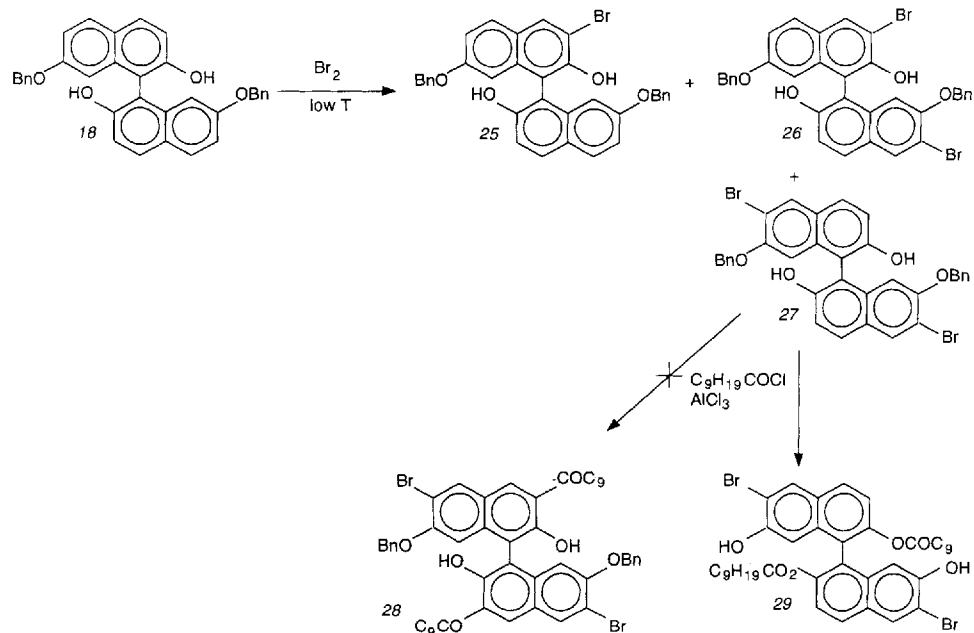
including using the C_9 acid chloride to acylate both the hydroxy group and the aromatic ring.

A different approach involved preparing the tetrol **19** from the naphthalene diol **16** (see scheme 3). It was necessary to first protect one of the hydroxy groups with a benzyl group **17** (this had to be separated from the diether) to avoid forming a poly(naphthol) in the oxidative coupling step. A number of reagents $\text{Mn}(\text{acac})_3$ [23], FeCl_3 [24], and CuCl_2 with *t*-butylamine [25], were tried in this reaction but the best results were obtained with the CuCl_2 method. It also has the advantage that a chiral





Scheme 3.

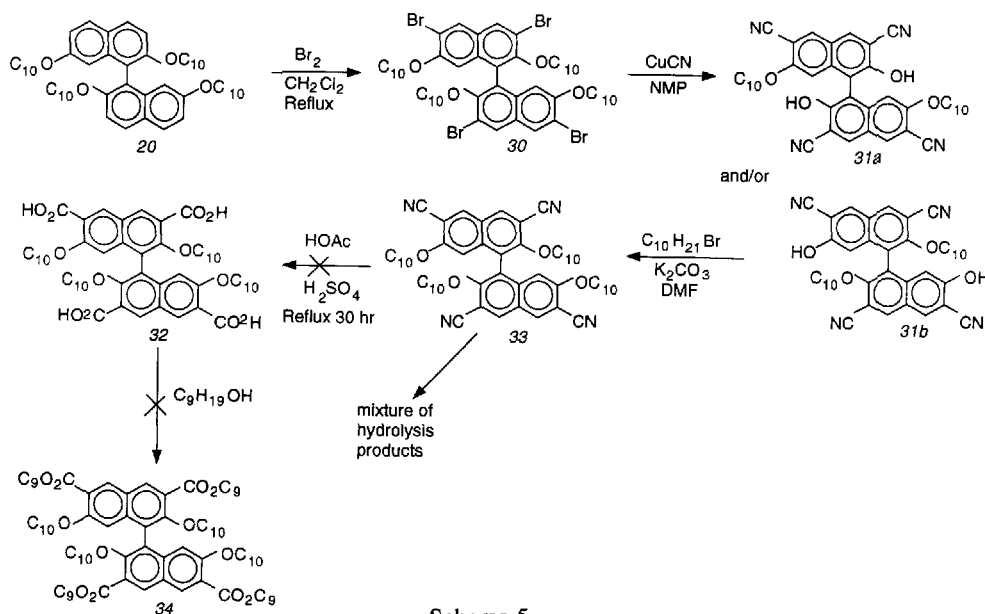


Scheme 4.

tertiary amine could be used to prepare the chiral binaphthyl compound. The diol **18** was isolated in a purified yield of 86 per cent. Catalytic hydrogenation removed the benzyl groups to give the tetrol **19** which was then converted to the tetraether **20**. Bromination of this compound at low temperatures gave a mixture of the di-**21** and tribromides **22**. A small amount of this mixture was separated by chromatography for characterization of the structures by NMR. The remainder was treated with CuCN to give a mixture of the di-**23** and tri-**24** nitriles. These

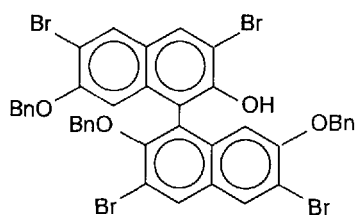
were separated by chromatography and characterized. The dinitrile **23** was found to be too impure to obtain a good elemental analysis and not enough material was available for further purification. Since no mesophases were detected by microscopy no additional material was prepared.

Low temperature (–78°C) bromination of the diol **18** also gave a mixture of bromides (see scheme 4). Three bromides **25–27** were separated by chromatography and characterized by NMR. Only one of these **27** has two



Scheme 5.

bromines in the positions needed to be converted to a desirable dinitrile. Bromination at 0°C gave primarily the tetrabromide:



Attempts at Friedel–Crafts acylation of this compound to obtain the ketone **28** again gave only an ester **29**.

High temperature bromination of the tetraether **20** gave the tetrabromide **30** (see scheme 5) but treatment with cuprous cyanide caused ether cleavage to the phenol **31** which could be either **31 a** or **31 b**. Alkylation of this diol was then needed to give the desired tetranitrile **33**. Hydrolysis of all four nitriles to the tetraacid **32** followed by esterification could yield the tetraester **34** but complete hydrolysis was not achieved as shown by IR and NMR spectra of the hydrolysis mixture which suggested that it contained nitrile, amide and acid groups in various combinations.

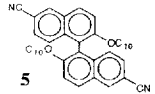
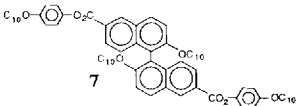
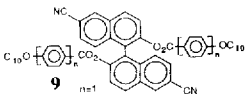
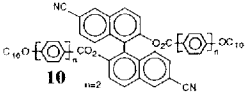
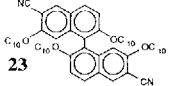
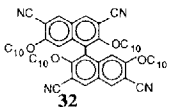
The difficulty of adding additional chains to the binaphthyl ring system in positions which would be the most favourable for mesomorphic properties and the absence of any mesophases in the compounds synthesized did not seem to warrant additional effort to incorporate more chains into the binaphthyl ring system.

3. Mesomorphic and optical properties

Transition temperatures (°C) for the binaphthyl compounds most likely to show mesophases were determined by hot-stage polarizing microscopy (see table 1). No mesophases were obtained in any of these compounds. Several of them, **9**, **10**, and (*R*)-(+)-**5** as well as the dibromide **3** formed very viscous liquids which did not crystallize on cooling suggesting that glasses may have formed.

