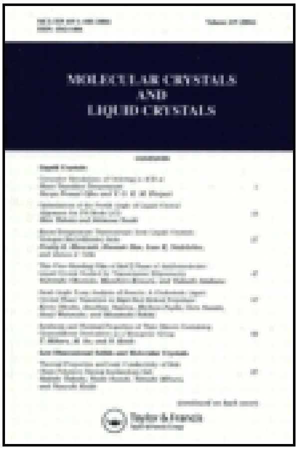

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Mesomorphic Properties of 4-[3′,4′,5′-tri(p-n-Dodecyloxybenzyloxy)]-Benzoyloxy-4‴-p-n-Dodecyloxybenzyloxybiphenyl

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Mesomorphic Properties of 4-[3′,4′,5′-tri(*p*-*n*-Dodecyloxybenzyloxy)]-Benzoyloxy-4‴-*p*-*n*-Dodecyloxybenzyloxybiphenyl

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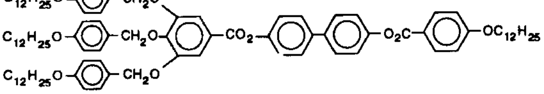
The diester was resynthesized to study its reported thermotropic biaxial nematic (N_b) phase. A slightly different synthesis route using a monoprotected biphenol was used. All intermediates, as well as the final diester, were thoroughly characterized by high resolution NMR and in some cases elemental analysis to be certain that the product isolated had the correct structure.

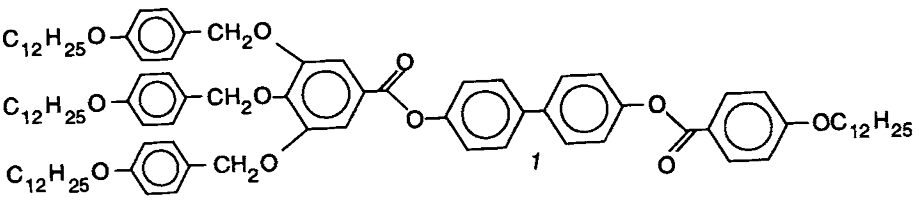


Mesomorphic properties were determined by both hot-stage polarizing microscopy and DSC. An *I*-nematic–smectic C sequence was observed rather than the N_b and N_u phases reported earlier. X-ray analysis confirmed the presence of a nematic above a smectic C phase.

Keywords: Biaxial nematic phase, X-ray analysis, plasmids, disk-rod shaped diester

INTRODUCTION

The report that the disk-rod shaped diester *1* showed both uniaxial $(N_u)^{1,2}$ and biaxial $(N_b)^{1,2}$ nematic phases prompted us to resynthesize this compound so that the properties of the N_b phase could be studied more extensively.



