(−)-Isocamphoric Acid Building Block for Chiral Liquid Crystals

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The synthesis and liquid-crystal properties of the novel chiral (−)-isocamphoric acid ester **8** are reported. Although the new material is not itself mesogenic, it induces chirality in the nematic and smectic-C phase of an achiral host. A proposed mechanism for the chiral induction according to the 'intercalated chirality' model opens the possibility for fine-tuning the chiroptical properties of the induced chiral mesophases.

1. Introduction. – Chirality in liquid crystals [1] has been the subject of intense research in recent years and is directly responsible for technological applications, *e.g.*, thermochromic thermometer devices that use chiral nematic materials, and far more important, fast-switching ferroelectric display devices that use the chiral smectic-C* phase. To fulfil the necessity of short response times in electro-optical devices, two main features are required for new ferroelectric liquid-crystal (FLC) materials: high spontaneous polarization (P_s) and low rotational viscosity. Because of the difficulty in obtaining substances which have both favorable properties, FLC materials are often prepared by doping non-chiral liquid-crystalline mixtures exhibiting low viscosity and a broad S_C-phase range, with chiral compounds having a large spontaneous polarization.

Many ferroelectric organic liquid crystals of low molecular weight bearing stereogenic centers either in the flexible hydrocarbon terminal chains [1–4] in the rigid core [5][6], or in the flexible spacer in dimeric structures [7–9], have been reported. Through diversity of chiral mesogens as well as chiral dopants that have been synthesized, certain structure-property relationships for good ferroelectric materials have been postulated. Thus, the spontaneous polarization is enhanced when the polar groups with a large lateral dipole are located close to the chiral center and rotation of the chiral center is restricted [5–7]. Such chiral units are often derived from α-amino acids because of their commercial availability as pure enantiomers and low cost [1].

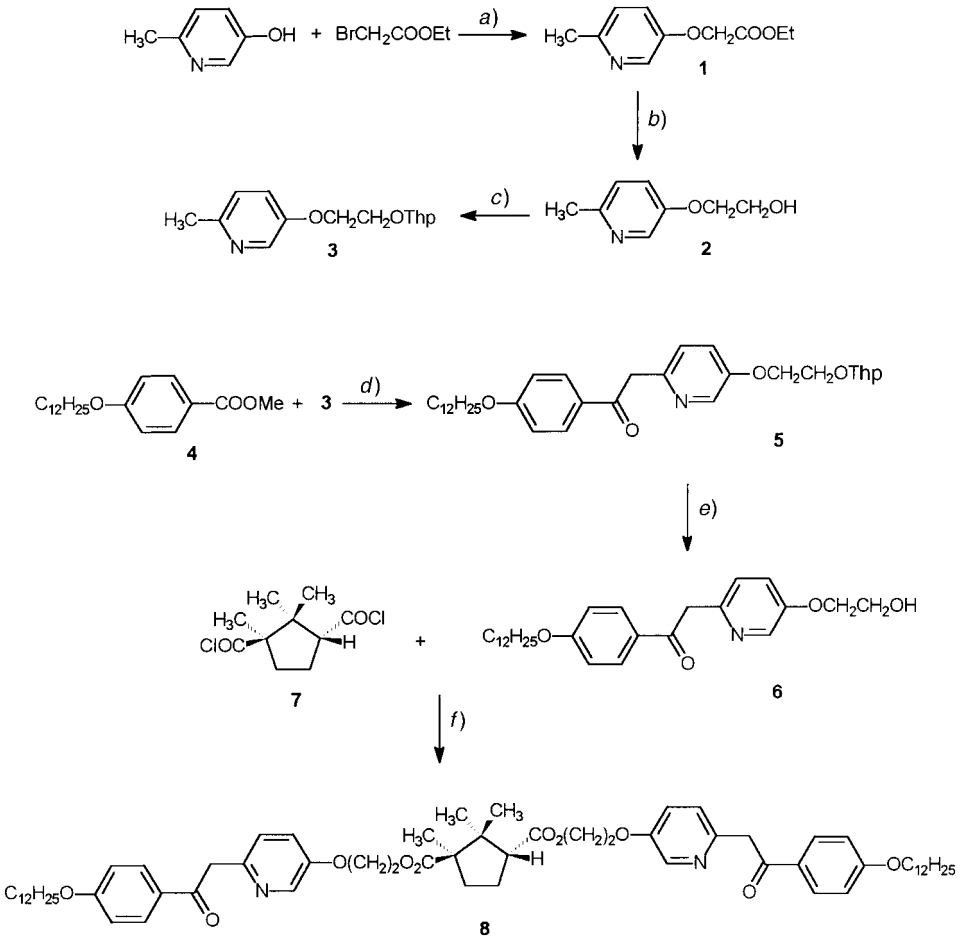
With these results in mind and our recent finding [10] that (4-alkoxyphenacyl)pyridines exhibit monotropic nematic phase transition, we envisaged their connection to (−)-isocamphoric acid to obtain chiral materials with potential liquid-crystalline properties. (−)-Isocamphoric acid with two chiral centers in the cyclopentane ring substituted by two carboxy groups in *trans* position fulfils the structural requirements for a good chiral unit. Beside, easy availability in the enantiomerically pure form makes it an interesting chiral building block for liquid crystals.