The observance of a melting temperature for the optical isomer of **5** which was considerably below that for the racemic material suggested that the racemic material is actually a racemic compound, i.e. the molecules prefer to pack in a crystal structure with molecules of opposite chirality rather than the same [26]. Further, evidence for this is the fact that the racemic material, once melted, recrystallized fairly quickly whereas the optical isomer did not crystallize even when cooled to -20° and allowed to stand at RT for a long time. If the molecules prefer to pack with opposite isomers, then crystallization with the same isomers would be more difficult. Formation of a racemic compound is obvious in a phase diagram of both optical isomers since two eutectics occur on either side of the racemic material (1:1) whereas only one occurs in a racemic mixture at a ratio of 1:1. An easy way to determine the phase diagram is to use the Kofler contact method [27 (a)]. Although we had only one optical isomer and the racemic mixture, we thought we could do one-half of the phase diagram, but the reluctance of the optical isomer to crystallize simply gave a solid for half of the sample with the remainder staying in the liquid phase. Since the eutectic can occur anywhere between the optically pure isomer and the racemic material [27 (b)],

Table 1. Transition temperatures of some binaphthyl derivatives.

Compound	Transition temperatures/°C	
	C†	I
	± 75.8 (R)-(+) [‡]	95.5–96.1 56.0–57.8
	75.4	81.8–82.0
	‡	103.9–105.7§
		160.3–162.6§
	15.2	~ 56.4¶
	95.2	100.4–100.7

† C = crystallization temperature obtained on cooling at 2° min^{-1} , I = isotropic liquid.

‡ Crystallization never occurred in this sample even after setting at RT for a long time.

§ Crystallization occurred only after the sample was allowed to set at RT for 8 days.

|| Melting temperatures were determined using the crystals obtained by recrystallization from solvent.

¶ This sample was not pure enough to obtain an elemental analysis and a sharp melting transition. It was, however, obvious that no mesophases were present. These are more likely to occur in an impure than in a pure compound.

this provides no indication of the optical purity of this isomer. We were unable to determine optical purity by other means but the sharp melting point suggests that the purity is high.

The optically active dibromidiol **3** also had a melting temperature below that of the racemic material (97° versus 200°C) and the optically active ether **4** never crystallized whereas the racemic material did. This suggests that these materials also form racemic compounds. Initially, melting of the optically active dibromide **3** seemed to be broad. However, with the purified material, it became obvious that this solid melts quickly to a highly viscous liquid which traps air bubbles. These are released with continued heating causing the effect of a broad melting temperature. This was also true of the racemic material.

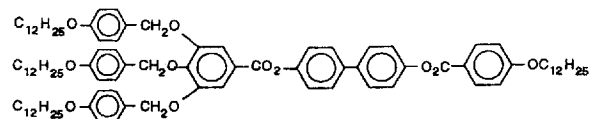
The optical rotations for these highly chiral compounds

were high. The starting diol **2** has a rotation of 34.1° . Converting this to the dibromide **3** gave an extremely large rotation with an opposite sign -120.6° . Rotations for the remaining compounds were **3a**, $+70.9^\circ$, **4**, $+32.8^\circ$, and **5**, $+40.7^\circ$.

Although these compounds showed no mesophases, their expected high chirality in the optical isomer could make them useful as dopants. The large difference in molecular shapes for these binaphthyl compounds and liquid crystalline materials of interest as hosts would likely give poor mixtures at higher concentrations of the dopant, but a high chirality would require less dopant. Since the easiest compound to prepare as a single optical isomer was the dinitrile **5** (BINAP), several mixture studies were done using this compound as a dopant and a variety of known liquid crystals as the host. The racemic material was used initially to determine the best mixtures. Then the optical isomer was tried with these better mixtures.

All mixtures were prepared by melting together the two components, stirring well and allowing the melt to crystallize. Transition temperatures and mesophase identification were determined by hot-stage polarizing microscopy (see table 2). Our goal was to obtain some idea if mixtures were feasible and what, if any, mesophases would be observed, not to obtain highly detailed and precise mixture phase diagrams. It was obvious from the mixed phase regions observed that only small concentrations of dopant would yield good mixtures. The most promising mixture was found in mixtures of 1–5 per cent of the BINAP dopant in 8OCB which showed a wider range nematic phase than found in 8OCB which also has a smectic A below the nematic phase (see figure 1). The smectic A phase disappeared in 2 per cent mixtures and mixed phase regions of nematic and isotropic liquid occurred above 6 per cent. Use of the optical isomer at 2 per cent gave a cholesteric phase.

Previously the diester **36**



36

was reported to show a thermotropic biaxial nematic (N_b) as well as a uniaxial nematic (N_u) phase [15, 16]. Our own studies of this compound showed a N– S_C combination [17] instead. However, the possibility exists that the nematic phase could have an undetectably small biaxiality. Therefore, this compound was tried as a host material for the BINAP dopant. A combination of nematic and smectic C phases were observed at concentrations of < 6 per cent (see table 2). Higher concentrations showed only a nematic phase which became monotropic at 20.9 per cent.

Table 2. Transition temperatures (°C) for binary mixtures of the binaphthyl dinitrile **5** with other mesomorphic compounds.

Compound	Mol% of 5	S†	S†	S†	S _B	S _C	S _A	N	I
Diester 36	0.0					67.4		78.0	93.7†
	4.0‡					70.5		77.1	91.4
	4.9					(68.0)		76.5	89.6
	5.9					(66.0)		76.1	86.2
	8.0							82.0	86.7
	20.9							(68.5)	85.1
	100.0								95.9
Biphenylester 37	0.0				81.4	111.3	115.9		181.3
	9.66								177.3
Biphenylthioester 38	0.0	96.0	138.4	151.8		153.8	209.0	217.2	229.7
	7.6	110.0	132.1	151.6		153.1	195.1	203.4	220.0
	12.1	114.2	~ 131	151.7		153.3		~ 194	> 210
	17.4	?	~ 114	~ 152		~ 153		?	~ 194
	30.7							92.3	170.8

† Smectic phases not totally characterized.

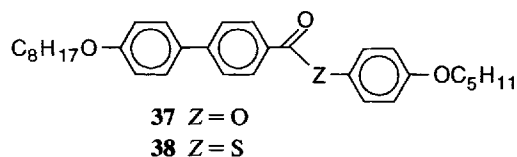
‡ Data from [17].

§ The (+) optical isomer was used giving a twisted N or cholesteric phase.

|| Unpublished data, see [28].

Use of the optical isomer gave a cholesteric phase which showed some luminescent colours in non-polarized light.

Mixtures of the BINAP dopant with the biphenyl ester **37** and the thioester **38**



were studied to determine if chiral smectic phases such as S_C^{*} would be observed. The ester **37** showed no

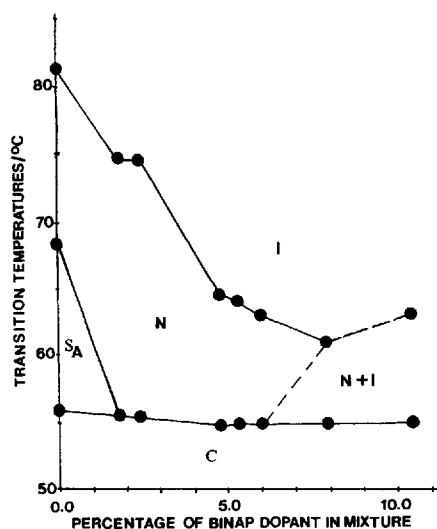


Figure 1. Phase diagram for mixtures of the BINAP **5** dopant in 8OCB

mesophases at a dopant concentration of 9.66 per cent. Conceivably smaller concentrations could yield mesophases but mixtures with the thioester **38** were more promising. Surprisingly, the extensive mesophase polymorphism was retained in a mixture of 7.6 per cent of the dopant. At 12.5 per cent, observing some of the transitions became difficult due to mixed phase regions. At 30.7 per cent only the nematic phase was present.