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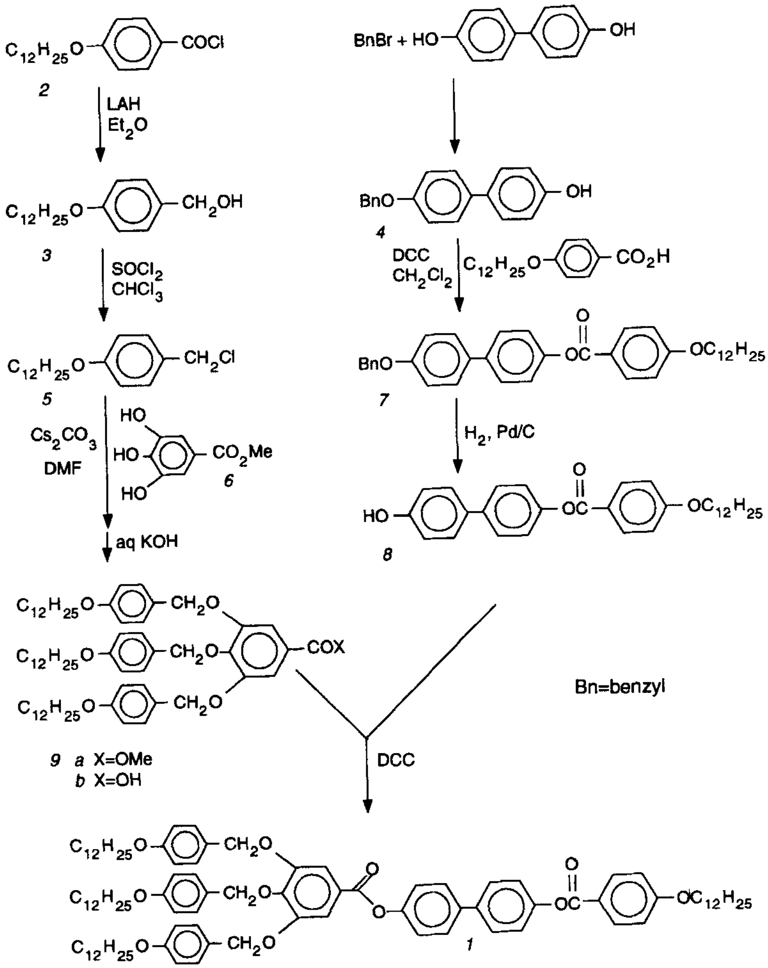
SYNTHESIS

Our synthesis procedure (Scheme 1) was similar but not identical to the one reported[1] in that a mono protected biphenol *4* was used to prepare the ester 8 before esterifying



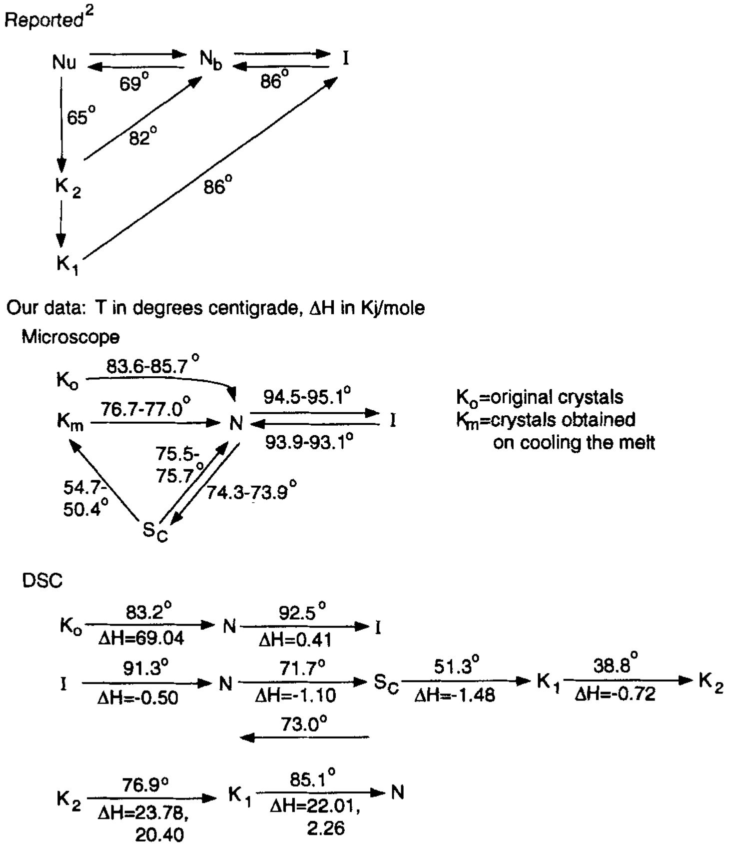
SCHEME 1

with the acid *9b*. In the alkylation of the triol *6*, the standard Williamson ether synthesis (bromide/KOH) method failed to give the ether. Alkylation was successful, however, when the chloride *5* was used in the presence of cesium carbonate in DMF.[3] Recently, synthesis of the acid *9b* via reduction of 4-dodecyloxybenzaldehyde to the alcohol *3* was reported.[4] All intermediates, as well as the desired ester *1* were checked for purity by TLC, purified by column chromatography if necessary and characterized by IR, high resolution (200 MHz) NMR and in some instances elemental analysis to be certain that the final product was indeed the diester *1*.

