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Soluble and Liquid-Crystalline Ovalenes[**]

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Dedicated to Dr. Nguyen Huu Tinh
on the occasion of his 65th birthday

Large polycyclic organic π systems of high symmetry, such as acenes,[1] rylenes,[2] and fullerenes,[3] are not only exciting objects of synthesis and of great fundamental interest, but are also gaining more and more importance as electronically and optically active components in devices such as field-ffect transistors[4] and solar cells.[5]

In 1948, Clar reported the synthesis of the orange compound **1**, which he called ovalene, which he obtained by treating either 1,14-benzobisanthene (**2**) or bisanthene (**3**) with maleic anhydride under oxidative conditions to obtain the corresponding carboxylic anhydrides **4** and **5**, respectively, followed by decarboxylation (Scheme 1).[6] Geometrically, ovalene may be regarded as a two-dimensional analogue of fullerene C_{70}, since their cross-sections are approximately equivalent, just as coronene corresponds in shape to a cross-section of C_{60}.

There have been no reports of soluble ovalene-di- or -tetracarboxylic acid derivatives derived from **4** or **5** in the literature since Clar's first synthesis of the insoluble parent hydrocarbon and the carboxylic anhydrides. Clar reported that **5** was dark brown, while **4** was dark red. Their large aromatic systems, which promise good orbital overlap between neighboring molecules in the solid state, makes ovalene derivatives interesting candidates for organic opto-electronics, provided that they can be processed, namely are

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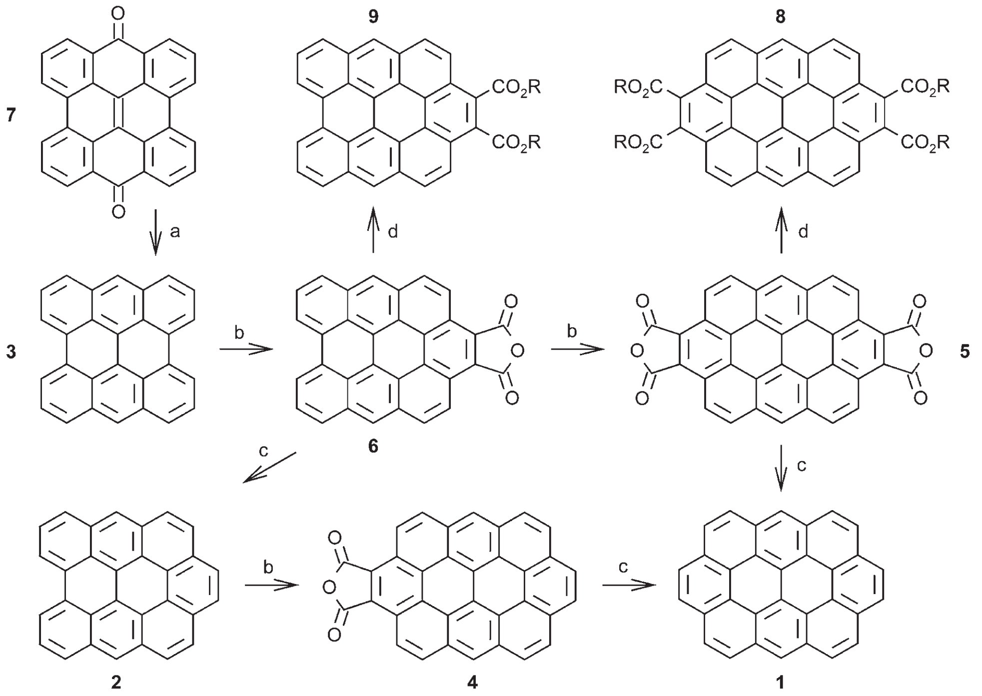


Scheme 1. Synthesis of **1** and **2** and of their carboxylic ester derivatives **8** and **9**: a) 1. Zn, pyridine, acetic acid; 2. chloranil; b) maleic anhydride, nitrobenzene; c) soda lime, 400 °C; d) RBr, ROH, DBU.