We were also interested in determining if the chiral BINAP dopant could be used to twist a known nematic phase to a highly chiral nematic phase giving the bright colours observed in the visible region which are usually seen only with the cholesteric compounds. A small amount of the BINAP dopant was added to the following room temperature nematic liquid crystals: MBBA, E7, and 5CB. All formed cholesteric (twisted nematic) phases as shown by the observance of oily streaks, focal-conic textures, and brilliant colours. These colours were also seen in the visible region. Heating the 5CB mixture to obtain a more consistent mixture and cooling gave only a cholesteric phase below room temperature whereas both MBBA and E7 retained the cholesteric phase at room temperature.

4. Conclusions

Synthetically, incorporating two pairs of long chains along with a pair of nitrile groups in the appropriate positions was feasible (for example, **23**) whereas adding an additional pair of chains was found to be difficult. No mesophases were observed in any of the compounds prepared. A review of the scant data provided for the phenanthrene compounds reported earlier [6, 7] raises the

question as to whether the transition observed was that for a mesophase as reported or was instead a crystal-to-crystal change.

The chiral binaphthyl compound **5** can be used as a dopant in mixtures of liquid crystals when used in small concentrations. A good nematic phase region was observed in the mixtures with 8OCB while the smectic A was suppressed. Both the nematic and smectic phases were retained in mixtures with a biphenyl thioester which shows extensive polymorphism. Highly coloured cholesteric phases were observed in mixtures with room temperature nematic phases.

5. Experimental

The starting materials 4-decyloxyphenol [28], 4-decyloxybenzoic acid [28], and 4'-decyloxybiphenyl-4-carboxylic acid [29], were prepared according to the literature. Optically active (*R*)-(+)-1,1'-bi-2-naphthol (99 per cent pure) was obtained from Aldrich Chemical Company and had a rotation of $[\alpha]_D^{21} + 34^\circ$ (1.0, THF). The liquid crystals 5CB, 8OCB, and E7 were obtained from EM Industries, Inc. (MBBA = 4'-methoxybenzylidene-4-butylaniline, 5CB = 4'-pentyl-4-cyanobiphenyl, 8OCB = 4'-octyloxy-4-cyanobiphenyl, and E7 = a mixture of 4'-alkyl-4-cyanobiphenyls). All other starting materials were commercially available and used without further purification. Anhydrous reactions were run under N₂ in glassware dried overnight at 130°C in an oven. Organic extracts were dried over anhyd Na₂SO₄. Flash column chromatography was done using E. Merck or Mallinckrodt silica gel (230–400 mesh) under N₂ (10–15 psi) by the method previously described [30]. TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and F₂ as the detectors. Preparative TLC was performed on Whatman silica gel 60A plates. Melting points were determined using a Thomas–Hoover Uni-melt apparatus and are corrected. All temperatures are given in °C. Melting points are not given when transition temperatures were determined by microscopy. Elemental analyses and mass spectra were obtained from Oneida Research Services, Inc., Whitesboro, New York. Optical rotations were determined using an Optical Activity Ltd AA-10 automatic polarimeter.

Sargent–Welch (Pye Unicam) 3-200 and a Nicolet Magna 550 spectrophotometer were used to record IR spectra (cm⁻¹) in Nujol unless otherwise noted. Both ¹H and ¹³C NMR spectra were run in CDCl₃ (unless otherwise specified) with TMS as the internal standard using a Varian Gemini-200 spectrometer equipped with a VXR-400 data station. The standard numbering system used for binaphthalene was used to identify the protons in interpretation of the ¹H NMR data with only one set indicated when the prime set was the same. Protons on the

benzene and biphenyl rings are differentiated from the binaphthalene protons by *be* and *biph* respectively.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a modified and calibrated Mettler FP2 heating stage at a heating rate of 2° min⁻¹. Crystallization temperatures were obtained by cooling the melt at 2° min⁻¹ until crystals were formed to ensure that all mesophases had been observed before this temperature. These crystals were reheated to obtain the melting temperatures and to confirm that these were not mesophases.

5.2.1. 6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl, **3**

This compound was prepared using the literature method [20] for the synthesis of the *R*-(–)-isomer. The crude product was recrystallized from benzene–hexane giving the purified (colourless) dibromide **3** (71.7 per cent): m.p. 200.0–202.5° (lit. [19] m.p. 199–199.5°); TLC (CH₂Cl₂) *R*_f = 0.19 (*R*_f for **2** = 0.15); IR 3250–2050 (OH) and 1590 (Ar); ¹H NMR 8.04 (d, 2, *J* = 1.91, H₅), 7.87 (d, 2, *J* = 9.08, H₄), 7.38 (d, 2, *J* = 8.95, H₈); 7.36 (dd, 2, *J* = 2.07 and 8.9, H₇), 6.95 (d, 2, *J* = 8.83, H₃) and 3.53 (br s, 2, OH); ¹³C NMR 152.94, 131.87, 130.84, 130.64, 130.54, 130.42, 125.86, 118.95, 117.99 and 110.68. Elemental analysis calculated for (C₂₀H₁₂Br₂O₂). C 54.07, H 2.72; found: C 53.67, H 2.67.

The optical isomer was prepared in the same manner from the (*R*)-(+)-isomer of the binaphthol **2** in a yield of 93.3 per cent. A purified sample (colourless) was obtained by preparing the *t*-butyldiphenylsilyl ether, chromatographing this material and then converting it back to the diol using the method described earlier [22]: m.p. 94.2–97.0°C (microscope) and $[\alpha]_D^{22} = -120.6^\circ$ (*c* 0.8, CH₂Cl₂) lit. [20] value = -129.0° (*c* 1 CH₂Cl₂), (+)isomer [21] 43.5° (*c* 1.83, THF) IR and NMR data were identical to those for the racemic material.

5.2.2. 6,6'-Dibromo-2,2'-didecyloxy-1,1'-binaphthyl, **4**

To a stirred solution of the diol **3** (2.0 g, 4.5 mmol) in DMF (10 ml) was added NaH (alkylation with KOH in THF gave a lower yield) (280 mg 80 per cent oil emulsion) at RT followed first by benzyltrimethylammonium bromide (~10 mg) within 10 min and then a solution of decyl bromide (1.94 g, 8.80 mmol) in DMF (5 ml) added dropwise 30 min later. The reaction mixture was stirred at RT under N₂ for 10 h, H₂O (40 ml) added, stirred for 0.5 h and the precipitate removed by filtration. This material was dissolved in CH₂Cl₂, dried, filtered and the filtrate rotovaped to give the crude product (3.24 g). Recrystallization of this material from hexane gave the purified (colourless) diether **4** (2.79 g, 87.8 per cent): m.p. 84.0–85.0°; IR 1580 (Ar); ¹H NMR 7.99 (dd, 2, *J* = 1.75, H₅), 7.83 (d, 2, *J* = 9.08, H₄), 7.40 (d, 2, *J* = 9.12, H₈), 7.26 (dd, 2, *J* = 2.00 and 8.99, H₇), 6.97 (d, 2, *J* = 9.16, H₃),

3.98–3.86 (m, 4, OCH₂), 1.39 (quint, 4, *J* = 6.92, OCH₂CH₂), 1.32–1.01 (m, 28, CH₂), and 0.89 (t, 6, *J* = 6.45, CH₃); ¹³C NMR 154.74, 132.56, 130.17, 129.74, 129.42, 128.35, 127.11, 120.03, 117.21, 116.38, 69.52, 31.92, 29.49, 29.34, 29.14, 29.01, 25.66 and 22.71. Elemental analysis: calculated for C₄₀H₅₀Br₂O₃: C 65.02, H 6.83; found: C 64.67, H 6.72.