In this work, we report the synthesis and mesomorphic properties of a novel chiral, 'dimeric' molecule **8**, consisting of two (4-alkoxyphenacyl)pyridine cores connected through a short flexible spacer to (−)-isocamphoric acid as a chiral unit.

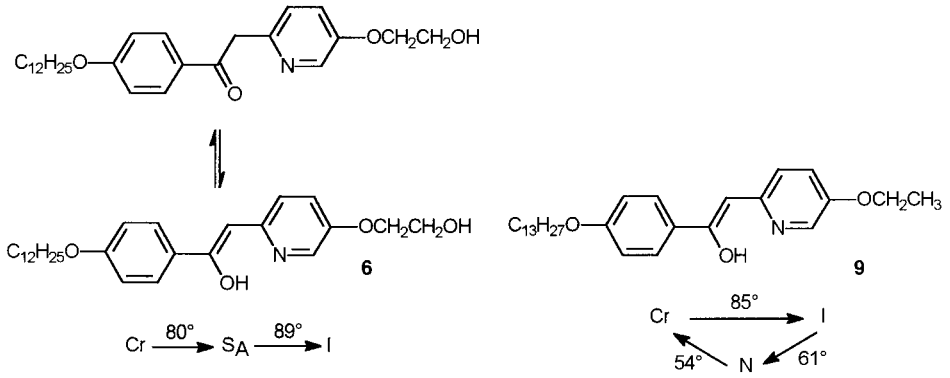
2. Results and Discussion. – 2.2. *Synthetic Considerations.* The synthesis of the 'dimeric' molecule **8**, according to the *Scheme* started by alkylation of 6-methypyridin-3-ol with $BrCH_2COOEt$. Due to the thermal sensitivity of both substrates, several different reaction conditions were examined [11–13], and the best yield of ethyl [(6-methylpyridin-3-yl)oxy]acetate (**1**) was achieved in CH_2Cl_2/H_2O with NaOH as a base in the presence of benzyltributylammonium bromide ($BnBu_3NBr$) as the phase-transfer catalyst [13]. Reduction of **1** by $LiAlH_4$ in THF [14] gave alcohol **2** in 93% yield. Protection of the OH group was performed by treatment with 3,4-dihydro-2*H*-pyran (Dhp) and pyridinium *p*-toluenesulfonate (PPTS) as a catalyst in CH_2Cl_2 [15] which yielded **3** (36%). Regioselective metallation of the Me group of picoline derivative **3** using $LiN(SiMe_3)_2$ [10] followed by the addition of methyl 4-(dodecyloxy)benzoate (**4**), prepared by alkylation of methyl 4-hydroxybenzoate with dodecyl bromide in the usual manner [10], afforded **5** as a yellow solid in 70% yield. The protecting tetrahydro-2*H*-pyran-2-yl group was best removed in DMSO in the presence of LiCl and a small amount of water [16], yielding the [(phenacylpyridinyl)oxy]ethanol **6** (73%). Isomerization of (+)-camphoric acid under acidic conditions followed by crystallization from aqueous ethanol gave enantiomerically pure (−)-isocamphoric acid in 28% yield [17]. Finally, esterification of (−)-isocamphoroyl dichloride (**7**) [18] with **6** followed by chromatographic purification afforded the 'dimeric' compound **8** as yellow solid. The structures of all the compounds prepared were confirmed by their NMR and IR spectra and elemental analyses.

2.2. *Liquid-Crystalline Properties.* The mesomorphic behavior of the chiral 'dimeric' molecule **8** and of its achiral monomer **6** were studied by polarizing optical microscopy. Upon heating, **6** started to melt at 70°, and until 80°, a heterogeneous mixture containing small crystals floating in an isotropic liquid was observed. The crystals then melted to give a smectic-A (S_A) phase characterized by the fan-shaped texture, and finally, complete isotropization was achieved at 89°. During the cooling cycle, the isotropic-to-smectic-A-phase transition was observed by the appearance of bâtonnets from the isotropic liquid which, on further cooling, developed into a fan-shaped texture; the sample also contained significant regions with the homeotropic texture of smectic-A phase. At 64°, the sample started to crystallize which took 5°; during that period, the coexistence of the crystals, isotropic liquid, and mesophase was observed. The explanation of this behavior can be found in the keto-enol tautomerism of the phenacylpyridine part of **6**. In a previous paper, we reported that in $CHCl_3$ solution, (alkoxyphenacyl)pyridines exist in the keto form, while in the solid state, the equilibrium is completely on the side of the enol form and that only the enol form displays a monotropic nematic phase [10]. Spectroscopic data revealed slightly different characteristics of **6**. (Alkoxyphenacyl)pyridine derivative **6** exists in solution completely in the keto form, as confirmed by the NMR spectra, whereas the solid-state IR spectrum of **6** shows bands at 1630 cm^{-1} (C=C stretch) and at 1680 cm^{-1} (C=O stretch), revealing the presence of both the non-mesomorphic keto and the mesomorphic enol form. Compared to the related asymmetric (alkoxyphenacyl)pyridine derivative **9**, addition of an OH group in the chain causes a change in the type of mesophase from monotropic nematic (N) into enantiotropic smectic-A phase.