soluble and film-forming. The elliptical shape of the aromatic core means that the introduction of solubilizing substituents may lead to columnar liquid-crystalline (LC) self-assembled systems with an associated efficient transport of excitons and charge along the columns.[7,8]

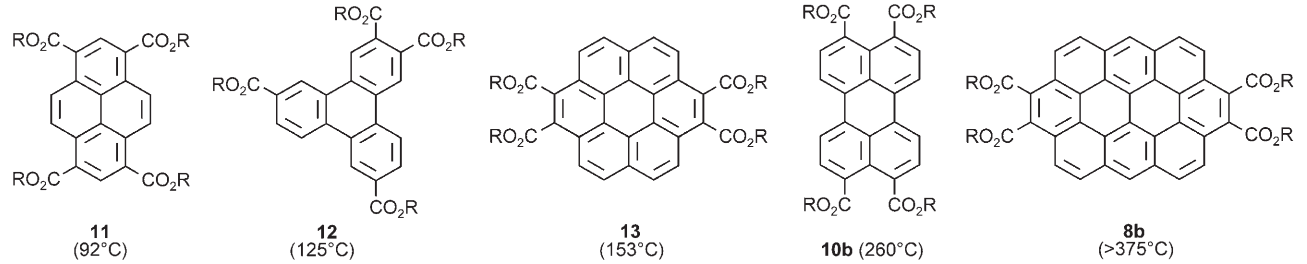
We therefore set out to prepare a soluble and columnar liquid-crystalline form of **5**, which is completely insoluble in organic solvents and hard to purify. The synthetic approach starting from **3** should also lead to soluble derivatives of the violet benzobisanthene dicarboxylic anhydride (**6**), which is obtained, instead of **5**, from the reaction of **3** and maleic anhydride in refluxing nitrobenzene if the reaction time is reduced to minutes instead of hours.[9]

We synthesized **5** starting from naphthadianthrone (**7**, which is obtained by photocyclization of commercial bianthrone).[10] To avoid isolation of the very unstable **3**, we followed the procedure developed by Brockmann and Randebrock. Treatment of **7** with zinc dust and acetic acid in pyridine gave a mixture of dihydro- and higher hydrogenated bisanthenes,[11,12] which we used directly in the benzogenic oxidative Diels–Alder reaction to give **6** and **5**, without attempting to prepare **3** by oxidation with chloranil.[11] Blue, fully aromatized bisanthene (**3**) is regenerated in situ during heating in nitrobenzene and adds maleic anhydride upon reaching reflux temperature.

To obtain esters **8** and **9**, we then faced the synthetic challenge of esterifying efficiently the quite unreactive insoluble anhydrides with long and branched alcohols, in particular 2-ethylhexanol, which we had used on other aromatic cores to induce high solubility as well as columnar liquid-crystalline self-assembly at room temperature.[13,14]

We had found previously that large aromatic dianhydrides such as perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), reported by other research groups as being difficult to esterify,[15] react with a mixture of propanol and bromopropane in the presence of potassium carbonate to give the tetrapropylester **10a** (R = *n*-propyl) in good yield.[13] However, this method is less efficient with longer, less-polar alcohols and bromoalkanes such as 2-ethylhexanol and 1-bromo-2-ethylhexane and gave only low yields after exceedingly long reaction times (on the order of a week). By modifying a procedure reported for the esterification of phthalocyanine-2,3,6,7,10,11,14,15-octacarboxylic acid[16] we succeeded in obtaining high yields of the 2-ethylhexyl esters **10b** and **8b** (Scheme 2, R = 2-ethylhexyl) overnight by esterification with 2-ethylhexanol and 1-bromo-2-ethylhexane in acetonitrile in the presence of the strong soluble base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

As expected, X-ray diffraction studies on **8b** showed the presence of a hexagonal columnar liquid-crystalline phase at room temperature, with a column-to-column distance of 22 Å and a disk-to-disk spacing of 3.5 Å (Figure 1). The mesophase is stable over a very large range of temperatures, and no



Scheme 2. Room-temperature liquid-crystalline arene tetracarboxylic tetra-2-ethylhexyl esters (R = 2-ethylhexyl). The transition temperatures from the columnar mesophase to the isotropic liquid are given in parentheses. **11** and **13** show subambient melting points of −28 °C and +12 °C, respectively. No transition to a crystalline phase was detected in **12**, **10b**, and **8b** by differential scanning calorimetry down to −60 °C.