The optically active isomer (colourless liquid) was synthesized from the (–)diol **3** either in the same manner (36.3 per cent) or via the (*R*)-(+) ether **3a**.

5.2.3. (*R*)-(+)–2,2′-Didecyloxy-1,1′-binaphthyl, **3a**

A mixture of (*R*)-(+)–1,1′-bi-2-naphthol **2** (4.0 g, 0.014 mol) and 60 per cent NaH in mineral oil (1.12 g, 0.028 mol, washed once with hexane) in DMF (11 ml) was stirred at RT for 2 h and then decylbromide (6.81 g, 0.031 mol) added dropwise. The reaction mixture was heated at 60°C for 22 h, cooled to RT and the DMF removed by vacuum distillation. Water was added to the remaining liquid and the mixture extracted with CHCl₃. The organic layer was washed with H₂O, 5 per cent aq KOH, H₂O, dried, filtered and the filtrate rotovaped to give 7.9 g of the crude product. Flash chromatography of this material on silica gel gave some starting material with hexane as the eluting solvent. Further elution with 20 per cent CH₂Cl₂ in hexane gave 6.13 g (77.3 per cent) of the purified ether **3a**, as a thick yellow liquid: TLC (CHCl₃) *R*_f = 0.86; IR (film) showed 1630, 1600 and 1517 (str, Ar) peaks and no OH absorption; ¹H NMR 7.90 (d, 2, *J* = 8.95, H₅) 7.84 (d, 2, *J* = 8.06, H₄), 7.40 (d, 2, *J* = 9.08, H₈), 7.35–7.10 (m; 6; H₃, H₆ and H₇), 3.92 (either 2d of t or 2t of d, 4, *J* = 6.23, OCH₂) and 1.48–0.72 (m, 38, 2C₉H₁₉) and [α]_D²² = +70.9° (c 1.1, CH₂Cl₂).

5.2.4. Bromination of the (*R*)-(+) diether **3a**

A solution of the (*R*)-(+) diether **3a** (690 mg, 1.20 mmol), Br₂ (390 mg, 2.43 mmol) in CH₂Cl₂ (7 ml) was refluxed 2 h and then stirred at RT for 17 h. A 10 per cent solution of NaHSO₃ was added; the organic layer separated, washed with H₂O, dried, filtered and the filtrate rotovaped to give 760 mg (61.4 per cent) of the crude product. Purification of this material by flash chromatography on silica gel eluting with hexane gave 240 mg (27.2 per cent) of the purified (*R*)-(+)–dibromide **4**: IR and NMR data were identical to those for the racemic material [α]_D²² = +32.8° (c 0.9, CH₂Cl₂). Further elution gave a second fraction as a yellow liquid (300 mg) giving a total yield of 61.4 per cent.

5.2.5. 2,2′-Didecyloxy-6,6′-dicyano-1,1′-binaphthyl, **5**

Cuprous cyanide (0.49 g, 5.5 mmol) was added in small portions to a stirred solution of the dibromide **4** (1.0 g, 1.4 mmol) in freshly distilled 1-methyl-2-pyrrolidinone (25 ml) at RT. This mixture was refluxed for 5 h, cooled

to RT and aq. FeCl₃ solution (1.30 g in 15 ml 1 N HCl) added. After stirring for an additional 0.5 h, this mixture was extracted with Et₂O (5–6 times), the combined Et₂O extracts washed with H₂O (2 × 50 ml), dried, filtered and the filtrate rotovaped to give the crude product (1.01 g). Purification of this material by flash chromatography using CH₂Cl₂ as the eluting solvent followed by recrystallization from hexane gave the purified dinitrile **6** (0.62 g, 72.9 per cent) as a colourless solid: TLC (CH₂Cl₂) *R*_f = 0.52, IR 3200–3060 (OH), 2210 (CN) and 1610 (Ar); ¹H NMR 8.25 (d, 2, *J* = 1.85, H₅), 8.01 (d, 2, *J* = 9.08, H₄), 7.50 (d, 2, *J* = 9.08, H₈), 7.34 (dd, 2, *J* = 1.69 and 8.81, H₇), 7.13 (d, 2, *J* = 8.83, H₃), 4.04–3.96 (m, 4, CH₂O), 1.42 (quint, 4, *J* = 6.82, OCH₂CH₂), 1.35–0.92 (m, 28, CH₂) and 0.89 (t, 6, *J* = 6.92, CH₃); ¹³C NMR 156.82, 135.37, 134.30, 130.32, 127.60, 126.68, 126.33, 126.04, 119.51, 118.94, 116.03, 106.56, 69.08, 31.83, 29.38, 29.23, 28.98, 25.53, 22.62 and 14.08; transition temperatures 95.5–96.1 (C–I), 75.8 (I–C). Elemental analysis: calculated for C₄₂H₅₂N₂O₂: C 81.78, H 8.50, N 4.54; found: C 81.79, H 8.53, N 4.48.

The optically active isomer was prepared in the same manner (60.5 per cent). Purification was by flash chromatography using 40 per cent CH₂Cl₂ in hexane followed by recrystallization from abs. EtOH giving a colourless solid: [α]_D²² = +40.7° (c 0.7, CH₂Cl₂) and transition temperature 56.3–58.1 (C–I). The NMR spectrum was identical to that for the racemic material.

5.2.6. 1,1′-Binaphthyl-2,2′-didecyloxy-6,6′-dicarboxylic acid, **6**

A mixture of the dinitrile **5** (1.75 g, 2.8 mmol) in glacial HOAc (21 ml) and 50 per cent H₂SO₄ (21 ml) was refluxed for 22 h and then poured into ice water (150 ml). The precipitate was removed by filtration, washed with water, dried, dissolved in acetone, filtered and the filtrate rotovaped to obtain the dicarboxylic acid **6** (1.34 g, 72.4 per cent): m.p. 218–219°; TLC (Et₂O) *R*_f = 0.1; IR 3200–2500 (CO₂H), 1680 (C=O), 1620 (Ar); ¹H NMR (*d*₆–DMSO) 8.63 (d, 2, *J* = 1.10, H₅), 8.24 (d, 2, *J* = 9.16, H₄), 7.72 (dd, 2, *J* = 1.38, 8.95 H₇), 7.65 (d, 2, *J* = 9.15, H₈), 7.01 (d, 2, *J* = 8.87, H₃), 4.02–4.00 (m, 4, CH₂O), 1.35–1.12 (m, 32, CH₂) and 0.85 (t, 6, *J* = 6.74, CH₃); ¹³C NMR (*d*₆–DMSO). 167.74, 156.23, 135.79, 131.37, 131.28, 127.88, 125.82, 125.73, 124.91, 118.90, 116.04, 68.65, 31.53, 29.15, 29.05, 28.92, 28.73, 25.34, 22.36 and 14.21. Elemental analysis: calculated for C₄₂H₅₄O₆: C 77.03, H 8.31; found: C 76.97, H 8.29.