Scheme 1



a) $BnBu_3NBr$, NaOH, CH_2Cl_2. *b*) $LiAlH_4$, THF/Et_2O. *c*) Dhp, PPTS, CH_2Cl_2. *d*) $LiN(SiMe_3)_2$, THF/Et_2O. *e*) LiCl, $DMSO/H_2O$. *f*) Et_3N, DMAP, CH_2Cl_2.



According to the IR spectrum, 'dimer' **8** also exists as a mixture of the ketone and enol forms in the solid state, but does not display any mesomorphism. This may be due to a combination of a flexible core with unfavorable steric interactions.

To explore the possibility to use **8** as a chiral dopant, the binary mixtures consisting of achiral 4-alkoxybenzoic acid doped by **8** were prepared. Mixtures *M1* and *M2* contained 8 wt.-% of **8** in 4-(hexyloxy)benzoic (*H1*) and 4-(tetradecyloxy)benzoic acid (*H2*), respectively. While 4-(hexyloxy)benzoic acid displays only a nematic phase, 4-(tetradecyloxy)benzoic acid shows a wide-range smectic-C and a very short-range nematic phase [1] (see *Table*). The *Table* shows that addition of 8% of 'dimer' **8** has a small influence on the temperature of the phase transition: the nematic-phase range is reduced, while the smectic-C-phase range is extended by a few degrees. According to optical textures, chiral induction is observed in both binary mixtures. Thus, mixture *M1* displays a chiral nematic phase characterized by the fingerprint texture (*Fig. 1,a*) indicating a relatively short pitch [19]. Mixture *M2* shows a chiral smectic-C phase and a very short-range chiral nematic phase; in the S_C* phase, only a few dechiralization lines are observed due to an incomplete helical structure (*Fig. 1,b*), indicating a very long S_C* pitch [19]. A miscibility study was performed between **8** and achiral host H2. The S_C* phase was found to disappear when the percentage of the 'dimer' was above 15 wt.-%, revealing relatively low miscibility of those two components.

Table 1. *Type of the Phase and Transition Temperatures for the Hosts* H1 *and* H2 *and the Mixtures* M1 *and* M2

Host or mixture	Temperature and phase sequence[a])
H1	Cr 105.4 N 153.2 I
M1 (8% **8** in *H1*)	Cr 105.0 N* 150.4 I
H2	Cr 98.5 S_C 135.1 N 135.6 I
M2 (8% **8** in *H2*)	Cr 92.4 S_C* 135.0 N* 135.4 I

[a]) Cr, crystal; N, nematic; N*, chiral nematic; S_C, smectic C; S_C*, chiral smectic C; I, isotropic liquid

2.3. *MM2 Calculations.* To get a closer look into the structure and possible mechanism of chiral induction, conformation analysis of the methoxy analogue of **8** was performed. Molecular-mechanic's calculations gave two energetically similar minima, corresponding to two stable conformers **A** ($E = 223.17$ kJ mol^{-1}) and **B** ($E = 232.76$ kJ mol^{-1}). In both conformers, the *trans*-situated carbonyl groups of the isocamphoric-acid moiety are oriented toward the atoms C(4) and C(5) of the cyclopentane ring, occupying the less-hindered position, and their rotation is blocked by the two geminal Me groups at C(2). The overall shape of the conformer is determined by the dihedral angle (φ) between the substituents at the ethane-1,2-diyl spacer. In the conformer **A**, this dihedral angle φ is 64°, leading to a bent-shaped molecule, while in the all-*trans* conformer **B**, the same angle is 180°, giving rise to a rod-shaped molecule. Due to the small energy difference ($\Delta E = 9.59$ kJ mol^{-1}) between those two conformers, interaction between host *H2* and the 'dimer' can determine the preferred conformer of the latter.

