

Synthesis and mesomorphic properties of calamitic malonates and cyanoacetates tethered to 4-cyanobiphenyls

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Full Research Paper

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Keywords:
cyanoacetates; 4-cyanobiphenyls; liquid crystals; malonates; nematic

Beilstein J. Org. Chem. **2012**, *8*, 371–378.
doi:10.3762/bjoc.8.40

Received: 08 November 2011
Accepted: 20 February 2012
Published: 09 March 2012

This article is part of the Thematic Series "Progress in liquid crystal chemistry II".

Associate Editor: P. J. Skabara

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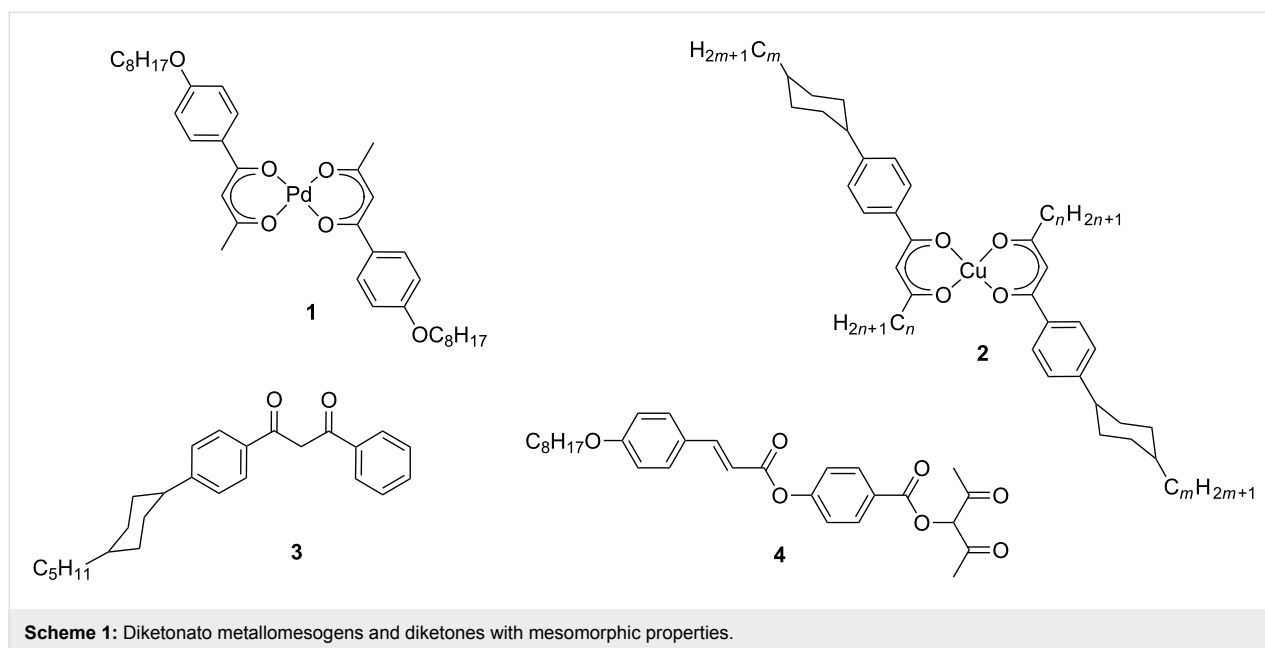
Abstract

4-Cyano-1,1'-biphenyl derivatives bearing ω -hydroxyalkyl substituents were reacted with methyl 3-chloro-3-oxopropionate or cyanoacetic acid, giving liquid-crystalline linear malonates and cyanoacetates. These compounds formed monotropic nematic phases at 62 °C down to ambient temperature upon cooling from the isotropic liquid. The mesomorphic properties were investigated by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction (WAXS).

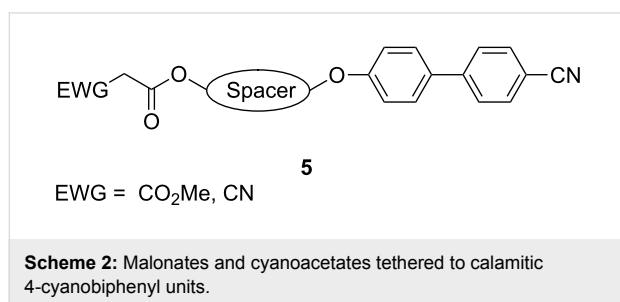
Introduction

Nematic liquid crystals display mesophases in which the molecules are oriented along one vector defined by the director axis, but with the molecular arrangement in random positional order [1]. Nematic phases typically display low viscosity [2-4]. Due to the long-range orientational order they reveal anisotropic properties. These features make nematic liquid crystals very attractive materials for electronics [5-8], for the construction of liquid crystal displays [9-11], or as anisotropic conductors [12,13]. Over the past few decades, a huge variety of organic calamitic compounds, which form nematic liquid crystals, have been synthesized and investigated [1,14].