5.2.7. 6,6′-Di(4-decyloxyphenyl)-2,2′-didecyloxy-1,1′-binaphthoate, **7**

A mixture of the diacid **6** (0.60 g, 0.9 mmol), 4-decyloxyphenol (0.57 g, 2.3 mmol, dicyclohexylcarbodiimide (0.47 g, 2.3 mmol) and dimethylaminopyridine (0.03 g,

0.23 mmol) in CH_2Cl_2 (20 ml) was refluxed for 4 h, cooled to RT and the precipitated DCU removed by filtration. The filtrate was extracted with 3*N* HCl (35 ml), 5 per cent aq. KOH (35 ml) and H_2O (3×35 ml), dried, filtered and the filtrate rotovapoured to give the crude product (1.60 g). This material was purified by flash chromatography using CH_2Cl_2 to elute the product (0.84 g, 81.6 per cent). Recrystallization of this material from hexane gave the purified diester **7**: TLC (CH_2Cl_2) $R_f = 0.68$; IR 1710 (CO_2R) and 1600 (Ar); ^1H NMR 8.82 (d, 2, $J = 1.47$, H_5), 8.13 (d, 2, $J = 8.79$, H_4), 7.93 (dd, 2, $J = 1.75$, 8.91, H_7), 7.51 (d, 2, $J = 9.08$, H_8), 7.22 (d, 2, $J = 8.88$, H_3), 7.15 (d, 4, $J = 9.04$, beH *ortho* to CO_2Ar), 6.94 (d, 2, $J = 9.12$, beH *ortho* to OC_{10}), 3.98 (m, 8, OCH_2), 1.80 (quint, 8, $J = 6.59$, OCH_2CH_2), 1.46–1.03 (m, 56, 28CH_2), 0.89 (t, 12, $J = 6.76$, CH_3); ^{13}C NMR 165.8, 156.8, 156.7, 144.4, 136.7, 132.2, 131.2, 127.9, 125.8, 125.5, 124.4, 122.4, 119.6, 115.7, 115.1, 69.2, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.6, 22.7 and 14.1; transition temperatures 81.8–82.0° (C–I) and 75.5° (I–C). Elemental analysis: calculated for $\text{C}_{74}\text{H}_{102}\text{O}_8$: C 79.38, H 9.18, found: C 79.17, H 9.12.

5.2.8. 1,1'-Binaphthyl-6,6'-dicyano-2,2'-diol, **8**

This dinitrile was prepared from the dibromide **3** in the same manner as the dinitrile **5** was synthesized to give a quantitative yield of the crude product. Purification of this material by flash chromatography using Et_2O as the eluting solvent gave the solid dinitrile **8** (0.89 g, 58.9 per cent): TLC (Et_2O) $R_f = 0.41$; IR 3500–3000 (OH), 2220 (CN) and 1610 (C=C); ^1H NMR 10.04 (br s, 2, OH), 8.52 (d, 2, $J = 1.47$, H_5), 8.07 (d, 2, $J = 8.87$, H_4), 7.49 (d, 2, $J = 8.95$), 7.48 (dd, 2, $J = 2.74$ and 8.75, H_7) and 7.03 (d, 2, $J = 8.79$, H_3), and ^{13}C NMR 156.82, 135.37, 134.30, 130.32, 127.60, 126.68, 126.33, 126.04, 119.51, 118.94, 116.03, 106.56, 69.08, 31.83, 29.38, 29.23, 28.98, 25.53, 22.62 and 14.08.

5.2.9. 6,6'-Dicyano-1,1'-binaphthyl-2,2'-di(4-decyloxybenzoate), **9**

This diester was prepared in the same manner as was the ester **7**. Purification of the crude product by flash chromatography on silica gel using CH_2Cl_2 as the eluting solvent followed by recrystallization from hexane gave the purified diester **9** (0.56 g, 87.5 per cent): TLC (CH_2Cl_2) $R_f = 0.31$; IR 2215 (CN), 1740 (CO_2R) and 1600 (Ar); ^1H NMR 8.30 (d, 2, $J = 1.01$, H_5), 8.05 (d, 2, $J = 8.95$, H_4), 7.68 (d, 2, $J = 8.95$, H_3), 7.59 (d, 4, $J = 8.96$, beH *ortho* to CO_2Ar), 7.48 (dd, 2, $J = 1.61$, 8.77, H_7), 7.38 (d, 2, $J = 8.79$, H_3), 6.74 (d, 4, $J = 8.96$, beH *ortho* to OC_{10}), 3.93 (t, 4, $J = 6.48$, OCH_2), 1.81–1.21 (m, 32, CH_2) and 0.88 (t, 6, $J = 5.17$, CH_3); ^{13}C NMR 163.96, 163.66, 149.80, 134.68, 134.24, 132.00, 130.43, 130.35, 127.57, 127.00, 124.16, 123.31, 120.25, 118.85, 114.19, 109.53,

68.29, 31.88, 29.54, 29.31, 29.02, 25.94, 22.68 and 14.11; transition temperature 102.7–108.6° (C–I) (since this sample was analytically pure, the broad melting transition is probably due to crystal–crystal changes near this transition), crystallization did not occur on cooling the sample to -20° but only after standing at RT for *c.* **8 d**. Elemental analysis: calculated for $\text{C}_{56}\text{H}_{60}\text{N}_2\text{O}_6$: C 78.48, H 7.06; found: C 78.59, H 7.09.

5.2.10. 6,6'-Dicyano-1,1'-binaphthyl-2,2'-di(4'-decyloxy-1,1''-biphenyl-4-carboxylate), **10**

This diester was synthesized in the same manner as was the diester **7**. Purification of the crude product by flash chromatography using 50 per cent CH_2Cl_2 in hexane as the eluting solvent gave the purified diester **10** (1.04 g, 69.3 per cent): TLC (CH_2Cl_2) $R_f = 0.41$; IR 2240 (CN), 1740 (CO_2R) and 1610 (Ar); ^1H NMR 8.34 (s, 2, H_5), 8.09 (d, 2, $J = 9.16$, H_4), 7.73 (d, 6, $J = 9.20$, bipH *ortho* to CO_2Ar), 7.55–7.40 (m, 12, H_3 , H_8 and 2,2'-bipH), 6.96 (d, 4, $J = 8.83$, bipH *ortho* to OC_{10}), 4.00 (t, 4, $J = 6.55$, OCH_2), 1.81 (quint, 4, $J = 7.18$, OCH_2CH_2), 1.47–1.20 (m, 28, CH_2) and 0.89 (t, 6, $J = 6.41$, CH_3); ^{13}C NMR 164.22, 159.62, 149.70, 146.16, 134.67, 134.31, 131.58, 130.63, 128.28, 127.70, 127.00, 126.44, 126.18, 124.03, 123.26, 118.81, 114.93, 109.67, 68.18, 31.89, 29.56, 29.38, 29.32, 29.22, 26.03, 22.68 and 14.12, transition temperature: 159.8–160.0° (C–I, from the virgin crystals), sample did not crystallize when cooled 2°min^{-1} to -20° nor after standing at RT for 1 month: Elemental analysis calculated for $\text{C}_{68}\text{H}_{68}\text{N}_2\text{O}_6$: C 80.92, H 6.79; N 2.78; found: C 80.67, H 6.78 and N 2.76.

