DOI: 10.1002/chem.201000542

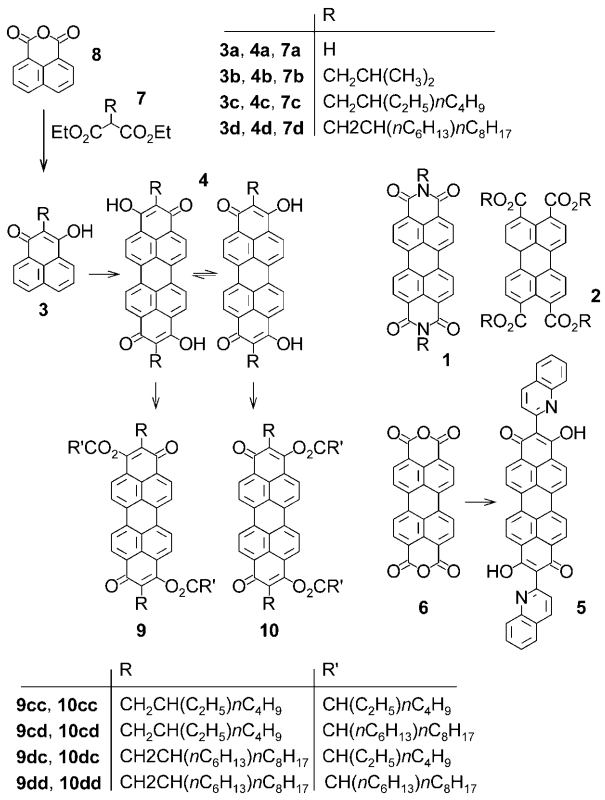
Soluble and Columnar Liquid Crystalline Peropyrenequinones by Coupling of Phenalenones in Caesium Hydroxide

Noémie Buffet,[a, b] Éric Grelet,[a] and Harald Bock*[a]

Perylene tetracarboxylic diimides (PTCDIs) **1** are very versatile, stable and synthetically very accessible red dyes with high extinction coefficients,[1] that have, amongst a variety of other applications,[2] found widespread use in molecular optoelectronics, including electrophotography,[3] solar cells[4] and light-emitting diodes.[5] When substituted with appropriate alkyl or trialkylaryl substituents, they exhibit lamellar or columnar liquid crystalline self-assembly, which gives rise to high intermolecular charge carrier mobilities.[6] The columnar liquid-crystalline state is also prominent in the corresponding orange perylene tetracarboxylic tetraalkyl esters (PTCTEs) **2** in which it can be stabilised at room temperature with racemically branched alkyl groups.[7] A key feature of tetracarboxylic perylene derivatives is their intense absorption at relatively long wavelengths (about 525 nm for dialkyl imides and about 475 nm for tetraalkyl esters in solution) with respect to their small chromophore size (which favours solubility), when compared with other relatively stable polycyclic aromatic hydrocarbon (PAH) derivatives.

Considerable efforts have been undertaken to obtain perylene derivatives that absorb at yet longer wavelengths, whilst maintaining solubility. These approaches include the introduction of arylimidazole moieties,[8] donor substitution in the bay regions,[9] extension of the core in the rylene series[10] and lateral oligomerisation.[11]

To shift the absorption maximum to longer wavelengths by a particularly simple approach that maintains the small chromophore size of **1**, and to ensure at the same time columnar liquid-crystalline self-assembly at room temperature, we have investigated the known base-induced dehydro-dimerisation of 3-hydroxy-1-phenalenone (**3a**).[12] The resulting violet dihydroxyperopyrenequinone **4** can be regarded as a homologue of **1** in which both nitrogen atoms have been exchanged for methine moieties (Scheme 1). Since **4** is enolised (no ^{1}H NMR coupling in alkyl-substituted **4** between the α protons of R with any ring proton), which yields to two fully sp^2-configured terminal rings, its colour is



	R	R'
9cc, 10cc	$CH_2CH(C_2H_5)nC_4H_9$	$CH(C_2H_5)nC_4H_9$
9cd, 10cd	$CH_2CH(C_2H_5)nC_4H_9$	$CH(nC_6H_{13})nC_8H_{17}$
9dc, 10dc	$CH2CH(nC_6H_{13})nC_8H_{17}$	$CH(C_2H_5)nC_4H_9$
9dd, 10dd	$CH2CH(nC_6H_{13})nC_8H_{17}$	$CH(nC_6H_{13})nC_8H_{17}$

Scheme 1. Approach to substituted peropyrenequinones, with related perylene derivatives.

[a] Dr. N. Buffet, Dr. É. Grelet, Dr. H. Bock
Centre de Recherche Paul Pascal
Université de Bordeaux
Centre National de la Recherche Scientifique (CNRS)
115 avenue Schweitzer, 33600 Pessac (France)
Fax: (+33) 556845600
E-mail: bock@crpp-bordeaux.cnrs.fr

[b] Dr. N. Buffet
Essilor International, R&D Technologies Digitales
rue Curie, 31682 Labège cedex (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000542.

considerably bathochromically shifted with respect to **1**. Accordingly, and in contrast to **1**, compound **4** is soluble in aqueous base. Apart from the unsubstituted chromophore, the doubly quinolinyl-substituted derivative **5** is known as well, which can be obtained from perylene tetracarboxylic dianhydride (PTCDA) **6** by double condensation with 2-methylquinoline (quinaldine); bay-substituted derivatives of this condensation product with quinaldine have recently been reported as soluble long-wavelength absorbing emitters.[13] No other substituted derivatives **4** ($R \neq H$ or quinolinyl) have been described.

We found that two-fold terminal substitution of **4** can conveniently be achieved by the use of accordingly 2-substituted 3-hydroxy-1-phenalenones, which are obtained by condensation of 2-substituted malonic esters **7** with naphthalic anhydride **8** in the presence of zinc chloride.[14]

Further solubility-enhancing substitution is subsequently accomplished by esterification at the two enolic hydroxy groups. Together with the two "malonic" substituents in positions 2 and 9, this leads to a sufficient number of flexible alkyl groups to hope for the formation of columnar liquid-crystalline self-assembly at moderate temperatures, as observed in PTCTEs **2**. Two regioisomers **9** and **10** are obtained, of which the former (*transoid*) is centrosymmetric, whereas the latter (*cisoid*) exhibits a lateral permanent dipole moment.