Considering the structure of **8** which is similar to that of its methoxy analogue and considering the lamellar organization in the smectic phase observed, chiral induction could be explained by the 'intercalated chirality' model [20]. In this model, two planar,

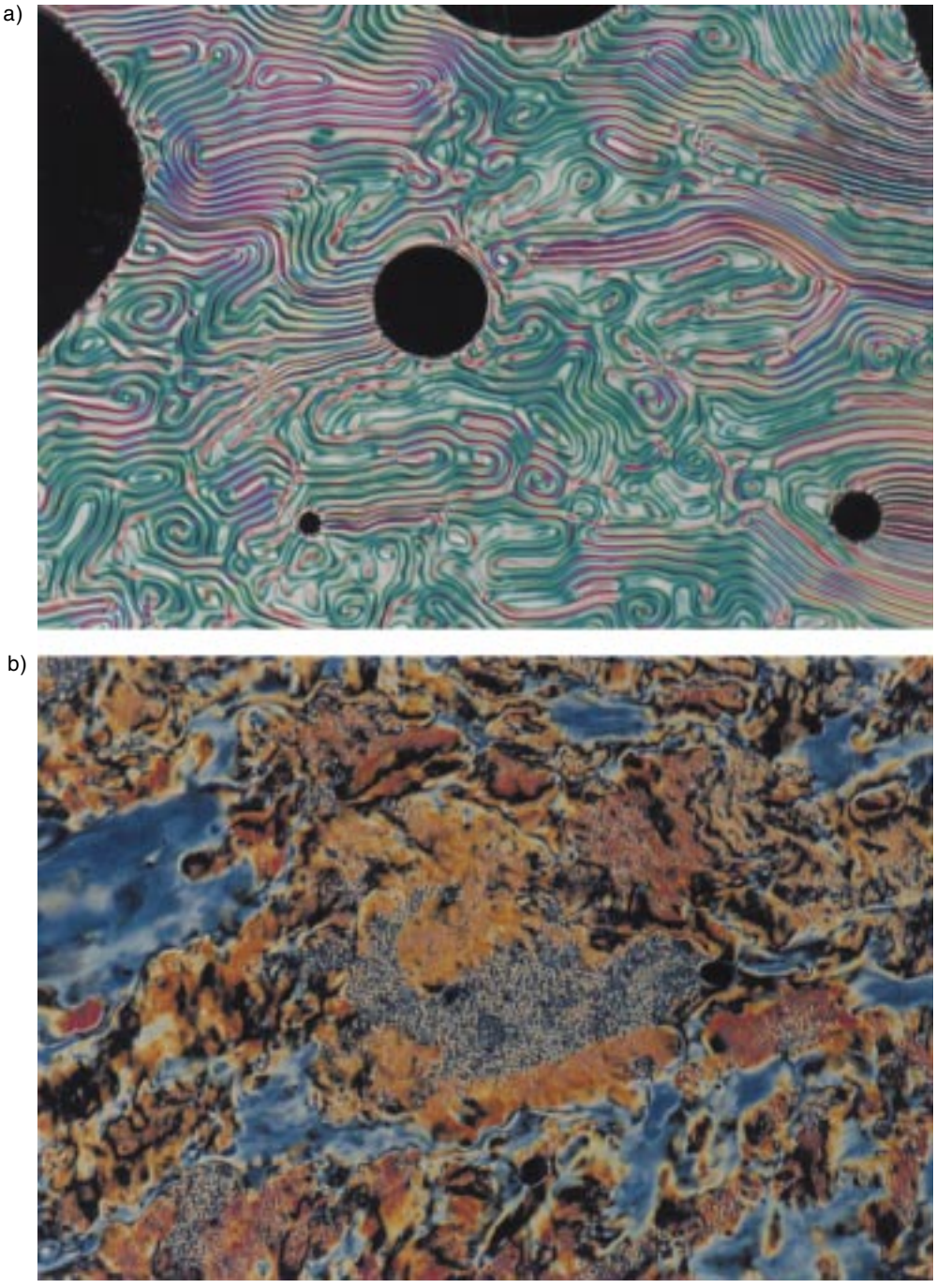


Fig. 1. *Photomicrographs of the liquid-crystal phases of the mixtures* M1 (**8** + *H1*) *and* M2 (**8** + *H2*) (× 100): a) *Fingerprint texture of the chiral nematic phase* (*M1*); b) *chiral smectic-C* phase characterized by a few dechiralization lines* (*M2*)

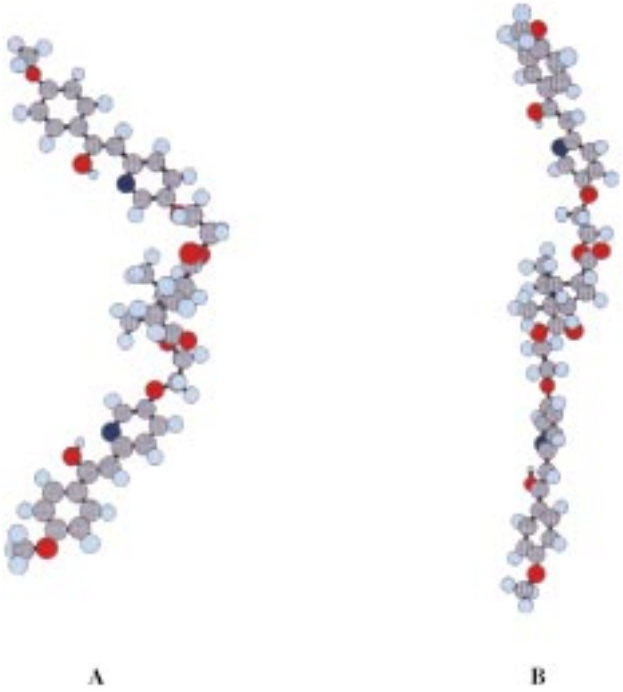


Fig. 2. *Ball-and-stick representation of MM2-calculated minimum-energy conformations of the methoxy analogue of* **8**