Bulkin et al. were the first to investigate the phase behaviour of metal β -diketonate complexes such as **1** [15] (Scheme 1). Although they were not able to detect any mesophases, their study motivated others to examine the mesomorphic properties of β -diketonates in more detail [16]. Among the first examples of a nematic β -diketonate is the Cu complex **2** described by Haase [17-21]. In contrast to the various diketonato metallo-mesogens only a little information is available about the mesomorphic properties of metal-free diketones. Among the few examples are the nematic compounds **3** [22] and **4** [23,24] (Scheme 1).



The corresponding malonates and cyanoacetates are well known as suitable ligands for strong coordination of main-group and transition metals [25]. Benzylidene derivatives of malonic esters, so called swallow-tailed liquid crystals, were described as forming smectic phases [26]. However, most work on liquid-crystalline malonates has been devoted to C₆₀ fullerene dendrimers [27–31]. Only a few liquid crystalline cyanoacetates have been described so far. The first example, a dihydrazide, was reported by Schubert [32]. Furthermore some calamitic and bent-core mesogens derived from α -cyanocinnamic acid were described in the literature [33,34]. Therefore, we decided to explore the synthesis and mesomorphic properties of malonates and cyanoacetates **5** tethered to calamitic 4-cyanobiphenyl units (Scheme 2).



Results and Discussion

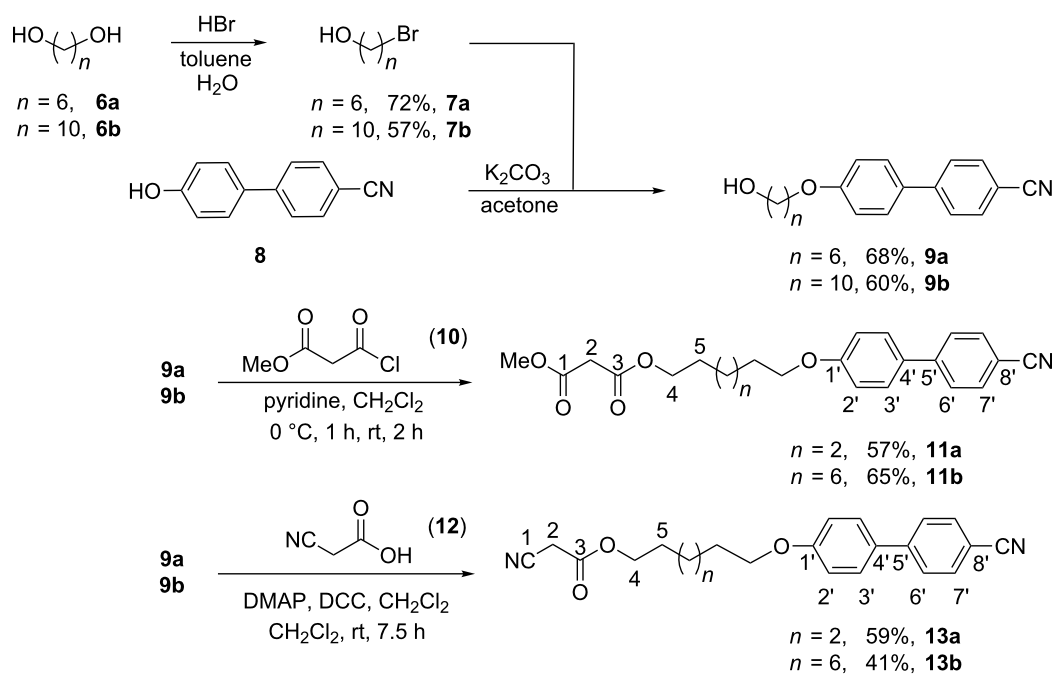
The syntheses of malonate and cyanoacetate derivatives **11**, **13** are shown in Scheme 3. Starting from the corresponding diols **6a,b**, 6-bromohexan-1-ol (**7a**) and 10-bromodecan-1-ol (**7b**) were obtained in moderate yields by bromination with aqueous HBr in toluene [35]. The bromides **7a,b** were reacted with

4-cyano-1,1'-biphenol (**8**) in acetone in the presence of K₂CO₃ giving compounds **9a,b**, bearing C₆- or C₁₀-spacers, in 68% and 60% yield, respectively [36–38] after recrystallization from methanol (Scheme 3).