MESOMORPHIC PROPERTIES

Intermediates which had molecular shapes favorable for forming mesophases were studied by hot-stage polarizing microscopy. Both the biphenyl esters *7* and *8* were found to show nematic and smectic C phases (see Experimental section). Mesomorphic properties for the acid *9b* determined by DSC wer reported earlier.[1,4] We found it difficult to obtain sharp and accurate transition temperatures by hot-stage microscopy due to decomposition.

Transition temperatures for the diester *1* were determined both by microscopy* and DSC. Our data are compared with the literature values in Scheme 2. The original crystals (K_0) melted to a nematic phase at 85.7°C with the nematic phase converting to the isotropic liquid at 95.1°C. This melting temperature corresponds to that previously reported for $K_1 \rightarrow I$. On cooling, a smectic C phase formed from the *N* phase at 74.3°C. Reheating this phase converted it back to the nematic phase at 75.7°C, confirming that this is a mesophase rather than a crystalline phase. Continued cooling of the smectic C phase at 2°/min to about 54.7°C caused crystals to grow slowly. The texture of the smectic C phase was not that of a typical smectic C phase, i.e., focal conic broken fans or



SCHEME 2

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* The temperatures for the X-ray studies may not be identical to those found in the microscope studies due to differences in the equipment used.

schlieren but a sanded texture[5] making it difficult to see the even finer textured crystals growing. Observing the melting transition then became quite difficult. After many attempts, this transition became more obvious by the observation that the crystals appeared more opaque than did the smectic C phase. These crystals melted to the nematic phase at 76.7–77.0°C. This temperature is only slightly higher than that observed for the smectic C to nematic phase transition but enough so to suggest that the smectic C phase is monotropic in relation to both crystal forms. No obvious changes were observed in the temperature region of 65–69°C although other crystal changes could occur in this region with varying conditions. Moving the cover slip did not yield either a homeotropic texture in the nematic phase or a schlieren texture in the smectic C phase. Although the schlieren texture is often observed in smectic C phases occurring below a smectic A phase, it is not unusual to have difficulty in observing this texture in smectic C phases that occur below nematic phases.[6] Broken fan textures are also often not observed and sometimes the texture even resembles that observed in a nematic phase.[6,7]

DSC scans confirmed the microscope data (Scheme 2). Melting from the original crystals gave one broad intense peak at 83.9°C for the melting transition and a weak one at 92.4°C for the clearing transition. Cooling showed a peak for the N–S_C transition at 71.7°. When the sample was cooled to 60°C and then reheated, the $S_C \rightarrow N$ transition occurred at 73.0°C. Cooling of the smectic C phase below 60° gave two broad peaks at 51.3° and 38.8°C. When the cooled sample was allowed to set a week and then reheated, two large peaks at 76.9°C (K_2–K_1, $\Delta H = 23.78$) and 85.1°C ($K_1 \rightarrow N$, $\Delta H = 22.01$) were observed. The sum of the ΔH values of these two peaks does not equal the value for $K_0 \rightarrow N$ nor does the sum of the ΔH values for the two crystallization peaks, suggesting there might be other crystal forms that were not detected. Reheating the crystals immediately gave a smaller ΔH value for the peak at 85.1°C ($\Delta H = 2.26$) again suggesting multicrystal forms. Obviously, there are several crystal forms present; their observance varies according to the conditions used.

X-ray crystallographic studies were done on a sample heated to 106°C in the presence of a magnetic field and then cooled to different temperatures while recording the diffraction patterns. X-ray patterns determined at three representative temperatures are shown in Figure 1.