mesogenic phenacylpyridine parts exist in neighboring smectic layers, while the bulky isocamphoric-acid unit occupies the space between flexible chains of the host molecules. Since two mesogenic parts are connected through a short, flexible spacer to (−)-isocamphoric acid as a chiral unit, a twist interaction is produced between adjacent layers, which induces a helical macrostructure in the S_C* phase. We assume that the low miscibility of dopant **8** and host *H2* lays in the mismatching in distance between the two aromatic core parts of **8** and the smectic-layer thickness. Owing to mismatching in distance, 'core-core' interaction is relatively poor causing weaker interlayer interactions and, therefore, a very long S_C* pitch, as observed by the appearance of a few dechiralization lines in the texture of the S_C* phase.

3. Conclusion. – A novel chiral (−)-isocamphoric-acid derivative, bis{2-{{6-{2-[4-(dodecyloxy)phenyl]-2-oxoethyl}pyridin-3-yl}oxy}ethyl} (1*R*,3*R*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate (**8**), was prepared. Investigation of mesogenic properties showed that unlike its achiral precursor **6**, chiral **8** displays no mesomorphism suggesting that the introduction of the isocamphoric-acid moiety suppresses liquid crystallinity. However, in the mixture with an achiral host, **8** induces a helical macrostructure in the mesophase. A proposed mechanism for the chiral induction opens a possibility for improving the interaction between the mesogenic part of the 'dimer' and the host molecules by changing the length of the flexible spacer, and thus for a fine-tuning of the chiroptical properties of the induced chiral mesophase.

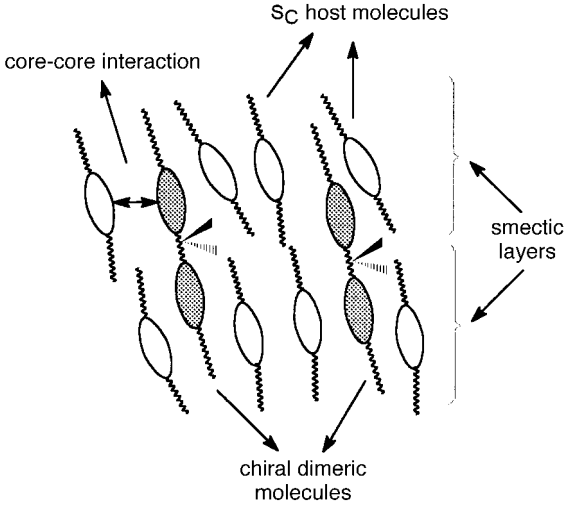


Fig. 3. *Schematic representation of a possible model for the chiral smectic-C* phase, consisting of the chiral dimer and the achiral S_C host, according to* [20]

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Experimental Part

1. General. All the solvents were either of *puriss p.a.* quality or distilled over appropriate drying reagents. All the other reagents were used as purchased from *Aldrich*. TLC: Al-sheets coated with silica gel *60* F_{254} (*Merck*) detection with a UV lamp (λ 254 nm). HPLC: *Hewlett Packard 1050* instrument equipped with a UV detector and *Hewlett Packard HP-3396A* integrator; reversed-phase column *Eurospher C-18* (4.6 mm × 150 mm × 5 μm); flow 0.9 ml min^{-1}, *c* (sample) ≈ 0.5 gdm^{-3}; mobile phases and gradient: from 90% to pure MeOH in 20 min; t_R 10.5 (**5**) and 5.5 min (**6**). GLC: *Hewlett Packard 5890 Series II*, equipped with a FI detector and a *Hewlett Packard HP-3396A* integrator; column *HP-17* (50% *Ph Me Silicone*), 0.53 mm × 10 m × 2 μm; conditions as follows: initial temp. 100°, final temp. 250°, injector and detector temp. 300°, heating rate 10° min^{-1}; t_R 11.2 (**1**), 9.1 (**2**), and 14.0 min (**3**). M.p.: electrothermal *9100* instrument. B.p.: *Büchi-GKR-51* instrument for distillation under reduced pressure. Phase temp. and textures: *Zeiss-Labpol* polarizing microscope equipped with a *Linkam-TH600* hot stage and a *PR600* temp. controller. Optical rotations: automatic polarimeter *AA-10* using the Na_D wavelength; *c* in g sample/100 ml of solvent. UV Spectra: *Phillips-PU-8700* UV/VIS spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer-297* spectrophotometer; absorption bands in cm^{-1}. ^{1}H- (300 MHz) and ^{13}C-NMR (75.5 MHz) Spectra: *Varian-XL-Gemini-300* instrument with $SiMe_4$ as internal standard; in $CDCl_3$ unless otherwise stated; δ in ppm, *J* in Hz. Conformational analysis: molecular-mechanics MM2 method with *ChemOffice Ultra, CambridgeSoft* software, No. *496311*.