Symmetrical long-chain secondary alkyl substituents, such as 1-hexylheptyl, on both nitrogen atoms have been shown to impart excellent solubilities to PTCDIs **1**.[15] We therefore aimed to introduce such swallow-tail substituents in **4** starting from diethyl isopropylmalonate and its longer homologues, but whilst we found that the reaction of straight-chain malonates, such as diethyl *n*-butylmalonate, with naphthalic anhydride and zinc chloride smoothly yields the corresponding 2-substituted phenalene-1,3-diones **3**, the reaction fails with diethyl isopropylmalonate ($R = CHMe_2$) and diethyl pent-3-ylmalonate ($R = CHEt_2$), yielding only small amounts of unsubstituted **3a**. It appears that Lewis acid assisted dealkylation dominates with secondary alkyl groups, and varying the reaction conditions (duration, temperature) was of no avail.

We then turned to 2-substituted alkyl substituents, such as 2-ethylhexyl, and obtained the desired 2-(2-alkylalkyl)-3-hydroxy-1-phenalenones **3b–d** without difficulty from the respective diethyl 2-(2-alkylalkyl)-malonates **7b–d** in moderate yield (39% with isobutyl, 31% with 2-ethylhexyl, 23% with 2-hexyldecyl). A marked alkyl-substituent dependence of the solution behaviour towards aqueous base is observed: When shaking the crude products during workup with dilute aqueous potassium hydroxide solution and ethyl acetate, the isobutyl homologue **3b** goes into the aqueous phase, whilst the 2-ethylhexyl and 2-hexyldecyl homologues **3c** and **3d** dissolve in the organic phase.

As the solubilising effect of β-branched primary alkyl substituents on PTCDI-type chromophores is weaker than secondary alkyl groups, we focussed on the relatively long 2-hexyldecyl substituent, as well as the shorter 2-ethylhexyl. We obtained the corresponding hydroxyphenalenones **3c** and **3d** on a 10 g scale, and then noted that the yield of **4** obtained by oxidising dimerisation in molten potassium hydroxide in the presence of oxygen, which is near quantitative with short or absent alkyl substituents (**4a** and **4b**), decreases to 33% with 2-ethylhexyl (**4c**). No dimerisation could be obtained with 2-hexyldecyl (**4d**). Such voluminous alkyl groups seem to hinder efficiently the interaction of the relatively small potassium cation with the keto/enol oxygen atoms. We therefore investigated the effect of the hydroxides of the larger and softer alkali metals rubidium and caesium. Whilst rubidium hydroxide only increased the yield with **4c** to 65%, but did not yield any product with **4d**, caesium hydroxide led not only to similarly improved yields of **4c** of 60% with 2-ethylhexyl, but also allowed the dimerisation to occur in moderate yield (21%) with 2-hexyldecyl to give **4d**.

Dihydroxyperopyrenequinones **4c** and **4d** form intensely violet solutions, the absorption spectra of which show two main peaks of nearly equal intensity at 556 and 591 nm (Figure 1).

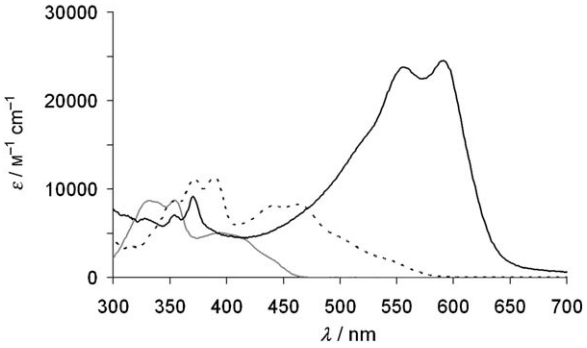
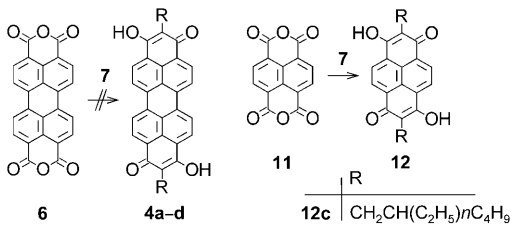


Figure 1. Absorption spectra of **3b** (grey), **12c** (dashed) and **4d** (black) in chloroform.

We failed to obtain any **4** by an alternative approach, that is, the two-fold reaction of PTCDA **6** with diethyl malonate **7a** or its 2-alkyl homologues **7b–d** in the presence of zinc chloride (Scheme 2). We were therefore surprised to find that malonates **7** do react twice with naphthalene-1,4,5,8-tetracarboxylic dianhydride **11** to give the dihydroxypyrenequinones **12**. The yield of this double condensation (9% of **12c**) with diethyl 2-ethylhexylmalonate **7c** corresponds to



Scheme 2. Approach to peropyrenequinones and pyrenequinones by condensation of malonic esters with dianhydrides.

the square of the yield (31%; $0.31^2 = 0.0961$) of the single condensation with naphthalic anhydride **8**, under similar reaction conditions. The condensation therefore proceeds with similar ease on **8** and on **11**, even if no conversion of highly insoluble **6** is observed under these conditions.

When **4c** or **4d** is esterified with either 2-ethylhexanoyl chloride or 2-hexyldecanoyl chloride in the presence of pyridine at room temperature, a mixture of the two possible products **9** and **10** is obtained in 22–63% combined isolated yield. These isomers are separated without difficulty by column chromatography due to the permanent dipole moment of the *cisoid* isomer **10**. They are of distinctively different hues, compound **9** is reddish violet in chloroform (absorption maximum at 598 nm), whereas **10** is bluish violet (absorption maximum at 611 nm) (Figure 2).

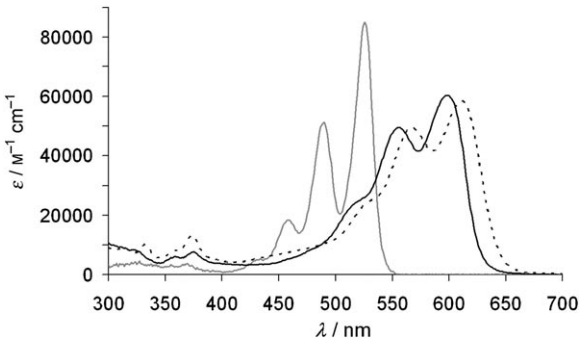


Figure 2. Absorption spectra of **9dd** (black), **10dd** (dashed) and **1** (R = $CHEt_2$, for comparison, grey) in chloroform.

The esters **9cc–dd** and **10cc–dd** all are viscous shearable waxes at room temperature, and exhibit typical fan-shaped focal conic or dendritic textures of columnar liquid crystals under polarising optical microscopy after cooling from the isotropic liquid (Figure 3). Only **9cc**, the liquid crystal to isotropic liquid transition temperature of which (>300 °C) is too high to be reached without substantial decomposition, does not yield such a characteristic texture. Some decomposition at the transition also renders the determination of the transition temperature approximate for **10cc** (≈280 °C), **9cd** (≈260 °C) and **10cd** (≈240 °C). Compounds **9dc**, **10dc**, **9dd** and **10dd** show their clearing transitions at 155, 228, 86 and 131 °C, respectively.