The malonate unit was attached by treatment of the compounds **9a,b** with methyl 3-chloro-3-oxopropionate (**10**) in the presence of pyridine in CH₂Cl₂ to yield the malonates **11a,b** in 57% and 65%, respectively, after column chromatography. In a parallel approach, the precursors **9a,b** were converted to the corresponding cyanoacetates **13a,b** by esterification of cyanoacetic acid (**12**) in the presence of DMAP and dicyclohexylcarbodiimide in CH₂Cl₂. After chromatography the cyanoacetates **13a,b** were isolated as colourless solids in 59% and 41% yield.

The obtained malonate and cyanoacetic esters **11a,b** and **13a,b** were subjected to differential scanning calorimetry (DSC) studies (Figure 1, Figure 2, and Table 1).

During the first heating runs all compounds did not show the appearance of any liquid-crystalline phase, but melted without decomposition into isotropic liquids. It was observed that the melting points increased with an increase of the spacer length between 4-cyanobiphenyl and ester groups. Thus, melting points were recorded at 49.1 °C/63.4 °C for the series of **11a/11b** and at 89.0 °C/93.2 °C for the series of **13a/13b**, respectively (Table 1). The cyano group is a stronger electron-acceptor than the ester function, and thus the cyanoacetic ester molecules are more polarized than the corresponding malonates. Stronger dipole–dipole interactions for cyano esters **13** led to an increase of their clearing points compared with malonates **11**.



Scheme 3: Synthesis of malonate and cyanoacetates tethered to 4-cyano-biphenyl moieties.

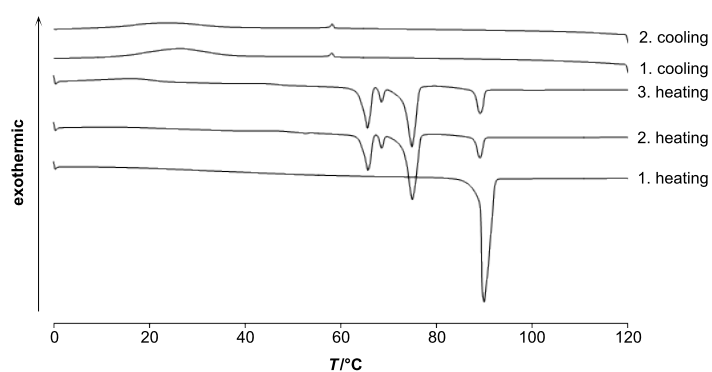


Figure 1: DSC traces of **13a** (heating/cooling rate 5 K/min).

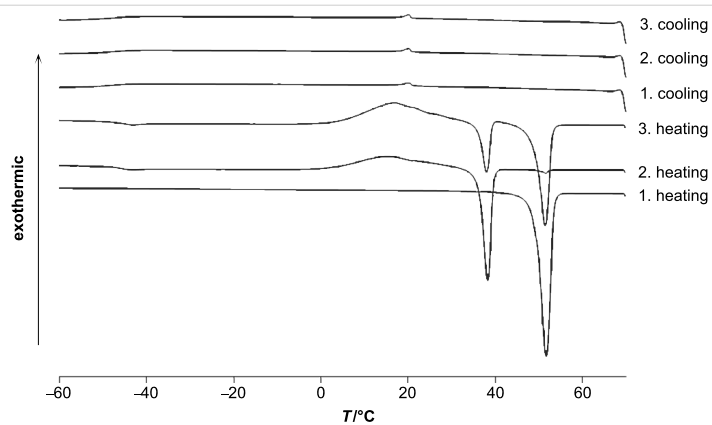


Figure 2: DSC traces of **11a** (heating/cooling rate 10 K/min).