At 96°C, the small and large angle rings [Figure 1(a)] correspond to the effective length and width of the molecule are symmetric as the molecules are randomly oriented in the isotropic phase. The inner ring is shown on an expanded 4X scale in Figure 1(b). The rings correspond to the 42.1 ± 1 and 4.73 Å length scales. We believe that 42.1 Å is less than the length of the molecule perhaps because of chain folding in the I phase. The usual separation between hydrocarbon chains is 4.71 Å.

At 75.5°C, in the middle of the nematic phase, the large angle ring breaks up into two crescents as molecules align parallel to the magnetic field. The small angle ring splits into two pairs of peaks due to the aligning effect of the magnetic field as clearly visible in Figure 1(c). One of the four spots is only partially visible as it is blocked by the beam-stop. Figure 1(d) shows these reflections more clearly on an enlarged scale. The magnetic field points exactly through the middle of the two pairs of reflections as shown. The angle between the two pairs allows us to calculate the molecular tilt to be ~41.5° in the cybotactic clusters of this nematic phase. The effective d spacing,

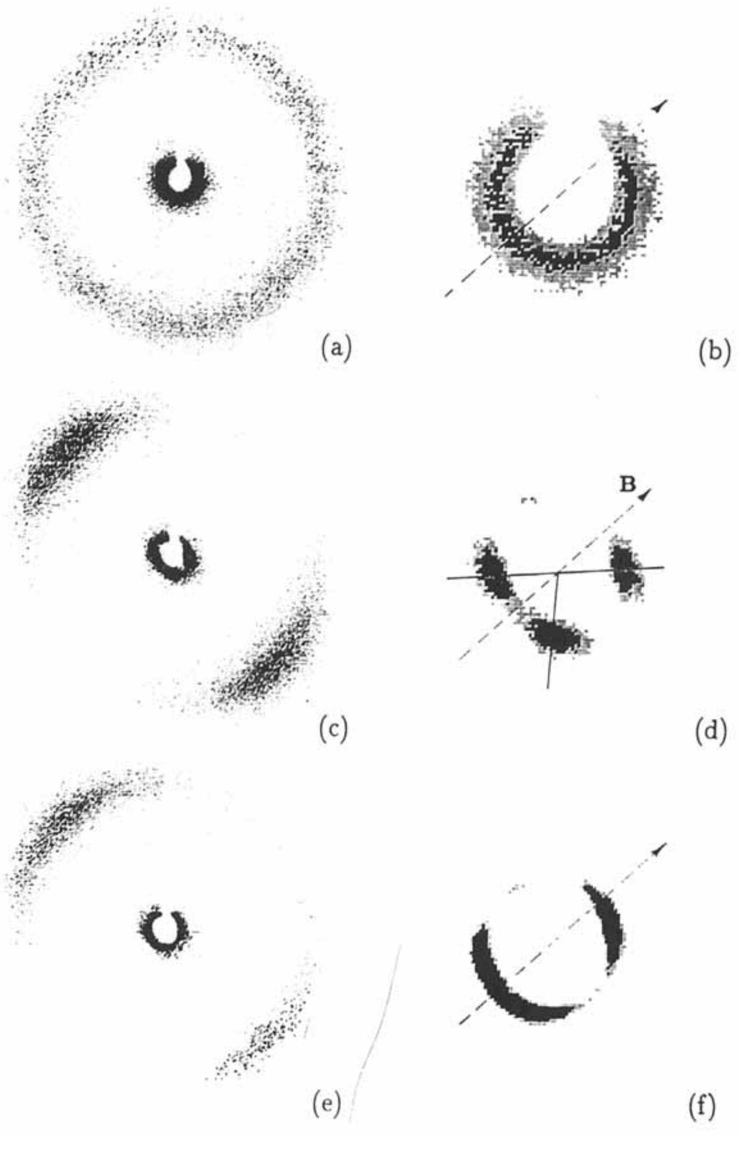

FIGURE 1 X-ray crystallographic patterns for the isotropic liquid (96°C, a and b), cybotactic nematic (75.5°C, c and d), and smectic C (70°C, e and f) phases for the ester *1*.

calculated from the diffraction angle of these peaks, is 43.5 Å. The tilt and *d* value of the cybotactic clusters allow us to calculate the length of the molecules as 58.1 ± 1 Å in good agreement with the 59 Å length obtained from a space-filling model.