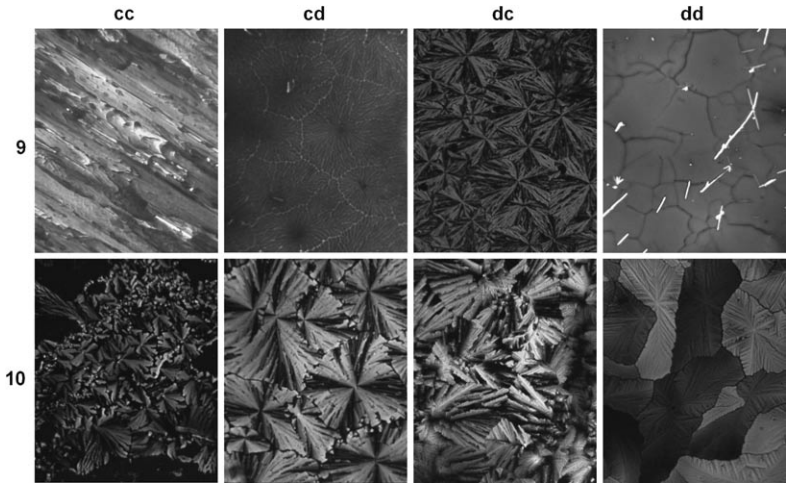


Figure 3. Textures observed by polarising optical microscopy in transmission at room temperature after cooling from the isotropic liquid (except **9cc**). All images are 300×240 μm. Compounds **9dc** and **10cc–dd**: crossed polarisers; **9cd** and **9dd**: slightly uncrossed polarisers to render visible the domain boundaries in the nonbirefringent homeotropic texture (**9dd** additionally shows a few needle-like birefringent planar domains); **9cc**: unheated sample sheared between glass plates at room temperature, uncrossed polarisers.

We performed wide-angle powder X-ray scattering experiments (Figure 4) at room temperature on the longest-chain

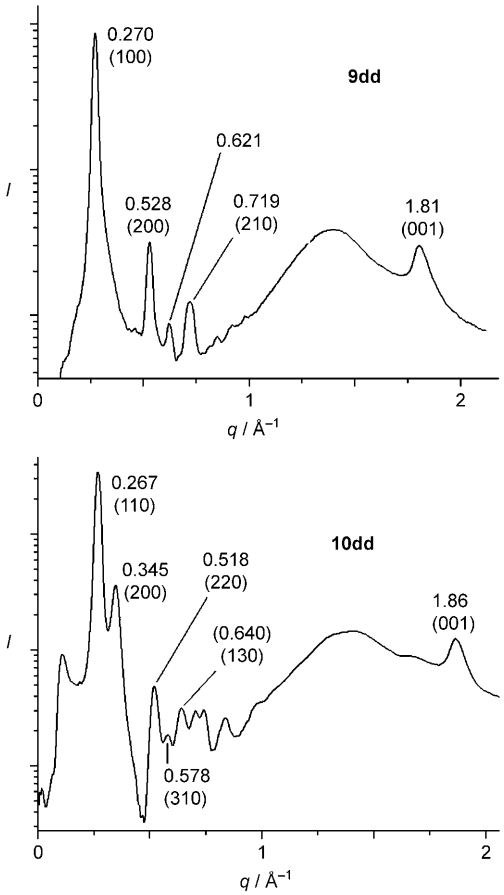


Figure 4. Powder X-ray diffraction spectra of **9dd** and **10dd** at room temperature (logarithmic intensity scaling). The indicated Miller indices correspond to column lattices of hexagonal symmetry for **9dd** and of rectangular symmetry for **10dd**.

homologues **9dd** and **10dd**. Compound **9dd** shows the (100), (200) and (210) reflections corresponding to a columnar mesophase of hexagonal symmetry, with a column-to-column distance (from the (100) peak) of 26.9 Å. An unexplained non-indexable reflection is observed between the (200) and (210) reflections. The diffractogram of polar **10dd** shows the typical splitting of the main peak in two ((110) and (200)) together with further characteristic peaks ((220), (310), (130)) that correspond to a rectangular column lattice of parameters $a=36.4$ Å and $b=30.8$ Å. This biaxial phase symmetry manifests itself also by the presence of birefringence in the pseudo-homeotropic texture (Figure 3). Both diffractograms also show the typical broadened peak corresponding to an intracolumnar disk-to-disk spacing of about 3.5 Å, as well as the usual very broad peak corresponding to the characteristic distance between aliphatic chains of 4–5 Å.

In summary, the oxidative dimerisation of 2-alkyl-3-hydroxy-1-phenalenones, the nitrogen-free carbon homologues of N-alkyl naphthalimides, in caesium hydroxide as a reaction medium opens access to a new class of intensely long-wavelength absorbing perylenic dyes that adopt columnar liquid-crystalline structures at ambient temperature, and which are obtained as separable pairs of centrosymmetric (*transoid*) and polar (*cisoid*) regioisomers. Their strong absorption in the long-wavelength part of the visible spectrum and their room temperature columnar self-assembly makes them promising materials for organic opto-electronics.

Experimental Section

General: X-ray scattering experiments were carried out by using a rotating anode generator (Rigaku, Japan) with a wavelength of 1.54 Å. The incident beam had a size of about 0.7 mm and the spectra were recorded with a bidimensional detector located at about 130 mm from the sample. Powder samples were placed in 1 mm diameter glass capillary tubes and the calibration of the experimental setup was performed with silver behenate. NMR spectra were recorded on a Nicolet Magna-IR 750 spectrometer UV/Vis spectra were recorded on a Unicam UV4 spectrometer.