2. *Ethyl [(6-Methylpyridin-3-yl)oxy]acetate* (**1**). A mixture of H_2O (100 ml), CH_2Cl_2 (100 ml), 6-methylpyridin-3-ol (10 g, 92 mmol), NaOH (5.5 g, 140 mmol), $BrCH_2COOEt$ (13.4 ml, 120 mmol), and $BnBu_3NBr$ (3.3 g, 9.2 mmol) was stirred at r.t. for 48 h. The org. layer was then separated, the aq. layer extracted with CH_2Cl_2 (3 × 30 ml each), the combined org. extract evaporated, and the residue mixed with H_2O (30 ml). The mixture was extracted with Et_2O (3 × 20 ml). The combined org. extract was washed twice with 2M NaOH (20 ml) and finally with H_2O, dried (Na_2SO_4), and evaporated and the oily residue purified by distillation under reduced pressure to give **1** (33%). Colorless liquid. B.p. 101–103°/0.4 Torr. IR (NaCl, liq.): 2980, 1575, 1490, 1300, 1200, 1080. ^{1}H-NMR: 1.30 (*t*, *J* = 7.2, 3 H); 2.49 (*s*, 3 H); 4.27 (*q*, *J* = 7.1, 2 H); 4.64 (*s*, 2 H); 7.06–7.16 (*m*, 2 H); 8.21 (*d*, *J* = 2.8, 1 H). ^{13}C-NMR: 13.68; 22.91; 61.13; 65.38; 122.22; 123.15; 136.58; 151.33; 151.98; 168.27. Anal. calc. for $C_{10}H_{13}NO_3$ (195.24): C 61.52, H 6.71, N 7.17; found: C 61.53, H 6.58, N 7.29.

3. *2-[(6-Methylpyridin-3-yl)oxy]ethanol* (**2**). To a suspension of $LiAlH_4$ (3 g, 80 mmol) in dry Et_2O (50 ml), a soln. of **1** (5.8 g, 30 mmol) in dry THF (70 ml) was added and the mixture stirred under N_2 for 2 h at r.t. Then

H_2O was added dropwise until the mixture became clear. The precipitate was filtered off, the filtrate dried (K_2CO_3) and evaporated, and the residue purified by distillation: **2** (93%). Colorless oil. B.p. 120–123°/0.4 Torr. IR (NaCl, liq.): 3700–3000, 2920, 1755, 1570, 1485, 1315, 1210, 1080. ^{1}H-NMR: 2.47 (*s*, 3 H); 3.96 (*t*, *J* = 4.5, 2 H); 4.08 (*t*, *J* = 4.6, 2 H); 7.03–7.15 (*m*, 2 H); 8.14 (*d*, *J* = 2.8, 1 H). ^{13}C-NMR: 22.62; 60.40; 69.72; 122.16; 123.39; 136.29; 150.14; 152.99. Anal. calc. for $C_8H_{11}NO_2$ (153.15): C 62.74, H 7.24, N 9.15; found: C 62.88, H 6.99, N 9.23.

4. *2-Methyl-5-{2-[(tetrahydro-2*H*-pyran-2-yl)oxy]ethoxy}pyridine* (**3**). A soln. of **2** (2.3 g, 15 mmol) and 3,4-dihydro-2*H*-pyran (2.7 ml, 30 mmol) in dry CH_2Cl_2 (60 ml) containing PPTS (0.38 g, 1.5 mmol) was heated under reflux for 48 h. Then the mixture was allowed to cool to r.t. and washed with brine (3 × 15 ml) and H_2O. The org. phase was dried (Na_2SO_4) and evaporated and the residue distilled: pure **3** (36%). Colorless oil. B.p. 140–142°/0.25 Torr. IR (NaCl, liq.): 2940, 1575, 1485, 1270, 1125, 1035, 985. ^{1}H-NMR: 1.53–1.83 (*m*, 6 H); 2.48 (*s*, 3 H); 3.77–3.92 (*m*, 2 H); 4.02–4.11 (*m*, 2 H); 4.16–4.19 (*m*, 2 H); 4.70 (*s*, 1 H); 7.04–7.18 (*m*, 2 H); 8.22 (*d*, *J* = 2.8, 1 H). ^{13}C-NMR: 19.00; 22.93; 25.03; 30.14; 61.95; 65.54; 67.75; 98.84; 122.23; 123.13; 136.75; 150.38; 153.03. Anal. calc. for $C_{13}H_{19}NO_3$ (237.30): C 65.80, H 8.07, N 5.90; found: C 65.52, H 8.35, N 6.08.