Table 1: Phase-transition temperatures [°C] and enthalpies [kJ/mol] of **11** and **13**.^a

	<i>n</i>	Cr ₁	<i>T</i>	ΔH	Cr ₂	<i>T</i>	ΔH	Cr ₃ /N	<i>T</i>	ΔH	I	
11a	6	•	49.1	32.4	–	–	–	–	–	–	•	1. heating ^b
		•	–	–	–	–	–	N	21.2	–0.32	•	1. cooling ^b
		•	4.1	–12.0	•	36.2	17.6	Cr ₃	49.9	0.27	•	2. heating ^b
		•	–	–	–	–	–	N	20.9	–0.29	•	2. cooling ^b
11b	10	•	5.0	–18.2	•	35.9	7.72	Cr ₃	48.8	20.7	•	3. heating ^b
		•	63.4	53.2	–	–	–	–	–	–	•	1. heating ^c
		•	10.0	–24.2	•	14.8	–3.45	N	35.6	–0.68	•	1. cooling ^{c,d}
		•	54.8	39.8	–	–	–	Cr ₃	59.9	7.35	•	2. heating ^c
13a	6	•	14.8	–24.2	•	31.1	–0.33	N	35.4	–0.46	•	2. cooling ^c
		•	89.0	39.6	–	–	–	–	–	–	•	1. heating ^c
		•	–	–	–	–	–	N	58.7	–0.38	•	1. cooling ^c
		•	64.1	9.19	•	73.0	22.7	Cr ₃	87.8	–4.34	•	2. heating ^{c,e}
13b	10	•	–	–	–	–	–	N	58.7	–0.41	•	2. cooling ^c
		•	63.9	11.6	•	72.9	19.8	Cr ₃	87.8	5.48	•	3. heating ^{c,f}
		•	93.2	49.1	–	–	–	–	–	–	•	1. heating ^c
		•	52.7	–41.1	–	–	–	N	61.8	–0.71	•	1. cooling ^c
		•	74.7	13.5	•	86.3	–7.41	Cr ₃	91.5	41.5	•	2. heating ^{c,g}
		•	52.7	–41.1	–	–	–	N	61.9	–0.98	•	2. cooling ^c

^aCr crystalline; N nematic; I isotropic; • phase was observed; – phase was not observed. ^bHeating and cooling rate: 10 K/min. ^cHeating and cooling rate: 5 K/min. ^dAnother crystal-to-crystal transition (31.2 °C, –0.24 kJ/mol) was observed. ^eAnother crystal-to-crystal transition (67.7 °C, 1.62 kJ/mol) was observed. ^fAnother crystal-to-crystal transition (67.6 °C, 1.86 kJ/mol) was observed. ^gAnother crystal-to-crystal transition (78.1 °C, 21.0 kJ/mol) was observed.

The additional Cr→Cr transitions in the 2nd and 3rd heating curves (Figure 1 and Figure 2) are probably due to equilibration and the presence of keto-enol tautomers. Molecular geometry phase-behaviour relationships in keto-enamine/imino-enol tautomers of ferrocenophanes have been previously studied by Galyametdinov [39]. In the first cooling runs the appearance of nematic mesophases was observed for both series **11a,b** and **13a,b**. All compounds displayed small transition enthalpies in a range between –0.3 and –0.7 kJ/mol (Table 1) for the transition from the isotropic liquid to the corresponding mesophases. While C₆-linked compounds displayed monotropic nematic mesophases at temperatures of 21 °C for **11a** and 59 °C for **13a**,

their longer and more flexible C₁₀-linked homologues showed higher transition temperatures at 36 °C for **11b** and 62 °C for **13b** upon cooling from the isotropic liquid. Due to supercooling, no crystallisation could be observed for compound **11a** and, therefore, no mesophase range could be determined. But the second and third heating runs of **11a** showed broad recrystallization peaks (Figure 2).

Polarizing optical microscope (POM) studies

POM observations of compounds **11a,b** and **13a,b** revealed textures typical for nematic phases, only upon cooling from the isotropic liquid (Figure 3 and Figure 4).