At 70°C, in the smectic-*C* phase, the molecular tilt increases to 43.3°. Since the magnetic field is unable to maintain the alignment as the system enters the smectic-*C* phase with a change in tilt, the three visible small angle reflections become elongated due to a broadened mosaic of the smectic layers [Figures 1(e) and 1(f)]. The smectic layer spacing decreases to 40.8 Å due to the increased tilt.

CONCLUSIONS

The diester *1* was resynthesized and thoroughly characterized to confirm its structure. Microscopic studies indicated the presence of a nematic above a smectic C phase as well as two different crystal forms with two melting temperatures with the smectic C phase being monotropic in both instances. Both DSC and X-ray studies confirmed the presence of these phases with X-ray studies indicating the presence of a cybotactic nematic phase above a smectic C phase.

No attempt was made to determine whether the nematic phase observed was optically uniaxial or biaxial. However, the absence of reflections corresponding to three lengths in X-ray scattering strongly suggests it to be a uniaxial *N* phase. Recently, the N_b phase reported in a cinnamic acid dimer[8] was found to be uniaxial by deuterium NMR studies.[9] Luckhurst is currently studying our sample 1 to try to resolve this question of biaxiality. These results will be reported in a later paper.

EXPERIMENTAL

Solvents for anhydrous reactions were dried by allowing them to set over Linde #4A molecular sieves for at least 17 hr. All organic extracts were dried over anhyd Na_2SO_4. Commercially available starting materials were used without further purification. 4-Dodecyloxybenzoic acid was obtained from Frinton Laboratories. Column chromatography was done using 60–100 mesh silica gel (Davidson) whereas Anal-Tech silica gel GHLF Uniplates with UV light as the detector were used for thin-layer chromatography. Melting points (°C) were determined using a Hoover–Thomas melting point apparatus and are corrected. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

IR spectra were run in Nujol using a Pye-Unicam 3–200 instrument. NMR spectra were determined in $CDCl_3$ using TMS as the internal standard and a Varian Gemini 200 MHz instrument. Biphenyl protons are identified by the abbreviation biph. X-ray data were obtained on an aligned sample in a sealed capillary using a Siemens polymer diffraction system with an area detector (512 × 512 pixels) and a 3-axis goniometer (diffractometer).

Transition temperatures (°C) were determined using a Leitz–Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/ min as previously described.[10] Samples were cooled at 2°/ min until they crystallized to obtain the crystallization temperature and so that no monotropic phases occurring before this temperature were missed. Mesophases were identified by the observance of textures typical of these phases as previously described.[6,5,11]

DSC scans were determined using a Perkin–Elmer DSC-7 instrument. The ΔH values of the mesophase transitions represents the average obtained from several scans.

The DSC instrument was not calibrated immediately before these scans were run. We have seen as much as 5° difference between the microscope and DSC data if this is not done which explains the differences in the transition temperatures reported from these two methods. Since we do not see large variations in the microscope data, we consider transition temperatures obtained on the microscope as the more accurate values.