Compound 4d: A mixture of monohydrated caesium hydroxide (9.00 g, 53.59 mmol) and **3d** (0.971 g, 2.31 mmol) was heated at 280 °C for 3 h in a metallic crucible open to air. After cooling, the crude product was dissolved in a mixture of water (250 mL) and acetone (250 mL). The resulting solution was acidified with 20% sulfuric acid (100 mL). Ethyl acetate (250 mL) and water (100 mL) were added and the phases were separated. The combined organic layers were washed with water (200 mL) and brine (50 mL) and the solvent was evaporated. The residue was purified by column chromatography (silica gel; chloroform→chloroform/ethyl acetate 5:1). The resulting oil was recrystallised from methanol to give the product as a dark violet solid (207 mg, 21%). ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta=8.78$ (d, 8 Hz, 4H; ArH), 8.60 (d, 8 Hz, 4H; ArH), 3.24 (d, 7 Hz, 4H; α-CH$_2$), 2.34 (m, 2H; CH), 1.60 (m, 12H; CH$_2$), 1.44 (m, 4H; CH$_2$), 1.29–1.16 (m, 32H; CH$_2$), 0.80 ppm (t, 7 Hz, 12H; CH$_3$); IR (KBr disk): $\tilde{\nu}=3238$ (br), 2953 (w), 2923 (s), 2852 (m), 1606 (m), 1588 (w), 1547 (s), 1456 (w), 1373 (m), 1294 (w), 1190 (m), 1134 (w), 1021 (w), 810 cm^{-1} (w); UV/Vis (chloroform): λ_{max} (ε) = 354 (7100), 370 (9200), 556 (24000), 591 nm (25000 mol^{-1}m^{3}cm^{-1}); elemental analysis calcd (%) for $C_{58}H_{76}O_4$: C 83.21, H 9.15; found: C 83.07, H 8.95.

Compounds 9dd and 10dd: 2-Hexyldecanoyl chloride (3.5 g, 13 mmol) was cautiously added to a solution of **4d** (406.6 mg, 0.49 mmol) and pyridine (5 mL) in chloroform (20 mL). After stirring at room temperature for 30 min under exclusion of water, the mixture was diluted with chloroform (250 mL), and acidified with 5% hydrochloric acid (300 mL). The organic layer was separated and dried over anhydrous sodium sulfate, and the solvent was evaporated. The resulting purple liquid was purified by column chromatography (silica gel; chloroform→chloroform/ethanol 165:1) to yield two dark violet waxes, which were both recrystallised from MeOH.

9dd: Yield: 134 mg (0.10 mmol, 21%); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta=8.65$ (d, 8 Hz, 2H; ArH), 8.53 (d, 8 Hz, 2H; ArH), 8.42 (d, 8 Hz, 2H; ArH), 7.75 (d, 8 Hz, 2H; ArH), 2.84 (quint, 7 Hz, 2H, CHCOO), 2.50 (br s, 4H; α-CH$_2$), 1.96 (m, 4H; CH$_2$), 1.87 (m, 2H, CH), 1.78 (m, 4H; CH$_2$), 1.56 (m, 8H; CH$_2$), 1.39–1.26 (m, 80H; CH$_2$), 0.96 (t, 7 Hz, 6H; CH$_3$), 0.94 (t, 7 Hz, 6H; CH$_3$), 0.85 ppm (t, 7 Hz, 12H; CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): $\delta=184.3$, 173.6, 154.6, 135.3, 132.1, 131.6, 130.7, 128.5, 127.0, 126.0 (×3: 3 overlapping signals), 123.0, 122.9, 45.7, 37.2, 33.9 (×2), 32.0, 31.95, 31.9, 31.8 (×3), 30.3, 30.2, 29.85, 29.8, 29.7, 29.6, 29.45, 29.4, 29.35, 27.7, 27.65, 26.7, 26.65, 22.74, 22.71, 22, 69, 22.67, 14.15 (×2), 14.0 ppm (×2); IR (KBr disk): $\tilde{\nu}=2954$ (m), 2925 (s), 2855 (m), 1751 (m), 1629 (m), 1587 (w), 1563 (m), 1464 (w), 1341 (w), 1167 (w), 1108 (m), 1027 (w), 808 cm^{-1} (w); UV/Vis (chloroform): λ_{max} (ε) = 375 (7700), 556 (49000), 598 nm (60000 mol^{-1}m^{3}cm^{-1}); elemental analysis calcd (%) for $C_{90}H_{136}O_6$: C 82.26, H 10.43; found: C 82.01, H 10.34.

10dd: Yield: 220 mg (0.17 mmol, 34%); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta=8.68$ (d, 8 Hz, 2H; ArH), 8.63 (d, 8 Hz, 2H; ArH), 8.37 (d, 8 Hz, 2H; ArH), 7.74 (d, 8 Hz, 2H; ArH), 2.83 (quint, 7 Hz, 2H, CHCOO), 2.50 (br s, 4H; α-CH$_2$), 1.95 (m, 4H; CH$_2$), 1.86 (m, 2H, CH), 1.78 (m, 4H; CH$_2$), 1.56 (m, 8H; CH$_2$), 1.38–1.26 (m, 80H; CH$_2$), 0.96 (t, 7 Hz, 6H; CH$_3$), 0.94 (t, 7 Hz, 6H; CH$_3$), 0.85 ppm (t, 7 Hz, 12H; CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): $\delta=184.6$, 173.5, 154.7, 135.2, 132.5, 131.4, 130.9, 129.0, 127.1, 126.3, 126.1, 125.7, 123.6, 122.4, 45.7, 37.2, 33.9 (×2), 32.0 (×3), 31.9 (×2), 31.8, 30.3, 30.1, 29.82, 29.78, 29.7, 29.6, 29.41, 29.38 (×2), 27.7, 27.65, 26.7 (×2), 22.73, 22.69 (×2), 22.66, 14.13, 14.12, 14.10 ppm (×2); IR (KBr disk): $\tilde{\nu}=2955$ (m), 2925 (s), 2854 (m), 1751 (m), 1631 (m), 1585 (m), 1563 (m), 1460 (w), 1349 (w), 1230 (w),1168 (w), 1110 (m), 1030 (w), 807 cm^{-1} (w); UV/Vis (chloroform): λ_{max} (ε) = 373 (13100), 567 (50000), 611 nm (58000 mol^{-1}m^{3}cm^{-1}); elemental analysis calcd (%) for $C_{90}H_{136}O_6$: C 82.38, H 10.43; found: C 82.01, H 10.05.