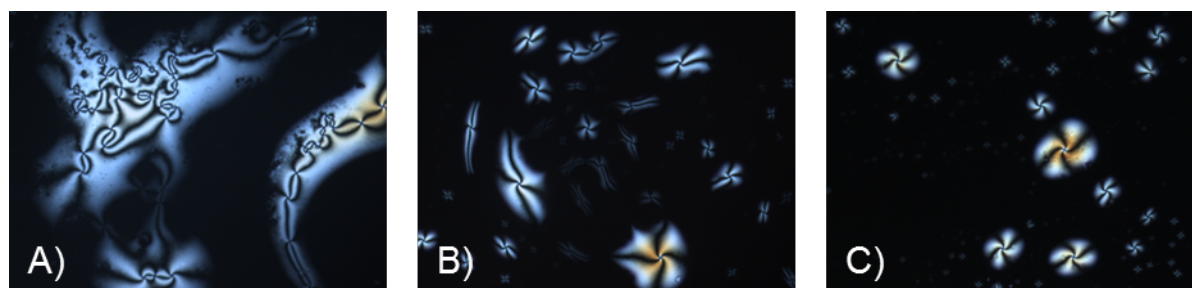


Figure 3: Schlieren textures of **11a** and **11b** under crossed polarizers, upon cooling (cooling rate 5 K/min) from the isotropic liquid (magnification 200×): (A) **11a** (20 °C), (B) **11a** (14 °C), (C) **11b** (29 °C).

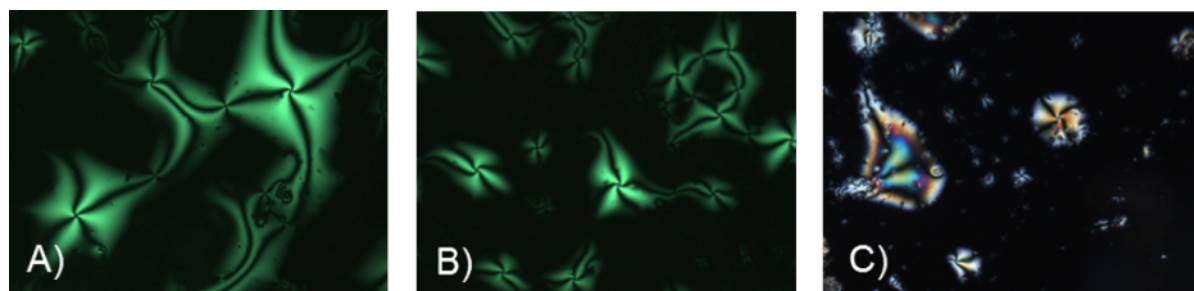


Figure 4: Schlieren textures of **13a** and **13b** under crossed polarizers upon cooling (cooling rate 5 K/min) from the isotropic liquid (magnification 200×): (A) **13b** (61 °C), (B) **13b** at 61 °C, different section, (C) **13a** (46 °C).

Schlieren textures with fourfold brushes were observed for compound **13b** at the transition from the isotropic liquid into the nematic phase. Quite similar textures were published by Dierking [40,41]. The areas without birefringence in Figure 3 and Figure 4 derive from homeotropic alignment of the molecules.

X-ray diffraction studies

The assignment of the nematic mesophases were exemplarily confirmed by wide-angle X-ray scattering (WAXS) experiments on compound **11a**. Representative 2D diffractograms of the crystalline phase, the isotropic phase and the nematic phase are shown in Figure 5.

In the isotropic phase (Figure 5, part B) only a diffuse symmetric halo is observed. The diffraction pattern of **11a** at 15 °C (Figure 5, part C) displays a halo split into two diffuse, crescent reflections, which is typical for nematic mesophases [42].

Conclusion

The mesogenic 4-cyano-1,1'-biphenyl group can be attached to either a malonate or a cyanoacetic ester scaffold by means of

simple reaction sequences and with the aid of cheap chemical precursors. Linked ester molecules **11a,b** and **13a,b** have a distinct linear shape and easily form monotropic mesophases at ambient temperature upon cooling from the isotropic liquid. Following POM and X-ray studies, nematic mesophases could be assigned to all the described compounds **11a,b** and **13a,b**.

Experimental

General information

All reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware. Solvents were dried and distilled under nitrogen prior to use. Flash chromatography was performed on silica gel, with grain size 40–63 μm (Macherey-Nagel).