4-Dodecyloxybenzyl Alcohol, 3

To a stirred mixture of $LiAlH_4$ (3.4g, 90.6 mmole) in anhyd Et_2O (90 ml) under N_2 at RT was added dropwise a solution of 4-dodecyloxybenzoyl chloride (9.80g, 30.2 mmole, prepared from the acid using the $SOCl_2$ method) in anhyd Et_2O (160 ml). This reaction mixture was refluxed for 24 hr, cooled to RT, poured into a mixture of ice and 36% HCl and stirred until complete hydrolysis of the excess $LiAlH_4$ was evident from the conversion of the gray to a white solid. The product was extracted into Et_2O, washed with H_2O, dried, filtered and the filtrate rotovaped to give the crude alcohol *3* (8.59g, 97.6%): mp 68° (lit[4] mp 66°), TLC ($CHCl_3$) $R_f = 0.21$ and faint spots with $R_f = 0.54, 0.68, 0.73$ and 0.86), IR 3320 (med, br OH) and 1610, 1580 cm^{-1} (wk, Ar) and NMR δ7.28 (*d*, 2, $J = 8.06$ Hz, ArH ortho to CH_2), 6.88 (*d*, 2, $J = 8.71$ Hz, ArH ortho to OR), 4.61 (*s*, 2, $ArCH_2$), 3.95 (*t*, 2, $J = 6.55$ Hz, $ArOCH_2$), 1.80–1.70 (*m*, 2, OCH_2CH_2), 1.40 – 1.10 (*m*, 18, $9CH_2$) and 0.85 (*t*, 3, $J = 6.76$ Hz, CH_3).

4-Dodecyloxybenzyl Chloride, 5

Thionyl chloride (33.4g, 0.28 mole) was added dropwise under anhydrous conditions to a stirred and cooled (0°) solution of the crude alcohol *3* in a mixture of anhyd $CHCl_3$ (200 ml) and DMF (20 drops). This reaction mixture was allowed to warm to RT over 2 hr and then extracted with Et_2O. The Et_2O extract was washed with 5% $NaHCO_3$ and H_2O, dried and filtered. The filtrate was treated with activated carbon, filtered through Celite and the solvent removed from the filtrate to give 9.12g (quant) of the crude chloride *5*: mp 40.0–42.0°C (lit[4] mp = 36°C); TLC (CH_2Cl_2) $R_f = 0.93$ and ^{1}H-NMR δ7.29 (*d*, 2, $J = 8.79$ Hz, ArH ortho to CH_2), 6.86 (*d*, 2, $J = 8.71$ Hz, ArH ortho to RO), 4.56 (s, 2, $ArCH_2$), 3.94 (*t*, 2, $J = 6.54$ Hz, $ArOCH_2$) and 0.88 (*t*, 3, $J = 6.41$ Hz, Me).

3,4,5-Tri(*p*-*n*-dodecyloxybenzyloxybenzoic) Acid, 9b

A stirred mixture of the chloride *5* (8.0 g, 25.8 mmole), methyl 3,4,5-trihydroxybenzoate (1.56 g, 8.4 mmole) and Cs_2CO_3 (25.5 g, 78.1 mmole) in anhyd DMF (80 ml) was refluxed under anhydrous conditions at 80°C for 8 hr. The reaction mixture was cooled to RT, H_2O added and the product extracted into CH_2Cl_2. The organic layer was dried, filtered and the filtrate rotovaped to give 8.45 g (quant) of the crude ester *9a*. This compound was refluxed with alc KOH (8.0 g in 240 ml 95% EtOH), for 2 hr, rotovaped, 36% HCL (160 ml) added to the residue, warmed for 30 min and then cooled to RT. The product was extracted into Et_2O which was then washed with H_2O, dried, filtered and the filtrate rotovaped to give the crude product. This material was purified by column chromatography on silica gel eluting with 9:1 CH_2Cl_2–MeOH to give the purified acid

9b (7.2 g, 86.4%): TLC (5% MeOH in $CHCl_3$) $R_f = 0.31$; IR 3500 – 2400 (br acid OH), 1680 (str, CO_2H) and 1610, 1585 cm^{-1} (str, Ar) and NMR δ7.43 (*s*, 2, ArH ortho to CO_2H), 7.32 (*d*, 4, $J = 8.34$ Hz, ArH ortho to CH_2 external) 7.25 (*d*, 2, $J = 8.14$ Hz, ArH ortho to CH_2 internal), 6.89 (*d*, 4, $J = 8.43$ Hz, ArH ortho to OR external), 6.75 (*d*, 2, $J = 8.43$ Hz, ArH ortho to OR central), 5.03 (*s*, 6, $3RCH_2O$), 3.95, 3.91 (2*t*, 6, $J = 6.59$ Hz, $3CH_2O$), 1.90 – 1.68 (*m*, 6, $3RCH_2CH_2O$), 1.68 – 1.00 (*m*, 54, $27CH_2$) and 0.88 (*t*, 3, $J = 6.0$ Hz, $3CH_3$); ^{13}C NMR ($CDCl_3$) δ159.56, 159.51, 153.16, 130.73, 129.91, 129.78, 128.98, 114.98, 114.61, 110.21, 75.24, 71.57, 68.56, 68.49, 32.44, 30.36, 30.15, 29.97, 29.88, 29.84, 29.73, 26.60, 23.21 and 14.63 and transition temperatures agreed with the literature values.[4]