Compound 12c: 1,4,5,8-Naphthalenetetracarboxylic dianhydride **11** (13.4 g, 50 mmol) and zinc dichloride (30 g, 220 mmol) were added to freshly distilled diethyl 2-ethylhexylmalonate 7c (54.5 g, 200 mmol) with vigorous stirring. The mixture, which partially solidified into an unstirrable mass during the reaction, was kept at 200 °C for 5 h, at which point gas evolution nearly ceased. The resulting blackish brown mass was transferred to a 1 L flask with the help of a little acetone, and ethyl acetate (400 mL) and a solution of potassium hydroxide (60 g) in water (400 mL) were added. After vigorous stirring for 15 min, the precipitated zinc salts were filtered off by passing the biphasic mixture though a large glass filter. The aqueous phase was washed with ethyl acetate and discarded, the united organic phases were washed with dilute hydrochloric acid, and the solvent was evaporated. After evaporation of the solvent, the product was precipitated by adding heptane, and then it was purified by column chromatography (silica gel; chloroform) and precipitated with heptane from solution in acetone (2.2 g, 4.5 mmol, 9%). M.p. 210 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=10.95$ (s, 2H; OH), 8.41 (s, 4H; ArH), 2.66 (d, 7 Hz, 4H; α-CH$_2$), 1.72 (m, 2H; CH), 1.42–1.31 (m, 16H; CH$_2$), 0.94 (t, 7 Hz, 6H; CH$_3$), 0.92 ppm (t, 7 Hz, 6H; CH$_3$); IR (KBr disk): $\tilde{\nu}=3267$ (br), 2957 (s), 2926 (s), 2858 (m), 1610 (m), 1566 (s), 1451 (m), 1398 (w), 1374 (w), 1301 (w), 1170 (s), 979 (m), 781 cm^{-1} (w); UV/Vis (chloroform): λ_{max} (ε) = 354 (8600), 372 (11100), 389 (11300), 440 (8100), 464 nm (8200 mol^{-1}m^{3}cm^{-1}); elemental analysis calcd (%) for $C_{52}H_{76}O_6$: C 78.65, H 8.25; found: C 78.79, H 8.26.

Acknowledgements

We are grateful to Mbolotiana Rajaoarivelo for his experimental support and to the Association Nationale pour la Recherche Technique for funding (CIFRE grant to N.B.).

Keywords: cesium hydroxide · dyes/pigments · liquid crystals · perylenes · regioisomers

[1] a) A. Rademacher, S. Märkle, H. Langhals, *Chem. Ber.* **1982**, *115*, 2927–2934; b) H. Langhals, *Helv. Chim. Acta* **2005**, *88*, 1309–1343.
[2] a) M. Berberich, A.-M. Krause, M. Orlandi, F. Scandola, F. Würthner, *Angew. Chem.* **2008**, *120*, 6718–6721; *Angew. Chem. Int. Ed.* **2008**, *47*, 6616–6619; b) K. Peneva, G. Mihov, F. Nolde, S. Rocha, J.-I. Hotta, K. Braeckmans, J. Hofkens, H. Uji-I, A. Herrmann, K. Müllen, *Angew. Chem.* **2008**, *120*, 3420–3423; *Angew. Chem. Int. Ed.* **2008**, *47*, 3372–3375; c) D. Baumstark, H.-A. Wagenknecht, *Angew. Chem.* **2008**, *120*, 2652–2654; *Angew. Chem. Int. Ed.* **2008**, *47*, 2612–2614.
[3] K.-Y. Law, *Chem. Rev.* **1993**, *93*, 449–486.
[4] a) A. K. Pandey, S. Dabos-Seignon, J.-M. Nunzi, *Appl. Phys. Lett.* **2006**, *89*, 113506; b) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122.
[5] A. K. Pandey, J.-M. Nunzi, *Appl. Phys. Lett.* **2007**, *90*, 263508.
[6] a) C. W. Struijk, A. B. Sieval, J. E. J. Dakhorst, M. van Dijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. van de Craats, J. M. Warman, H. Zuilhof, E. J. R. Sudhölter, *J. Am. Chem. Soc.* **2000**, *122*, 11057–11066; b) J. van Herrikhuyzen, A. Syamakumari, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2004**, *126*, 10021–10027; c) Z. Chen, V. Stepanenko, V. Dehm, P. Prins, L. D. A. Siebbeles, J. Seibt, P. Marquetand, V. Engel, F. Würthner, *Chem. Eur. J.* **2007**, *13*, 436–449; d) A. Wicklein, A. Lang, M. Muth, M. Thelakkat, *J. Am. Chem. Soc.* **2009**, *131*, 14442–14453.
[7] a) T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, H. Bock, *Angew. Chem.* **2001**, *113*, 2119–2122; *Angew. Chem. Int. Ed.* **2001**, *40*, 2060–2063; b) S. Saïdi-Besbes, É. Grelet, H. Bock, *Angew. Chem.* **2006**, *118*, 1815–1818; *Angew. Chem. Int. Ed.* **2006**, *45*, 1783–1786.
[8] a) M. Adachi, Y. Nagao, *Chem. Mater.* **1999**, *11*, 2107–2114; b) H. Langhals, S. Sprenger, M.-T. Brandherm, *Liebigs Ann.* **1995**, 481–486; c) H. Quante, Y. Geerts, K. Müllen, *Chem. Mater.* **1997**, *9*, 495–500.
[9] a) H. Langhals, S. Kirner, *Eur. J. Org. Chem.* **2000**, 365; b) H. Langhals, P. Blanke, *Dyes Pigm.* **2003**, *59*, 109; c) Z. Chen, U. Baumeister, C. Tschierske, F. Würthner, *Chem. Eur. J.* **2007**, *13*, 450–465.
[10] a) F. Nolde, W. Pisula, S. Müller, C. Kohl, K. Müllen, *Chem. Mater.* **2006**, *18*, 3715–3725; b) N. G. Pschirer, C. Kohl, F. Nolde, J. Qu, K. Müllen, *Angew. Chem.* **2006**, *118*, 1429–1432; *Angew. Chem. Int. Ed.* **2006**, *45*, 1401–1404.
[11] a) H. Qian, Z. Wang, Y. Wan, D. Zhu, *J. Am. Chem. Soc.* **2007**, *129*, 10664–10665; b) H. Qian, F. Negri, C. Wang, Z. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 17970–17976.
[12] a) Badische Anilin- und Soda-Fabrik, German Patent 283365, **1915**; [*Chem. Abstr.* **1915**, 9:20290]; b) N. Buffet, H. Bock, PCT Int. Appl. WO2009141562, **2009**; [*Chem. Abstr.* **2009**, 151:550314].
[13] a) A. E. Porai-Koshits, I. I. Chizhevskaya, *Zh. Obshch. Khim.* **1956**, *26*, 1950–1958; b) J. Feng, B. Liang, D. Wang, L. Xue, X. Li, *Org. Lett.* **2008**, *10*, 4437–4440.
[14] G. Errera, *Gazz. Chim. Ital.* **1911**, *41*, *I*, 191–197.
[15] S. Demmig, H. Langhals, *Chem. Ber.* **1988**, *121*, 225–230.