5.2.11. Friedel–Crafts acylation of 6,6-dibromo-2,2-didecyloxy-1,1'-binaphthyl, **4**

Aluminium chloride (0.65 g, 4.9 mmol) was added in small portions to a stirred solution of decanoyl chloride (0.93 g, 2.2 mmol) in CH_2Cl_2 (8 ml). This mixture was stirred at RT for 10 min, a solution of the dibromide **4** (1.60 g, 2.2 mol) in CH_2Cl_2 (10 ml) was added dropwise within 45 min, stirring at RT was continued for 15 h followed by refluxing for 12 h, H_2O (50 ml) was added and then the mixture extracted with CH_2Cl_2 . The organic layer was washed with 5 per cent aq. KOH solution (30 ml), H_2O (2×50 ml), dried, filtered and the filtrate rotovapoured to give a thick oil (2.23 g): TLC (1:1 CH_2Cl_2 –pentane) showed 4 spots. When this material was flash chromatographed using 1:1 CH_2Cl_2 –pentane, an oil (1.78 g) which still showed two spots ($R_f = 0.70$ and 0.80, 1:1 CH_2Cl_2 –pentane) was isolated. A second chromatography using 1:4 CH_2Cl_2 –pentane as the eluting solvent gave two major fractions. Fraction 1 was shown to be the monoester **12**: 0.82 g (50.2 per cent yield); m.p. 65–66°; TLC (1:1 benzene–pentane) $R_f = 0.5$; IR: 1750 (CO_2R) and 1600 (Ar); ^1H NMR 8.08 (d, 2, $J = 1.91$, H_5 or H_5'), 7.98 (d, 2,

$J = 2.08$, H₅ or H₅), 7.87 (d, 2, $J = 8.79$, H₄ or H₄'), 7.85 (d, 2, $J = 8.80$, H₄' or H₄), 7.44–7.26 (m, 4, H₇, H₇', H₈ and H₈'), 7.07 (d, 2, $J = 9.07$, H₃ or H₃'), 6.98 (d, 2, $J = 8.87$, H₃' or H₃), 3.97–3.92 (m, 2; OCH₂), 2.04 (t, 2, $J = 7.29$, O₂CCH₂) and 1.55–0.83 (m, 36, aliph) and MS (rel. intensity) m/z 739 (M + isotropic cluster, 11.4), 289 (C₁₉H₂₅O₂, 100) and 155 (C₉H₁₉CO + , 93.68). Characterization data showed that fraction 2 was the diester **13**: 0.60 g (36.2 per cent, liquid); TLC (1:1 benzene–pentane) $R_f = 0.37$; IR (CHCl₃) 1750 (CO₂R) and 1600, 1570 (Ar); and ¹H NMR 8.08 (s, 2, H₅), 7.90 (d, 2, $J = 8.87$, H₄), 7.43 (d, 2, $J = 8.95$, H₈), 7.37 (dd, 2, $J = 1.46$, 8.51, H₇), 7.05 (d, 2, $J = 9.08$, H₃), 2.10 (t, 4, $J = 7.29$, O₂CCH₂), 1.35–0.93 (m, 28, CH₂) and 0.90 (t, 6, $J = 6.41$, CH₃).

5.2.12. 6,6'-Dibromo-1,1'-binaphthyl-2,2'-diacetate, **14**

A solution of acetyl chloride (0.78 g, 9.9 mmol) in CH₂Cl₂ (8 ml) was added dropwise to a stirred solution of the diol **3** (2.0 g, 4.5 mmol) and Et₃N (1.4 ml) in CH₂Cl₂ (15 ml) and this mixture stirred at RT for 2 h and then H₂O (30 ml) added. The organic layer was separated; extracted with 3*N* HCl (35 ml), 5 per cent aq KOH (35 ml), and H₂O (2 × 35 ml); dried; filtered and the filtrate rotovapoured to give the diacetate **14** (2.36 g, 99.2 per cent): m.p. 176–177°, TLC (CH₂Cl₂) $R_f = 0.45$; IR 1760 (CO₂R) and 1600 (Ar); ¹H NMR 8.11 (d, 2, $J = 2.04$, H₅), 7.92 (d, 2, $J = 9.23$, H₄), 7.45 (d, 2, $J = 8.92$, H₈), 7.37 (dd, 2, $J = 2.02$, 9.02, H₇), 7.01 (d, 2, $J = 8.88$, H₃) and 1.88 (s, 6, CH₃) and ¹³C NMR 168.1, 145.9, 131.5, 130.7, 129.2, 129.1, 127.8, 126.7, 122.1, 119.0 and 19.5.

5.2.13. 7-Benzoyloxy-2-naphthol, **17**

Sodium hydride (10.0 g, 80 per cent oil emulsion) was added in small portions to a stirred solution of the diol **16** (58.50 g, 365.6 mmol) in DMF (100 ml) at RT, stirred for 0.5 h, benzyltrimethylammonium bromide (50.00 g, 292.4 mmol) in DMF (15 ml) added dropwise and stirring continued at RT for 20 h. Water (300 ml) was added, the mixture stirred for 1 h and the aqueous layer decanted. Another aliquot of H₂O was added, the mixture stirred for 1 h and the resulting precipitate removed by filtration. This material was stirred in hot (60°) water to extract any unreacted diol **16**. The insoluble product was removed by filtration, washed with H₂O and dried to give the crude product. This material was recrystallized from MeOH to remove the dibenzyl ether (11.8 g, 11.9 per cent): ¹H NMR 7.67 (d, 2, $J = 8.85$, H₄), 7.55–7.30 (m, 5, C₆H₅), 7.09 (2d; 4; $J = 8.85$; H₁, H₃) and 5.16 (s, 2, OCH₂) and ¹³C NMR 157.37, 136.95, 135.79, 129.20, 128.60, 127.28, 127.53, 124.54, 116.53, 106.67 and 70.0. Concentration of the mother liquor gave the monoether which was recrystallized to give the purified benzyl ether **17** (20.7 g, 29.6 per cent): m.p. 145–147 (lit. [31, 23] m.p. 151–152); TLC (CH₂Cl₂) $R_f = 0.40$; IR, NMR agree with literature [31]

data and ¹³C NMR 154.45, 153.85, 136.88, 135.89, 129.57, 129.32, 129.21, 128.72, 128.60, 128.01, 127.56, 124.48, 116.04, 115.29, 108.82, 100.03 and 70.02.

5.2.14. 7,7'-Dibenzoyloxy-1,1'-binaphthyl-2,2'-diol **18**

A 1 M solution of *t*-BuNH₂ in MeOH (538 ml, degassed) was added dropwise to a stirred solution of the phenol **17** (16.0 g, 64.0 mmol) in MeOH (400 ml, degassed) containing CuCl₂ (18.10 g, 134.5 mmol). A stream of N₂ was bubbled through this solution for 3–4 min and stirring continued for 24 h. This reaction mixture was then cooled to 20°, 6*N* HCl (7–800 ml added), stirred for 1 h and extracted with CH₂Cl₂ (8–10 times). The organic layer was washed with H₂O (2 × 200 ml), dried, filtered and the filtrate rotovapoured to give 17.0 g (106.6 per cent) of the crude product. Purification of this material by flash chromatography using toluene followed by recrystallization from CHCl₃–hexane gave the binaphthyl diol **18** (13.65 g, 85.6 per cent): m.p. 105–107°; TLC (CH₂Cl₂) $R_f = 0.24$ and ¹H NMR 7.88 (d, 2, $J = 8.87$, H₄), 7.79 (d, 2, $J = 8.88$, H₅), 7.23 (d, 2, $J = 8.58$, H₃), 7.23–7.16 (m, 10, C₆H₅), 7.10 (dd, 2, $J = 2.44$, 8.91, H₆), 6.48 (d, 2, $J = 2.48$, H₈), 4.98 (br, s, 2, OH), 4.81 (d, 2, $J = 11.72$, PhOCH_a, H_b) and 4.73 (d, 2, $J = 11.72$, PhOCH_a, H_b).