4-Benzyloxy-4′-hydroxybiphenyl, 4

To a stirred solution of biphenol (18.6 g, 0.10 mole) and K_2CO_3 (34.5 g, 0.25 mole) in acetone (400 ml) containing Linde #4A molecular sieves at RT was added dropwise, benzyl bromide (17.1 g, 0.10 mole). The reaction mixture was refluxed for 24 hr, cooled to RT and rotovaped to remove the acetone. An equal volume of H_2O was added to the residue and the mixture acidified with 36% HCl, boiled for 15 min and cooled in an ice bath. The resulting precipitate was collected by filtration, washed with H_2O, dried *in vacuo* and recrystallized from abs EtOH to give 12.1 g (43.8%) of the phenol *4*: mp 210–212° (lit mp 213°,[12] 203°[13]) and TLC (CH_2Cl_2) $R_f = 0.26$; IR 3400 cm^{-1} (OH); NMR δ7.46 (*d*; 2; $J = 8.67$ Hz; 2′, 6′-biph); 7.40 – 7.30 (*m*; 7; C_6H_5 and 2, 6-biph); 7.00 (*d*, 2, $J = 8.79$ Hz, 3′, 5′-biph); 6.85 (*d*, 2, $J = 8.58$ Hz, 3, 5-biph) and 5.09 (*s*, 2, OCH_2).

4-Benzyloxy-4′-*p*-*n*-Dodecyloxybenzyloxybiphenyl, 7

To a stirred solution of 4-dodecyloxybenzoic acid (6.64 g, 21.7 mmole), the phenol *4* (6.0 g, 21.7 mmole) and 4-pyrrolidinopyridine (0.32 g, 2.17 mmole) in anhyd CH_2Cl_2 (100 ml) at RT was added dropwise a solution of DCC (4.92 g, 23.9 mmole) in anhyd CH_2Cl_2 (30 ml) within 15 min. This reaction mixture was stirred at RT for 24 hr, an additional 100 ml CH_2Cl_2 added and then chromatographed on a column of silica gel. Elution with CH_2Cl_2 gave the ester *7* (7.35 g, 60.0%). Further purification by recrystallization and obtaining an NMR spectrum were not possible due to the poor solubility of this material in organic solvents: mp 131–133°C, TLC (CH_2Cl_2), $R_f = 0.87$, IR 1680 cm^{-1} (wk, Ar) and anal calcd for $C_{38}H_{44}O_4$: C 80.81, H 7.85. Found: C 80.73, H 7.94.

4′-*p*-*n*-Dodecyloxybenzyloxy-4-hydroxybiphenyl, 8

A solution of the ester *7* (7.20 g, 12.8 mmole) in THF (200 ml) containing 5% Pd/C (0.7 g) was hydrogenated at 50°C and 60 psi for 48 hr. The catalyst was removed by filtration through Celite and the filtrate rotovaped to give 5.6 g (92.6%) of the crude phenol. Recrystallization of this material from benzene gave the purified phenol *8*: TLC (5% MeOH in $CHCl_3$) $R_f = 0.60$; IR 3400 (wk, br OH), 1720 (str CO_2R) and 1600 cm^{-1} (wk, Ar) and NMR (DMSO, $CDCl_3$), 9.24 (*s*, 1, OH), 8.11 (*d*, 2, $J = 8.87$ Hz, ArH ortho to CO_2 biph), 7.57 (*d*, 2, $J = 8.95$ Hz; 2′, 6′-biph), 7.43 (*d*, 2, $J = 8.62$ Hz, 2, 6-biph), 7.22 (*d*, 2,