The following instruments were used for physical characterization of the compounds. Elemental analyses: Carlo Erba Strumentazione Elemental Analyzer, Modell 1106. NMR: Bruker ARX-500 (^1H , 500 MHz; ^{13}C , 125 MHz). Assignments of the resonances are supported by 2D experiments and chemical shift calculations. ^1H and ^{13}C NMR spectra were referenced to an internal Me_4Si (TMS) standard. IR: Bruker 22 FT-IR spectrometer with a golden-gate single-reflection diamond ATR system. MS: Bruker Daltonics mikro-TOF-Q (ESIMS). Differ-

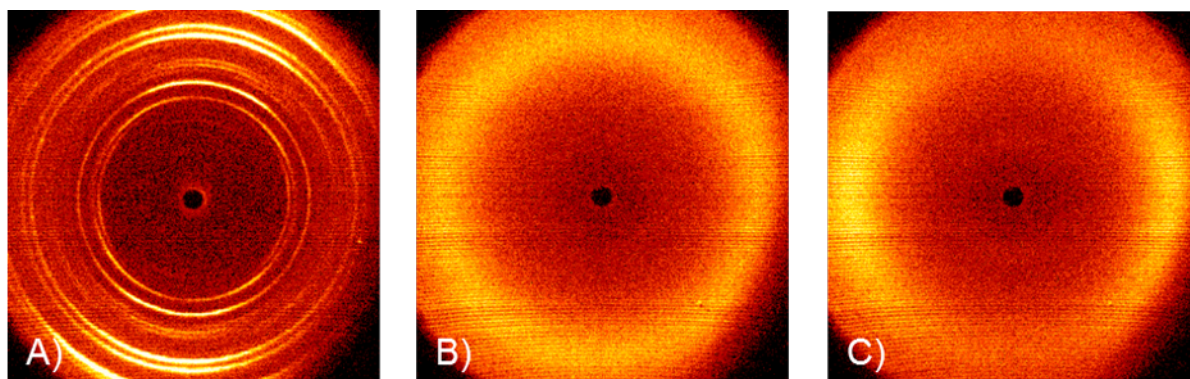


Figure 5: 2D X-ray scattering patterns of **11a**: (A) crystalline phase at 50 °C, (B) isotropic phase at 25 °C, and (C) nematic phase at 15 °C.

ential scanning calorimetry (DSC): Mettler-Toledo DSC 822e (heating/cooling rates were 5 or 10 K·min⁻¹). Polarizing optical microscopy: Olympus BX50 polarizing microscope combined with a Linkam TP93 central controller. X-ray diffraction (WAXS): Bruker AXS Nanostar C diffractometer employing Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

6-[(4'-cyano-[1,1'-biphenyl]-4-yl)oxy]hexyl methyl malonate (**11a**)

Pyridine (150 mg, 1.69 mmol) and then methyl 3-chloro-3-oxopropionate (**10**) (114 mg, 0.84 mmol) were added over 10 min at 0 °C under a N₂ atmosphere to a solution of 4'-((6-hydroxyhexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (**9a**) (500 mg, 1.69 mmol) in abs. CH₂Cl₂ (5 mL). The reaction mixture was stirred at 0 °C for 1 h, then for 2 h at rt. The reaction was quenched with 1 N H₂SO₄ (3 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were washed with brine (40 mL), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc 20:1) to give **11a** as a colourless solid (188 mg, 0.48 mmol, 57%). Mp 49.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.41–1.47 (m, 2H, 6-H), 1.49–1.55 (m, 2H, 7-H), 1.67–1.73 (m, 2H, 5-H), 1.79–1.85 (m, 2H, 8-H), 3.39 (s, 2H, 2-H), 3.74 (s, 3H, OCH₃), 4.01 (t, $J = 6.4 \text{ Hz}$, 2H, 9-H), 4.17 (t, $J = 6.4 \text{ Hz}$, 2H, 4-H), 6.98 (d, $J = 8.5 \text{ Hz}$, 2H, 2'-H), 7.52 (d, $J = 8.5 \text{ Hz}$, 2H, 3'-H), 7.64 (d, $J = 8.5 \text{ Hz}$, 2H, 6'-H), 7.69 (d, $J = 8.5 \text{ Hz}$, 2H, 7'-H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 25.6, 25.7 (C-6, C-7), 28.4 (C-5), 29.0 (C-8), 41.4 (C-2), 52.5 (OCH₃), 65.6 (C-4), 67.8 (C-9), 110.0 (C-8'), 115.0 (C-2'), 119.1 (CN), 127.0 (C-6'), 128.3 (C-3'), 131.3 (C-5'), 132.6 (C-7'), 145.3 (C-4'), 159.7 (C-1'), 166.6 (C-3), 167.0 (C-1) ppm; ATR–FTIR $\tilde{\nu}$: 2936 (m), 2858 (w), 2224 (m), 1967 (w), 1730 (s), 1602 (m), 1494 (m), 1246 (s), 1014 (m), 822 (s); ESIMS (m/z): 343.1 [M + K]⁺, 418.1 [M + Na]⁺, 396.1 [M + H]⁺, 278.15 [C₁₉H₂₀NO]⁺; Anal. calcd for C₂₃H₂₅NO₅: C, 69.86; H, 6.37; N, 3.54; found: C, 69.47; H, 6.37; N, 3.47; R_f 0.56 (hexanes/EtOAc 2:1).