5. *Methyl 4-(Dodecyloxy)benzoate* (**4**). Compound **4** was prepared by alkylation of methyl 4-hydroxybenzoate with dodecyl bromide in acetone with K_2CO_3 as base according to [10]. Crystallization from hot MeOH gave **4** (95%). Colorless crystals. M.p. 57–58°. IR (KBr): 2920, 2860, 1730, 1610, 1320, 1260, 1170, 1110, 850, 765. ^{1}H-NMR: 0.88 (*t*, *J* = 6.6, 3 H); 1.26–1.45 (*m*, 18 H); 1.75–1.84 (*m*, 2 H); 3.88 (*s*, 3 H); 3.99 (*t*, *J* = 6.7, 2 H); 6.89 (*d*, *J* = 8.5, 2 H); 7.97 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR: 13.79; 22.37; 25.68; 28.81; 29.06; 29.28; 29.34; 31.63; 51.54; 67.95; 113.90; 122.14; 131.43; 162.89; 166.86. Anal. calc. for $C_{20}H_{32}O_3$ (320.47): C 74.96, H 10.07; found: C 75.00, H 10.13.

6. *1-[4-(Dodecyloxy)phenyl]-2-{5-{2-[(tetrahydro-2*H*-pyran-2-yl)oxy]ethoxy}pyridin-2-yl}ethan-1-one* (**5**). At r.t. 1M $LiN(SiMe_3)_2$ in THF (12.5 mmol) was added dropwise to **3** (1.5 g, 6.3 mmol) under Ar and stirred for 3 h. Then, a soln. of **4** (1 g, 3.1 mmol) in anh. Et_2O (8 ml) was added dropwise. The mixture was stirred overnight at r.t. and then at 55° for additional 24 h. An aq. NH_4Cl soln. (30 ml) was added to the cold mixture until it became slightly basic (pH *ca.* 8). The org. phase was separated and the aq. layer extracted with Et_2O (2 × 20 ml). The org. extracts were washed with H_2O, dried (Na_2SO_4), and evaporated. The crude product was purified by CC (Et_2O/toluene 2.5 : 1) and crystallized from hot hexane: **5** (70%). Yellow crystals. M.p. 55–56°. IR (KBr): 2920, 2860, 1630, 1600, 1510, 1260, 1180, 1120, 835. ^{1}H-NMR: 0.87 (*t*, *J* = 6.9, 3 H), 1.25–1.82 (*m*, 26 H); 3.49–3.53 (*m*, 2 H); 3.76–3.89 (*m*, 2 H); 3.96–4.08 (*m*, 2 H), 4.15–4.18 (*m*, 2 H); 4.37 (*s*, 2 H); 4.68 (*s*, 1 H); 6.89 (*d*, *J* = 9.0, 2 H); 7.16–7.20 (*m*, 2 H); 8.02 (*d*, *J* = 9.0, 2 H); 8.27 (*s*, 1 H). ^{13}C-NMR: 13.87; 19.08; 22.45; 25.12; 25.72; 28.85; 29.12; 29.35; 29.41; 30.23; 31.69; 47.10; 62.06; 65.57; 67.75; 68.09; 98.92; 114.11; 122.22; 124.19; 129.29; 131.11; 137.41; 147.62; 153.88; 163.25; 195.88. Anal. calc. for $C_{32}H_{47}NO_5$ (525.73): C 73.11, H 9.01, N 2.66; found: C 73.04, H 9.22, N 2.77.

7. *1-[4-(Dodecyloxy)phenyl]-2-[5-(2-hydroxyethoxy)pyridin-2-yl]ethan-1-one* (**6**). A stirred mixture of **5** (0.72 g, 1.4 mmol), LiCl (0.29 g, 7 mmol), and H_2O (0.25 g, 14 mmol) in DMSO (7 ml) was heated at 90° for 24 h under Ar. The mixture was allowed to cool, then diluted with H_2O (10 ml), and extracted with Et_2O (3 × 20 ml). The org. extract was dried (Na_2SO_4) and evaporated and the product purified by CC (Et_2O/toluene 2.5 : 1). Crystallization from hot hexane gave **6** (73%). Yellow crystals. M.p. 86–87°. UV (THF): 231 (4.17), 282 (4.57), 349 (3.71). IR (KBr): 3600–3100, 2920, 2860, 1600, 1570, 1510, 1470, 1250, 1045, 830. ^{1}H-NMR: 0.88 (*t*, *J* = 6.5, 3 H); 1.26–1.53 (*m*, 18 H); 1.75–1.82 (*m*, 2 H); 3.99–4.04 (*m*, 4 H); 4.20 (*t*, *J* = 4.5, 2 H); 4.39 (*s*, 2 H); 6.91 (*d*, *J* = 9.0, 2 H); 7.16–7.27 (*m*, 2 H); 8.02 (*d*, *J* = 9.0, 2 H); 8.30 (*d*, *J* = 2.6, 1 H). ^{13}C-NMR: 13.85; 19.10; 22.72; 26.00; 29.13; 29.36; 29.39; 29.59; 31.94; 47.23; 61.31; 68.40; 69.85; 114.43; 122.33; 124.67; 129.53; 131.36; 137.48; 148.17; 153.93; 163.59; 196.11. Anal. calc. for $C_{27}H_{39}NO_4$ (441.61): C 73.43, H 8.90, N 3.17; found: C 73.31, H 9.02, N 3.25.