$J=8.59$ Hz; 3′, 5′-biph), 7.01 (*d*, 2, $J=8.87$ Hz, ArH ortho to OR), 6.88 (*d*, 2, $J=8.59$ Hz; 3, 5-biph), 4.07 (*t*, 2, $J=6.41$ Hz, $ArOCH_2$), 1.82 (*q*, 2, $J=6.96$ Hz, $ArOCH_2CH_2$), 1.62–1.18 (*m*, 18, $9CH_2$) and 0.88 (*t*, 3, $J=6.45$, CH_3) with the aromatic proton assignment confirmed by 2D-NMR and transition temperatures 160.5–162.0°C (K–S_C), 187.5–188.5°C (S_C–N), 212–214°C (N–I) and 139°C (S_C–K).

4-[3′,4′,5′-Tri(*p*-*n*-dodecyloxybenzyloxy)]-benzyloxy-4″-*p*-*n*-dodecyloxybenzyloxybiphenyl, 1

To a stirred solution of the acid *9b* (7.00 g, 7.05 mmole), phenol *8* (3.36g, 7.05 mmole) and 4-pyrrolidinopyridine (0.1 g, 0.7 mmole) in anhyd CH_2Cl_2 (425 ml) at RT was added a solution of DCC (1.6 g, 7.8 mmole) in anhyd CH_2Cl_2 (35 ml). The reaction mixture was stirred at RT for 20 hr, the insoluble material removed by filtration and the filtrate rotovaped to give the crude product. This material was purified by column chromatography on silica gel eluting with CH_2Cl_2 to obtain the diester *1* (5.0 g, 49.0%) which was recrystallized from Et_2O: TLC (5% MeOH in $CHCl_3$) $R_f=0.86$; IR 1730 cm^{-1} (str, CO_2R), ^{1}H-NMR δ8.15 (*d*, 2, $J=8.15$ Hz, disubstituted benzene H ortho to CO_2 biph), 7.62 (*d*, 4, $J=8.71$ Hz; 2, 6 and 2′, 6′-biph), 7.53 (*s*, 2, tetrasubstituted benzene H), 7.34 (*d*, 4, $J=8.71$ Hz, ArH_B ortho to CH_2), 7.28 (*d*, 4, $J=8.71$ Hz; 3, 5 and 3′, 5′-biph), 7.26 (*d*, 2, $J=8.63$ Hz, $ArH_{B'}$, ortho to CH_2), 6.96 (*d*, 2, $J=9.03$ Hz, ArH ortho to OR), 6.89 (*d*, 4, $J=8.59$ Hz, ArH_A ortho to OR), 6.77 (*d*, 2, $J=8.63$ Hz, $ArH_{A'}$, ortho to OR), 5.07 (*s*, 6, $3CH_2O$), 4.10–3.80 (*m*, 8, $4RCH_2O$), 1.90 – 1.60 (*m*, 8, $4RCH_2CH_2O$), 1.50 – 1.10 (*m*, 62, $36CH_2$) and 0.88 (*t*, 12, $J=6.04$ Hz, $4CH_3$); ^{13}C-NMR 159.62, 159.57, 153.29, 132.82, 130.78, 129.92, 129.83, 129.00, 128.64, 122.68, 122.58, 115.02, 114.84, 114.66, 110.36, 75.28, 71.71, 68.85, 68.57, 68.51, 32.46, 30.18, 29.98, 29.89, 29.64, 26.62, 26.53, 23.23 and 14.65; transition temperatures are given in Scheme 2 and anal calcd for $C_{95}H_{132}O_{11}$: C 78.68, H 9.18. Found: C 78.61, H 8.97.

Acknowledgements

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