Received: November 26, 2009
Published online: March 31, 2010

CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Soluble and Columnar Liquid Crystalline Peropyrenequinones by Coupling of Phenalenones in Caesium Hydroxide

Noémie Buffet,[a, b] Éric Grelet,[a] and Harald Bock*[a]

chem_201000542_sm_miscellaneous_information.pdf

SUPPORTING INFORMATION

Experimental Section: 3b, 3c, 3d, 4c, 9cc & 10cc, 9cd & 10cd, 9dc &10dc

2-isobutyl-3-hydroxy-phenalen-1-one (**3b**)
To diethyl isobutylmalonate **7b** (65g, 300mmol) are added 1,8-naphthalic anhydride **8** (19.8g, 100mmol) and zinc dichloride (30g, 220mmol) with vigorous stirring. The mixture, which partially solidifies to an unstirrable mass during the reaction, is kept at 200°C for 5h, at which point gas evolution has nearly ceased. The resulting blackish brown viscous mass is transferred to a 1L flask with the help of a little acetone, and ethyl acetate (400ml) and a solution of potassium hydroxide (60g) in water (400ml) are added. After vigorous stirring for 15 minutes, the precipitated zinc salts are filtered off by passing the biphasic mixture though a large glass filter. Heptane (400ml) is added, the phases are separated, the organic phase is washed three times with aqueous potassium hydroxide solution, the organic phase is discarded, and the combined aqueous phases are acidified with concentrated hydrochloric acid. Ethyl acetate is added to dissolve the precipitating product, the phases are separated and the organic phase is dried over sodium sulfate and evaporated. The residue is purified by column chromatography (chloroform/silica) and recrystallisation from chloroform:heptane 1:1. Yield: 9.8g (39mmol, 39%) of orange-yellow crystals.
mp. 176°C;
^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C, TMS): *d*= 10.30 (broad s, 1H; OH), 8.38 (d, 8Hz, 2H; ArH), 8.30 (d, 8Hz, 2H; ArH), 7.80 (t, 8Hz, 2H; ArH), 2.60 (d, 7Hz, 2H, CH_2), 1.93 (nont, 7Hz, 1H; CH), 0.94 ppm (d, 7Hz, 6H; CH_3)
UV/Vis (chloroform): $?_{max}$ (*e*)= 331 (9000), 354 (9000), 394 nm (5000 mol^{-1}dm^{3}cm^{-1})
elemental analysis calcd (%) for $C_{17}H_{16}O_2$: C 80.93, H 6.39; found: C 80.88, H 6.30

2-(2-ethylhexyl)-3-hydroxy-phenalen-1-one (**3c**)
Sodium ethylate (13.6g, 200mmol) is dissolved in anhydrous ethanol (100ml) at reflux. Diethyl malonate **7a** (32g, 200mmol) is added at reflux, followed after 30min by 2-ethyl-1-bromohexane (38.6g, 200mmol). After a few minutes, sodium bromide starts to precipitate. After 12h at reflux, the reaction mixture is added to 5% hydrochloric acid (500ml), and the resulting mixture is extracted with ethyl acetate (500ml). The organic phase is dried over sodium sulfate, and the solvent is evaporated. Remaining diethyl malonate is distilled off with a water-jet pump at 170°C, and the residue, raw diethyl (2-ethyl-hexyl)malonate **7c**, is used without further purification. In a 250ml flask, to this malonate are added 1,8-naphthalic anhydride **8** (19.8g, 100mmol) and zinc dichloride (30g, 220mmol) with vigorous stirring. The mixture is stirred at 200°C for 5h, at which point gas evolution has nearly ceased. The resulting brown viscous fluid is transferred to a 1L flask, and ethyl acetate (400ml) and a solution of potassium hydroxide (60g) in water (400ml) are added. After vigorous stirring for 15 minutes, the precipitated zinc salts are filtered off by passing the biphasic mixture though a large glass filter. The aqueous phase is washed with ethyl acetate and discarded, the united organic phases are washed with dilute hydrochloric acid, and the solvent is evaporated. The residue is dissolved in chloroform and filtered through a short and wide silica gel column to separate dark polar impurities. After evaporation of the solvent, the product is recrystallised from heptane. Yield: 9.6g (31mmol, 31%) of yellow sticky solid.
mp. 117°C;
^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C, TMS): *d*= 10.25 (broad s, 1H; OH), 8.38 (d, 8Hz, 2H; ArH), 8.29 (d, 8Hz, 2H; ArH), 7.80 (t, 8Hz, 2H; ArH), 2.63 (d, 7Hz, 2H, α-CH_2), 1.68 (m, 1H; CH), 1.30 (m, 7Hz, 8H; CH_2), 0.88 (t, 7Hz, 3H; CH_3), 0.86 ppm (t, 7Hz, 3H; CH_3)
elemental analysis calcd (%) for $C_{21}H_{24}O_2$: C 81.78, H 7.84; found: C 81.49, H 7.66

2-(2-hexyldecyl)-3-hydroxy-phenalen-1-one (**3d**)
Sodium ethylate (13.6g, 200mmol) is dissolved in anhydrous ethanol (100ml) at reflux. Diethyl malonate **7a** (32g, 200mmol) is added at reflux, followed after 30min by 2-hexyl-1-bromodecane (61g, 200mmol). After a few minutes, sodium bromide starts to precipitate. After 12h at reflux, the reaction mixture is added to 5% hydrochloric acid (500ml), and the resulting mixture is extracted with ethyl acetate (500ml). The organic phase is dried over sodium sulfate, and the solvent is evaporated. Remaining diethyl malonate is distilled off with a water-jet pump at 170°C, and the residue, raw diethyl (2-hexyl-decyl)malonate **7d**, is used without further purification. In a 250ml flask, to this malonate are added 1,8-naphthalic anhydride **8** (19.8g, 100mmol) and zinc dichloride (30g, 220mmol) with vigorous stirring. The mixture is stirred at 200°C for 5h, at which point gas evolution has nearly ceased. The resulting brown viscous fluid is transferred to a 1L flask, and ethyl acetate (400ml) and a solution of potassium hydroxide (60g) in water (400ml) are added. After vigorous stirring for 15 minutes, the precipitated zinc salts are filtered off by passing the biphasic mixture though a large glass filter. The aqueous phase is washed with ethyl acetate and discarded, the united organic phases are washed with dilute hydrochloric acid, and the solvent is evaporated. The residue is dissolved in chloroform and filtered through a short and wide silica gel column to separate dark polar impurities. After evaporation of the solvent, the product is recrystallised from pentane (3L, 3d in the freezer; smaller quantities of pentane give less precipitate). Yield: 9.8g (23mmol, 23%) of yellow sticky solid.
mp. 86°C;
^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C, TMS): *d*= 10.23 (broad s, 1H; OH), 8.34 (d, 8Hz, 2H; ArH), 8.25 (d, 8Hz, 2H; ArH), 7.76 (t, 8Hz, 2H; ArH), 2.59 (d, 7Hz, 2H, α-CH_2), 1.71 (m, 1H; CH), 1.40-1.05 (m, 7Hz, 24H; CH_2), 0.79 (t, 7Hz, 3H; CH_3), 0.77 ppm (t, 7Hz, 3H; CH_3)
elemental analysis calcd (%) for $C_{29}H_{40}O_2$: C 82.81, H 9.59; found: C 82.84, H 9.90