8. *(−)-Isocamphoroyl Dichloride* (=*(1*R*,3*R*)-1,2,2-Trimethylcyclopentane-1,3-dicarbonyl Dichloride*; **7**). (−)-Isocamphoric acid (=(1*R*,3*R*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid) was prepared by isomerization of (+)-camphoric acid in 28% yield according to [17]. M.p. 171–172°. $[\alpha]_D^{25} = -44.6$ (*c* = 8.3, EtOH). IR (KBr): 3700–2300, 1700, 1460, 1405, 1280, 1000-800. ^{1}H-NMR (DMSO): 0.81 (*s*, 3 H); 1.01 (*s*, 3 H); 1.05 (*s*, 3 H); 1.48–1.57 (*m*, 1 H); 1.75–1.88 (*m*, 1 H); 1.92–2.09 (*m*, 2 H); 2.83 (*t*, *J* = 9.0, 1 H); 12.13 (*s*, 2 H). ^{13}C-NMR (DMSO): 19.30; 19.96; 24.45; 24.76; 33.69; 46.06; 53.47; 55.59; 175.54; 178.60.

To a suspension of PCl_5 (1 g, 5 mmol) in anh. Et_2O (20 ml) at 0° (−)-isocamphoric acid (0.5 g, 2.5 mmol) was added in portions. The soln. was stirred at 0° for 1 h and then overnight at r.t. Any remaining solid was filtered off, the filtrate evaporated, and the yellow, smelly oil distilled under reduced pressure: **7** (89%) which was immediately used in the following reaction. Colorless oil. B.p. 77–79°/0.25 Torr.

9. *Bis{2-{{6-{2-[4-(dodecyloxy)phenyl]-2-oxoethyl}pyridin-3-yl}oxy}ethyl} (1*R,*3*R*)-1,2,2-Trimethylcyclopentane-1,3-dicarboxylate* (**8**). A mixture of **7** (0.53 g, 2.3 mmol), **6** (2 g, 4.5 mmol), 4-(dimethylamino)pyridine (DMAP; 0.05 g, 0.45 mmol), and Et_3N (0.45 g, 4.5 mmol) in anh. CH_2Cl_2 (60 ml) was heated under reflux for 24 h under Ar. After cooling, the mixture was washed with H_2O (3×60 ml), dried (Na_2SO_4), and evaporated. Purification by CC (CH_2Cl_2/MeOH 75 : 1) gave pure **8** (29%). Yellow solid. M.p. 96–98°. $[\alpha]_D^{25} = -13.9$ ($c =$ 3.02, CH_2Cl_2). UV (THF): 231 (4.23), 280 (4.60), 350 (3.97). IR (KBr): 2920, 2850, 1800, 1730, 1690, 1600, 1570, 1510, 1470, 1250, 1170, 890. ^{1}H-NMR: 0.83–0.93 (*m*, 9 H); 1.00–1.45 (*m*, 43 H); 1.62–2.69 (*m*, 1 H); 1.73–1.80 (*m*, 4 H); 1.98–2.03 (*m*, 1 H); 2.15–2.21 (*m*, 1 H); 2.96 (*t*, $J = 9.6$, 1 H); 3.98 (*t*, $J = 6.3$, 4 H); 4.18 (*t*, $J = 5.1$, 4 H); 4.32–4.41 (*m*, 4 H); 4.37 (*s*, 4 H); 6.90 (*d*, $J = 9.0$, 4 H); 7.13–7.24 (*m*, 4 H); 8.02 (*d*, $J = 9.0$, 4 H); 8.22 (*d*, $J = 2.6$, 2 H). ^{13}C-NMR: 13.88; 18.45; 20.00; 22.45; 23.97; 24.31; 25.71; 28.78; 29.10; 29.35; 29.41; 31.69; 33.84; 47.69; 53.37; 57.55; 61.72; 66.37; 68.29; 114.62; 120.60; 125.06; 126.08; 131.98; 138.38; 145.15; 157.82; 164.42; 172.81; 173.72; 194.76. Anal. calc. for $C_{64}H_{90}N_2O_{10}$ (1047.43): C 73.39, H 8.66, N 2.67; found: C 73.28, H 8.70, N 2.76.

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