10-[(4'-cyano-[1,1'-biphenyl]-4-yl)oxy]decyl methyl malonate (**11b**)

The ester **11b** was obtained by the same procedure as described above for **11a** from 4'-((10-hydroxydecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (**9b**) (560 mg, 1.60 mmol), methyl 3-chloro-3-oxopropionate (**10**) (109 mg, 0.80 mmol) and pyridine (126 mg, 1.60 mmol) in abs. CH₂Cl₂ (5 mL). The crude product was purified by column chromatography on silica gel (gradient: hexanes/EtOAc, 20:1, then 15:1) to give **11b** as a colourless solid (240 mg, 0.53 mmol, 65%). Mp 63.4 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.31–1.35 (m, 10H, 6-H, 7-H, 8-H, 9-H, 10-H), 1.44–1.50 (m, 2H, 11-H), 1.61–1.67 (m, 2H, 5-H), 1.77–1.83 (m, 2H, 12-H), 3.38 (s, 2H, 2-H), 3.75 (s, 3H,

OCH₃), 4.00 (t, $J = 6.5 \text{ Hz}$, 2H, 13-H), 4.14 (t, $J = 6.8 \text{ Hz}$, 2H, 4-H), 6.98–6.99 (m, 2H, 2'-H), 7.51–7.53 (m, 2H, 3'-H), 7.63–7.64 (m, 2H, 6'-H), 7.68–7.69 (m, 2H, 7'-H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 25.7 (C-6), 26.0 (C-11), 28.4 (C-5), 29.15 (C-12), 29.21, 29.33, 29.41, 29.45 (C-7, C-8, C-9, C-10), 41.4 (C-2), 52.4 (OCH₃), 65.7 (C-4), 68.1 (C-13), 110.0 (C-8'), 115.0 (C-2'), 119.1 (CN), 127.0 (C-6'), 128.3 (C-3'), 131.3 (C-5'), 132.6 (C-7'), 145.3 (C-4'), 159.8 (C-1'), 166.6 (C-3), 167.0 (C-1) ppm; ATR–FTIR $\tilde{\nu}$: 2927 (m), 2854 (w), 2225 (m), 1735 (s), 1603 (m), 1494 (m), 1249 (s), 1180 (m), 903 (m), 823 (m); ESIMS (m/z): 474.2 [M + Na]⁺, 452.2 [M + H]⁺; Anal. calcd for C₂₇H₃₃NO₅: C, 71.82; H, 7.37; N, 3.10; found: C, 71.66; H, 7.34; N, 3.03; R_f 0.76 (hexanes/EtOAc 2:1).

6-[(4'-cyano-[1,1'-biphenyl]-4-yl)oxy]hexyl 2-cyanoacetate (**13a**)