2,9-di(2-ethylhexyl)-3,10-dihydroxy-peropyrene-1,8-quinone (**4c**)
A mixture of monohydrated caesium hydroxide (10.40g, 61.93mmol) and **3c** (1.015g, 3.29mmol) is heated at 280°C for 3 hours in a metallic crucible open to air. After cooling down the crude product is dissolved in water (300mL) and the resulting purple solution is acidified with 20% sulphuric acid (100mL) to yield a black solid, which is washed with water and recrystallised from methanol (627mg, 60%).
^{1}H NMR (400 MHz, [D$_5$]pyridine, 25°C, TMS): *d*= 8.79 (d, 8Hz, 4H; ArH), 8.64 (d, 8Hz, 4H; ArH), 3.20 (d, 7Hz, 4H; α-CH_2), 2.23 (m, 2H; CH), 1.65-1.40 (m, 10H; CH_2), 1.40-1.20 (m, 6H; CH_2), 1.01 (t, 7Hz, 6H; CH_3), 0.83 ppm (t, 7Hz, 6H; CH_3)
elemental analysis calcd (%) for $C_{42}H_{44}O_4$: C 82.32, H 7.24; found: C 82.11, H 7.31

2,9-di(2-ethylhexyl)-3,10-di(2-ethylhexanoyloxy)-peropyrene-1,8-quinone (**9cc**) & **2,9-di(2-ethylhexyl)-3,8-di(2-ethylhexanoyloxy)-peropyrene-1,10-quinone** (**10cc**)
2-ethylhexanoyl chloride (4mL, 23mmol) is cautiously added to a solution of **4c** (677.5mg, 1.11mmol) and pyridine (5mL) in chloroform (20mL). After stirring at room temperature for 30 minutes under exclusion of humidity, the mixture is diluted with chloroform (250mL), and acidified with 5% hydrochloric acid (300mL). The organic layer is separated and dried over anhydrous sodium sulphate, and the solvent is evaporated. The resulting purple liquid is purified by silica gel column chromatography (1.chloroform, 2. chloroform:ethanol 165:1) to yield two dark violet waxes, which are both recrystallised from MeOH.
9cc: 326mg (0.38mmol, 34%)
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *d*= 8.61 (d, 8Hz, 2H; ArH), 8.48 (d, 8Hz, 2H; ArH), 8.37 (d, 8Hz, 2H; ArH), 7.73 (d, 8Hz, 2H; ArH), 2.81 (quint, 7Hz, 2H, CHCOO), 2.55 (broad s, 4H; α-CH_2), 2.00 (m, 4H; CH_2), 1.88 (m, 2H, CH), 1.82 (m, 4H; CH_2), 1.52 (m, 8H; CH_2), 1.45-1.25 (m, 16H; CH_2), 1.18 (t, 7Hz, 6H; CH_3), 1.03 (t, 7Hz, 6H; CH_3), 0.94 (t, 7Hz, 6H; CH_3), 0.90 ppm (t, 7Hz, 6H; CH_3)
elemental analysis calcd (%) for $C_{58}H_{72}O_6$: C 80.52, H 8.39; found: C 80.61, H 8.51
10cc: 273mg (0.32mmol, 29%)
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *d*= 8.66 (d, 8Hz, 2H; ArH), 8.60 (d, 8Hz, 2H; ArH), 8.36 (d, 8Hz, 2H; ArH), 7.72 (d, 8Hz, 2H; ArH), 2.79 (quint, 7Hz, 2H, CHCOO), 2.55 (broad s, 4H; α-CH_2), 1.99 (m, 4H; CH_2), 1.87 (m, 2H, CH), 1.81 (m, 4H; CH_2), 1.51 (m, 8H; CH_2), 1.45-1.25 (m, 16H; CH_2), 1.17 (t, 7Hz, 6H; CH_3), 1.02 (t, 7Hz, 6H; CH_3), 0.93 (t, 7Hz, 6H; CH_3), 0.89 ppm (t, 7Hz, 6H; CH_3)
elemental analysis calcd (%) for $C_{58}H_{72}O_6$: C 80.52, H 8.39; found: C 80.28, H 8.24

2,9-di(2-ethylhexyl)-3,10-di(2-hexyldecanoyloxy)-peropyrene-1,8-quinone (**9cd**) & **2,9-di(2-ethylhexyl)-3,8-di(2-hexyldecanoyloxy)-peropyrene-1,10-quinone** (**10cd**)
The preceding procedure was followed using 207.4mg (0.34mmol) of **4c**, with 2-hexyldecanoyl chloride (3.0g, 11mmol) instead of 2-ethylhexanoyl chloride.
9cd: 39mg (0.04mmol, 10%)
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *d*= 8.66 (d, 8Hz, 2H; ArH), 8.54 (d, 8Hz, 2H; ArH), 8.43 (d, 8Hz, 2H; ArH), 7.76 (d, 8Hz, 2H; ArH), 2.85 (quint, 7Hz, 2H, CHCOO), 2.50 (broad s, 4H; α-CH_2), 1.96 (m, 4H; CH_2), 1.81 (m, 6H; CH & CH_2), 1.55 (m, 8H; CH_2), 1.50-1.20 (m, 48H; CH_2), 0.94 ppm (t, 7Hz, 24H; CH_3)
elemental analysis calcd (%) for $C_{74}H_{104}O_6$: C 81.57, H 9.62; found: C 81.65, H 9.75
10cd: 62mg (0.06 mmol, 17%)
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *d*= 8.68 (d, 8Hz, 2H; ArH), 8.62 (d, 8Hz, 2H; ArH), 8.34 (d, 8Hz, 2H; ArH), 7.72 (d, 8Hz, 2H; ArH), 2.84 (quint, 7Hz, 2H, CHCOO), 2.50 (broad s, 4H; α-CH_2), 1.96 (m, 4H; CH_2), 1.79 (m, 6H; CH & CH_2), 1.55 (m, 8H; CH_2), 1.50-1.20 (m, 48H; CH_2), 0.93 ppm (t, 7Hz, 24H; CH_3)
elemental analysis calcd (%) for $C_{74}H_{104}O_6$: C 81.57, H 9.62; found: C 81.37, H 9.70