5.2.15. 2,2',7,7'-Tetrahydroxy-1,1'-binaphthalene, **19**

A solution of the diether **18** (2.3 g, 4.6 mmol) in THF (50 ml) containing 10 per cent Pd-C (100 mg) was hydrogenated at 35° and 50 psi for 24 h, filtered and the filtrate rotovapoured to give the tetrol **19** (1.47 g, 100 per cent): m.p. 68–72°; TLC (CH₂Cl₂) $R_f = 0.05$, (Et₂O) $R_f = 0.90$; IR 3600–3100 (OH) and 1690, 1610 (Ar); ¹H NMR (*d*₆-DMSO) 9.26 (s, 2, OH), 8.98 (s, 2, OH), 7.74 (d, 2, $J = 8.79$, H₅), 7.25 (d, 2, $J = 8.79$, H₄), 7.13 (d, 2, $J = 8.75$, H₃), 6.85 (dd, 2, $J = 2.40$, 8.71, H₆) and 6.36 (d, 2, $J = 2.44$, H₈) and ¹³C NMR (DMSO-*d*₆) 155.69, 153.50, 136.26, 129.65, 128.50, 123.30, 115.56, 155.10, 114.58, 106.47 and 60.08.

5.2.16. 2,2',7,7'-Tetradecyloxy-1,1'-binaphthalene, **20**

A solution of the tetrol **19** (1.47 g, 4.60 mmol) in DMF (15 ml) containing K₂CO₃ (2.90 g, 20.8 mol) was stirred at RT for 0.5 h, benzyltrimethylammonium chloride (100 mg) added followed by a dropwise addition of a solution of decyl bromide (4.30 g, 19.4 mmol) in DMF (5 ml). The reaction mixture was stirred at 50° for 24 h H₂O (100 ml) added and the mixture extracted with CH₂Cl₂. The organic layer was separated, washed with H₂O (3 × 100 ml), dried, filtered and the filtrate rotovapoured to give the crude product (5.90 g). Purification of this material by flash chromatography using 1:4 CH₂Cl₂–hexane gave the tetraether **20** (3.40 g, 84.0 per cent) as a liquid: TLC (CH₂Cl₂) $R_f = 0.88$; IR (film) no OH at 3400, has 1615 (Ar) and ¹H NMR 7.80 (d, 2, $J = 8.79$, H₅), 7.71 (d,

2, $J = 8.95$, H₄), 7.21 (d, 2, $J = 8.95$, H₃), 6.96 (dd, 2, $J = 2.44$, 8.87, H₆), 6.46 (d, 2, $J = 2.36$, H₈), 3.98–3.78 (m, 4, OCH₂), 3.67–3.41 (m, 4, OCH₂), 1.57–1.00 (m, 64, CH₂) and 0.98–0.85 (m, 12, CH₃); ¹³C NMR 157.23, 154.97, 135.45, 129.11, 128.56, 124.73, 119.72, 116.20, 112.97, 104.87, 67.51, 31.89, 29.54, 29.48, 29.37, 29.31, 29.22, 29.00, 26.00, 25.66, 22.66 and 14.10. Elemental analysis calculated for C₆₀H₉₄O₄: C 81.94, H 10.78; found: 81.96, H 10.69.

5.2.17. Bromination of the tetraether **20**

The tetraether **20** (7.4 mmol) was brominated in the same manner as the diol **3** using a reaction time of 6 h and no Norit treatment. The organic layer gave the crude liquid product (4.43 g) which TLC showed consisted of three similar compounds (3 spots at $R_f \sim 0.85$). A small amount was separated by preparative TLC on silica gel using 1:1 CH₂Cl₂–hexane to give three fractions: the unreacted tetraether **20**, a liquid identified by NMR as the tribromide **22**: ¹H NMR 8.03, 8.00, 7.97, (3s; 3; H₄ H₅ and H_{5'}), 7.78 (d, 1, $J = 8.83$, H₄), 7.23 (d, 1, $J = 8.50$, H_{3'}), 6.41, 6.38 (2s, 2, H₈ and H_{8'}), 4.00–3.80 and 3.70–3.60 (m, 8, OCH₂) and another liquid identified as the dibromide **21**: ¹H NMR 8.02 (s, 2, H₅), 7.74 (d, 2, $J = 8.87$, H₄), 7.24 (d, 2, $J = 10.05$, H₃), 6.42 (s, 2, H₈), 4.00–3.80 and 3.70–3.60 (2m, 8, OCH₂) and 1.60–0.80 (m, C₉H₁₉).

5.2.18. Preparation of the nitriles **23** and **24**

The crude bromide mixture from the above reaction (1.80 g) was treated with CuCN in the same manner as was the dibromide **4** using a reflux time of 6 h to give the crude product as a liquid (2.30 g). Flash chromatography of this liquid using 2:3 CH₂Cl₂–hexane gave three fractions: the tetraether **20** (120 mg, 5.2 per cent of the mixture) with TLC $R_f = 0.50$ (1:1 CH₂Cl₂–hexane); the dinitrile **23** (740 mg, 32.2 per cent of the mixture, 20.6 per cent yield based on **20**): $R_f = 0.45$; IR 2210 (CN), 1620, 1600 (Ar); ¹H NMR 8.14 (s, 2, H₅), 7.88 (d, 2, $J = 9.07$, H₄), 7.31 (d, 2, $J = 9.16$, H₃), 6.42 (s, 2, H₈), 4.05–3.92 and 3.74–3.60 (2m, 8, OCH₂), 1.67–1.02 (m, 32, CH₂) and 0.88 (t, 12, $J = 6.40$, CH₃); transition temperatures 56.4° (C–I) and < 15° (I–C, slow). Elemental analysis calculated for C₆₂H₉₂N₂O₄: C 80.12, H 9.98, N 3.01; found: C 78.97, H 9.84, N 2.79. The trinitrile **24** as an orange solid (520 mg, 22.6 per cent of the mixture, 14.2 per cent yield): m.p. 75.0–77.0°; TLC $R_f = 0.32$; ¹H NMR: 8.25, 8.22, 8.17 (3s; 3; H₄, H₅, H_{5'}), 7.96 (d, 1, $J = 8.95$, H_{4'}), 7.32 (d, 1, $J = 9.16$, H_{3'}), 6.46, 6.33 (2d; 2; H₈, H_{8'}), 4.05–3.96, 3.76–3.63 (2m, 4, CH₂) and 1.69–0.75 (m, 76, C₉H₁₉); ¹³C NMR 158.10, 157.23, 157.14, 156.70, 139.21, 138.52, 136.41, 136.10, 131.41, 124.45, 123.32, 122.79, 116.37, 115.55, 115.41, 112.28, 109.59, 104.44, 103.33, 101.97, 74.79, 69.10, 68.95, 68.87, 68.78, 31.86, 29.75, 29.45, 29.28, 29.01, 28.54, 28.38, 25.84, 25.78, 25.70, 25.34,

22.66, 14.10. Elemental analysis calculated for C₆₃H₉₁N₃O₄: C 79.33, H 9.62, N 4.41; found: C 79.34, H 9.86, N 4.47.