To a solution of 4'-((6-hydroxyhexyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (**9a**) (100 mg, 338 μ mol) in abs. CH₂Cl₂ (2.5 mL) were added sequentially a solution of cyanoacetic acid (**12**) (32 mg, 376 μ mol) in EtOAc (0.4 mL), a solution of DMAP (12 mg, 98 μ mol) in abs. CH₂Cl₂ (0.8 mL) and then at 0 °C a solution of dicyclohexylcarbodiimide (77 mg, 376 μ mol) in abs. CH₂Cl₂ (2.5 mL). The reaction mixture was stirred at rt for 7.5 h, then evaporated under vacuum. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc 12:1) to give **13a** as a colourless solid (72 mg, 190 μ mol, 59%). Mp 89.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.43–1.49 (m, 2H, 6-H), 1.51–1.56 (m, 2H, 7-H), 1.71–1.76 (m, 2H, 5-H), 1.80–1.85 (m, 2H, 8-H), 3.45 (s, 2H, 2-H), 4.01 (t, $J = 6.4 \text{ Hz}$, 2H, 9-H), 4.23 (t, $J = 6.3 \text{ Hz}$, 2H, 4-H), 6.98–6.99 (m, 2H, 2'-H), 7.52–7.53 (m, 2H, 3'-H), 7.63–7.64 (m, 2H, 6'-H), 7.68–7.69 (m, 2H, 7'-H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 24.7 (C-2), 25.5 (C-6), 25.6 (C-7), 28.3 (C-5), 29.0 (C-8), 66.9 (C-4), 67.8 (C-9), 110.0 (C-8'), 112.9 (C-1), 115.0 (C-2'), 119.1 (CN), 127.0 (C-6'), 128.3 (C-3'), 131.3 (C-5'), 132.5 (C-7'), 145.2 (C-4'), 159.6 (C-1'), 162.9 (C-3) ppm; ATR–FTIR $\tilde{\nu}$: 2941 (m), 2866 (w), 2225 (w), 1746 (m), 1602 (m), 1494 (m), 1249 (m), 1180 (m), 903 (s), 723 (s); ESIMS (m/z): 385.1 [M + Na]⁺, 363.1 [M + H]⁺; Anal. calcd for C₂₂H₂₂N₂O₃: C, 71.91; H, 6.12; N, 7.57; found: C, 71.44; H, 6.06; N, 7.73; R_f 0.68 (hexanes/EtOAc 2:1).

10-[(4'-cyano-[1,1'-biphenyl]-4-yl)oxy]decyl 2-cyanoacetate (**13b**)

The cyanoacetic ester **13b** was obtained by the same procedure as described above for **13a** from 4'-((10-hydroxydecyl)oxy)-[1,1'-biphenyl]-4-carbonitrile (**9b**) (120 mg, 341 μ mol), cyanoacetic acid (**12**) (32 mg, 376 μ mol), DMAP (13 mg, 102 μ mol), and dicyclohexylcarbodiimide (77 mg, 376 μ mol) in abs. CH₂Cl₂ (6.5 mL). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc 10:1) to give **13b**

as a colourless solid (57 mg, 140 μmol , 41%). Mp 93.2 °C; ^1H NMR (500 MHz, CDCl_3) δ 1.32–1.36 (m, 10H, 6-H, 7-H, 8-H, 9-H, 10-H), 1.44–1.50 (m, 2H, 11-H), 1.65–1.71 (m, 2H, 5-H), 1.78–1.83 (m, 2H, 12-H), 3.44 (s, 2H, 2-H), 4.00 (t, J = 6.5 Hz, 2H, 13-H), 4.20 (t, J = 6.9 Hz, 2H, 4-H), 6.98–6.99 (m, 2H, 2'-H), 7.51–7.53 (m, 2H, 3'-H), 7.63–7.64 (m, 2H, 6'-H), 7.68–7.69 (m, 2H, 7'-H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 24.7 (C-2), 25.6 (C-6), 26.0 (C-11), 28.3 (C-5), 29.11 (C-12), 29.21, 29.32, 29.36, 29.40 (C-7, C-8, C-9, C-10), 67.1 (C-4), 68.1 (C-13), 110.0 (C-8'), 113.0 (C-1), 115.0 (C-2'), 119.1 (CN), 127.0 (C-6'), 128.3 (C-3'), 131.3 (C-5'), 132.5 (C-7'), 145.2 (C-4'), 159.7 (C-1'), 162.9 (C-3) ppm; ATR-FTIR $\tilde{\nu}$: 2928 (m), 2855 (w), 2225 (w), 1747 (m), 1603 (m), 1494 (m), 1250 (m), 1180 (m), 903 (s), 725 (s); ESIMS (m/z): 457.1 [$\text{M} + \text{K}$] $^+$, 441.2 [$\text{M} + \text{Na}$] $^+$, 436.2, 419.2 [$\text{M} + \text{H}$] $^+$; Anal. calcd for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_3$: C, 74.61; H, 7.22; N, 6.69; found: C, 74.04; H, 7.18; N, 6.54; R_f 0.58 (hexanes/EtOAc 2:1).

Supporting Information

Supporting Information File 1

Full experimental procedures and DSC traces of **11b** and **13b**.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-8-40-S1.pdf>]

Acknowledgements

Generous financial support by the Bundesministerium für Bildung und Forschung, the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg and the Max-Planck-Gesellschaft (International Max Planck Research School for Advanced Materials fellowship for M.K.) is gratefully acknowledged. We would like to thank Ingo Dierking for helpful discussions and suggestions.

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