2,9-di(2-hexyldecyl)-3,10-di(2-ethylhexanoyloxy)-peropyrene-1,8-quinone (**9dc**) & **2,9-di(2-hexyldecyl)-3,8-di(2-ethylhexanoyloxy)-peropyrene-1,10-quinone** (**10dc**)
The preceding procedure was followed using **4d** (336.4mg, 0.40mmol) and 2-ethylhexanoyl chloride (4mL, 23mmol).
9dc: 24mg (0.02mmol, 5%)
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *d*= 8.63 (d, 8Hz, 2H; ArH), 8.52 (d, 8Hz, 2H; ArH), 8.42 (d, 8Hz, 2H; ArH), 7.75 (d, 8Hz, 2H; ArH), 2.80 (quint, 7Hz, 2H, CHCOO), 2.50 (broad s, 4H; α-CH_2), 2.00 (m, 4H; CH_2), 1.87 (m, 4H, CH), 1.78 (m, 2H; CH_2), 1.51 (m, 8H; CH_2), 1.45-1.15 (m, 48H; CH_2), 1.18 (t, 7Hz, 6H; CH_3), 1.03 (t, 7Hz, 6H; CH_3), 0.85 ppm (t, 7Hz, 12H; CH_3)
elemental analysis calcd (%) for $C_{74}H_{104}O_6$: C 81.57, H 9.62; found: C 81.63, H 9.47
10dc: 73mg (0.07mmol, 17%)
^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): *d*= 8.71 (d, 8Hz, 2H; ArH), 8.68 (d, 8Hz, 2H; ArH), 8.44 (d, 8Hz, 2H; ArH), 7.76 (d, 8Hz, 2H; ArH), 2.79 (quint, 7Hz, 2H, CHCOO), 2.55 (broad s, 4H; α-CH_2), 1.99 (m, 4H; CH_2), 1.86 (m, 4H, CH), 1.75 (m, 2H; CH_2), 1.51 (m, 8H; CH_2), 1.45-1.15 (m, 48H; CH_2), 1.17 (t, 7Hz, 6H; CH_3), 1.02 (t, 7Hz, 6H; CH_3), 0.85 ppm (t, 7Hz, 12H; CH_3)
elemental analysis calcd (%) for $C_{74}H_{104}O_6$: C 81.57, H 9.62; found: C 81.76, H 9.70

Colour version of figure 3

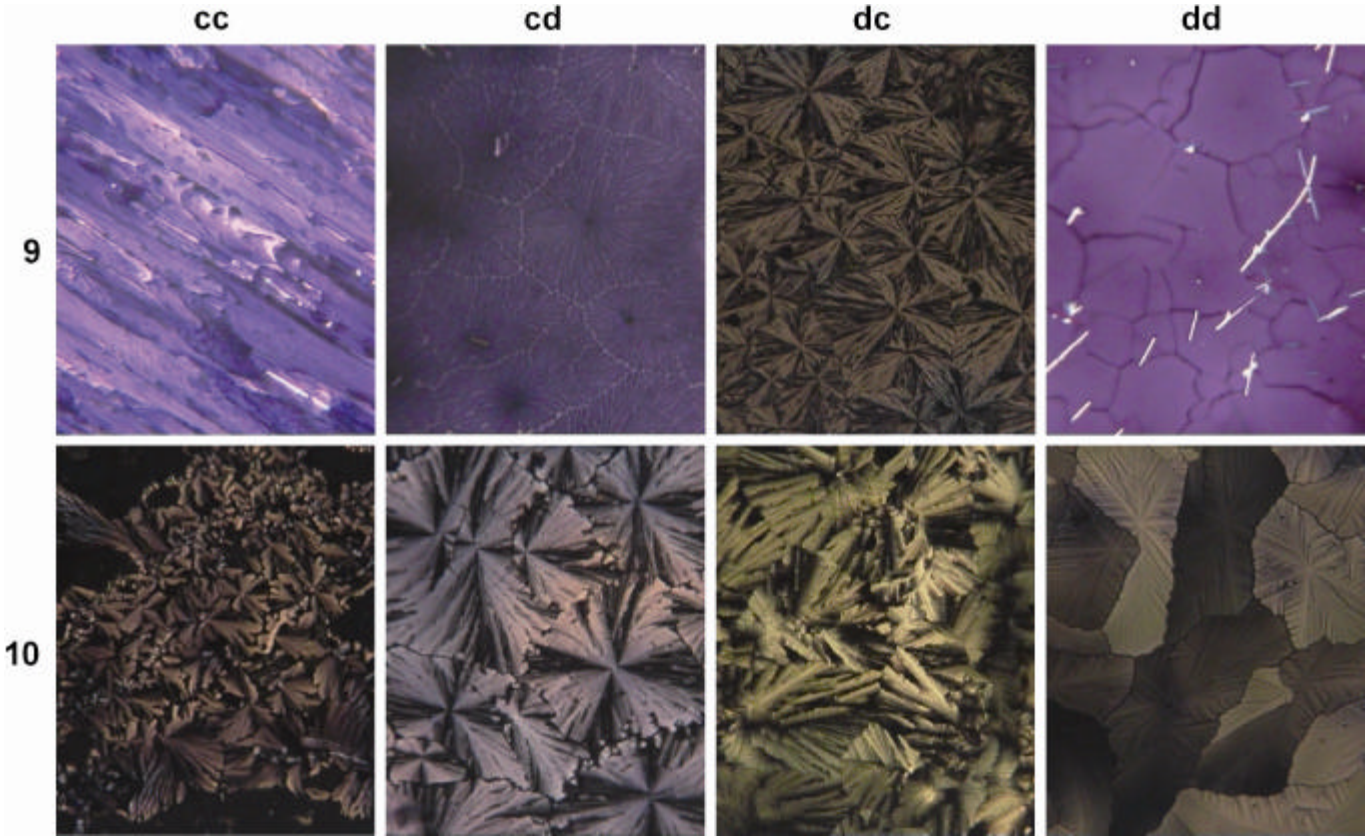


Figure 3. Textures observed by polarising optical microscopy in transmission at room temperature after cooling down from the isotropic liquid (except **9cc**). 300μm × 240μm each. **9dc** and **10cc-dd**: crossed polarisers; **9cd** and **9dd**: slightly uncrossed polarisers to render visible the domain boundaries in the nonbirefringent homeotropic texture (**9dd** additionally shows a few needle-like birefringent planar domains); **9cc**: unheated sample sheared between glass plates at room temperature, uncrossed polarisers.