5.2.19. Bromination of 7,7'-dibenzoyloxy-2,2'-dihydroxy-1,1'-binaphthyl, **18**

The diol **18** (3.55 g, 7.1 mmol) was brominated at –78° in the same manner as was the diol **2** to give 5.30 g of the crude product. Three fractions were obtained when this material was flash chromatographed using CH₂Cl₂: the 3,3'-dibromide **25** 1.40 g (26.4 per cent of the mixture, 29.6 per cent yield); TLC (CH₂Cl₂) $R_f = 0.60$; ¹H NMR 8.14 (s, 2, H₄), 7.71 (d, 2, $J = 9.04$, H₅), 7.27–7.16 (m, 10, C₆H₅), 7.11 (dd, 2, $J = 2.49$ and 8.96, H₆), 6.37 (d, 2, $J = 2.48$, H₈), 5.43 (s, 2, OH), 4.77 (d, 2, $J = 12.04$, OCH₂H_b) and 4.71 (d, 2, $J = 12.10$, OCH₂H_b); 3,6'-dibromide **26** 1.60 g (35.8 per cent of the mixture, 33.8 per cent yield), m.p. 156.0–158.0°; TLC (CH₂Cl₂) $R_f = 0.51$; IR 3200 (OH) and 1631 (Ar), ¹H NMR 8.18, 8.09 (2s, 2, H₄ and H_{5'}), 7.79, 7.75 (d, 2, $J = 9.15$, and 10.18, H₅ and H₄), 7.27–7.04 (m, 12, H_{3'}, H₆ and C₆H₅), 6.32 (d, 1, $J = 2.48$, H₈), 6.29 (s, 1, H₈), 4.88 (br s, 2, OH) and 4.84–4.64 (m, 4, OCH₂) and ¹³C NMR 158.11, 153.46, 152.66, 149.18, 136.09, 135.94, 134.18, 133.34, 132.90, 132.54, 129.79, 128.01, 128.38, 127.82, 127.70, 127.62, 127.51, 127.42, 127.21, 126.88, 125.26, 125.22, 118.26, 116.19, 112.29, 111.81, 111.54, 111.30, 108.99, 105.70, 105.53, 104.48, 70.40, 70.30 and 69.71 and 6,6'-dibromide **27** 0.80 g (16.9 per cent yield); TLC (CH₂Cl₂) $R_f = 0.23$; ¹H NMR 8.10 (s, 2, H₅), 7.80 (d, 2, $J = 9.04$, H₄), 7.20 (d, 2, $J = 8.87$, H₃), 7.18–6.98 (m, 10, C₆H₅), 6.24 (s, 2, H₈), 4.92 (br s, 2, OH), 4.81 (d, 2, $J = 12.82$, OCH₂) and 4.65 (d, 2, $J = 12.54$, OCH₂) and ¹³C NMR 153.57, 153.23, 135.72, 133.58, 132.56, 130.07, 128.30, 127.63, 126.68, 125.18, 116.16, 111.68, 109.70, 105.41 and 70.25.

5.2.20. 2,2'-(7,7'-Dihydroxy-6,6'-dibromo-1,1'-binaphthyl)-nonanoate, **29**

A solution of decanoyl chloride (0.51 g, 2.7 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a stirred solution of the dibromide **27** (0.80 g, 1.2 mmol) in CH₂Cl₂ (30 ml) containing AlCl₃ (0.34 g, 2.7 mmol) at 0°. This mixture was stirred at RT for 1 h, refluxed for 4 h, cooled to RT and poured into ice. The separated organic layer was washed with H₂O (2 × 100 ml), dried, filtered and the filtrate rotovapoured to give the crude product (0.89 g, 94.7 per cent). Purification of this material by flash chromatography using 1:1 Et₂O–hexane gave two unidentified fractions (0.44 g) followed by the diester **29** (0.65 g, 66.7 per cent): TLC (1:1 Et₂O–hexane) $R_f = 0.40$; IR (CHCl₃) 3600–3200 (OH), 1770 (CO₂R) and 1620, 1590 (Ar); ¹H NMR 7.99 (s, 2, H₅), 7.63 (d, 2, $J = 8.79$, H₄), 7.07 (d, 2, $J = 8.92$, H₃), 6.66 (s, 2, H₈), 2.38 (t, 4, $J = 7.61$,

OCOCH₂), 1.59 (quint, 4, 7.29, OCOCH₂CH₂), 1.35–1.05 (m, 24, CH₂) and 0.90–0.77 (m, 6, CH₃).

5.2.21. 2',2',7,7'-Tetradecyloxy-3,3',6,6'-tetrabromo-1,1'-binaphthyl, **30**

A solution of Br₂ (2.23 g, 13.9 mol) in CH₂Cl₂ (40 ml) was added dropwise to a stirred solution of the tetraether **20** in CH₂Cl₂ (100 ml) which then refluxed for 36 h, cooled to RT and a 10 per cent Na₂SO₃ solution (100 ml) added. The separated organic layer was washed with 5 per cent aq. KOH (50 ml), H₂O (2 × 100 ml), dried, filtered and the filtrate rotovapoured to give the liquid tetrabromide **30** (3.95 g): TLC (1:1 CH₂Cl₂-hexane) R_f = 0.84 (9:1 hexane-CH₂Cl₂) R_f = 0.47 (major), 0.55 and 0.50; ¹H NMR 8.06, 8.02 (2s, 4, H₄ and H₅), 6.35 (s, 2, H₈), 4.90–3.75 and 3.50–3.30 (2m, 8, OCH₂), 1.70–1.20 (m, 64, CH₂) and 0.95–0.80 (m, 12, CH₃) and ¹³C NMR 153.68, 152.98, 133.19, 131.48, 131.30, 127.08, 125.44, 115.92, 113.96, 105.41, 73.66, 68.88, 31.90, 29.72, 29.50, 29.27, 29.08, 28.49, 25.85, 25.43, 22.68 and 14.11.

5.2.22. Reaction of the tetrabromide **30** with cuprous cyanide

The tetrabromide **30** (3.96 g, 3.3 mmol) was treated with CuCN as described for the synthesis of the dinitrile **5**. The organic layer yielded 3.24 g of the crude product. Purification of this material by flash chromatography using CH₂Cl₂ followed by EtOAc as eluting solvents gave the tetranitrile **31 a** and/or **31 b** as a gooey solid (0.60, 26.0 per cent). Recrystallization of this material from CHCl₃-hexane gave purer material: TLC R_f = 0.42 (Et₂O), 0.1 (CH₂Cl₂); IR 3500–3000 (OH), 2200 (CN) and 1620 (Ar) and ¹H NMR 8.26, 8.17 (2s, 4, H₄ and H₅), 6.28 (s, 2, H₈), 3.85–3.55 (m, 8, OCH₂), 1.75–1.05 (m, 64, CH₂) and 0.86 (t, 12, J = 6.67, CH₃).

5.2.23. 2,2',7,7'-Tetradecyloxy-3,3',6,6'-tetracyano-1,1'-binaphthyl, **33**

A stirred mixture of the phenol **31** (600 mg, 0.86 mmol), decylbromide (380 mg, 0.172 mmol) and 240 mg K₂CO₃ (0.172 mmol) in DMF was heated at 50°C for 18 h and water added. The resulting precipitate was removed by filtration, dissolved in EtOAc, dried, filtered and the filtrate rotovapoured to give the crude product (0.90 g). Purification of this material by flash chromatography using CH₂Cl₂ gave the tetraether **33** (0.53 g, 63.1 per cent): TLC (CH₂Cl₂) R_f = 0.80; IR 2200 (CN) and 1610 (Ar); ¹H NMR 8.33, 8.27 (2s, 4, H₄ and H₅), 6.36 (s, 2, H₈), 4.00–3.60 (m, 8, OCH₂), 1.70–1.00 (m, 64, CH₂) and 0.90–0.85 (m, 12, CH₃); ¹³C NMR 158.60, 157.27, 138.54, 137.32, 136.76, 123.11, 122.76, 105.55, 105.19, 104.09, 69.31, 31.84, 29.79, 29.45, 29.26, 28.96, 28.38, 25.77, 25.38, 22.65 and 14.08 and transition temperatures: 100.4–100.7° (C–I) and 95.2–92.8° (I–C) followed by a

second fraction (0.07 g): TLC (CH₂Cl₂) R_f = 0.23; IR 3425 and 3340, 2200 (CN), 1650, and 1600 (Ar); ¹H NMR 8.81 (s, 1), 8.34, 8.33 (2s, 3), 6.36 (s, 2), 6.32 (s), 4.10–3.40 (m, 8), 1.80–1.00 (CH₂) and 1.00–0.81 (m, 12).

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