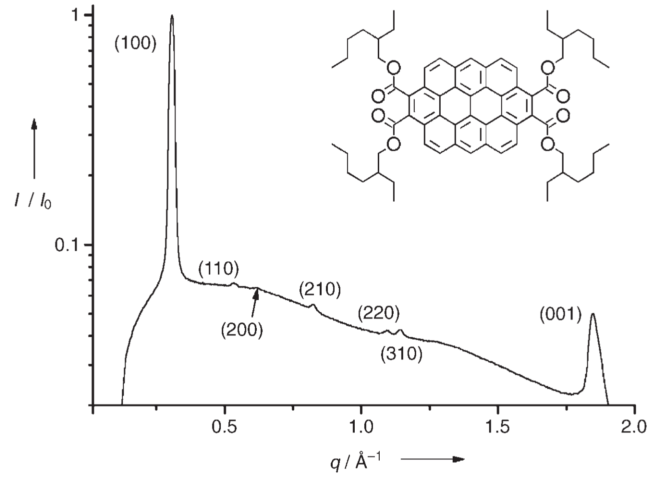


Figure 1. Room-temperature powder X-ray diffractogram of **8b**.

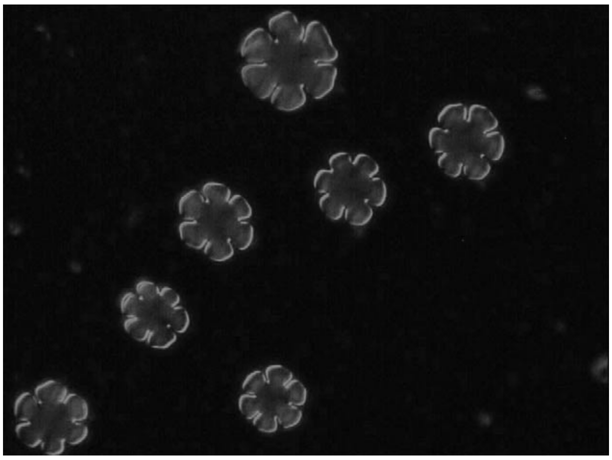


Figure 2. Growth of homeotropically aligned hexagonal columnar domains of **8c** upon cooling through the liquid-to-mesophase transition. The image was taken by differential interference contrast (DIC) microscopy in the reflection mode (350 μm × 450 μm) of a thin film between a silicon wafer and a glass slide.

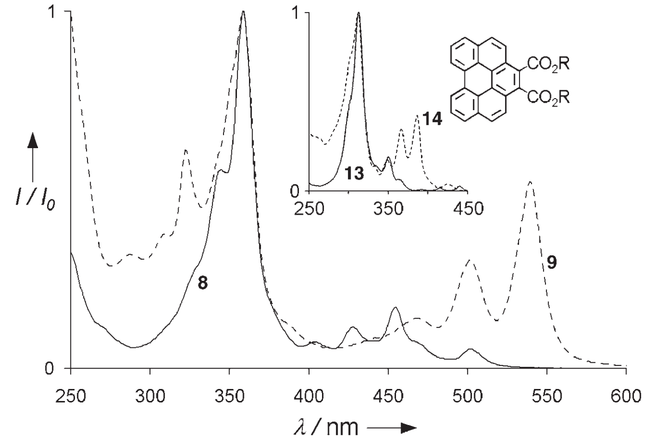


Figure 3. Normalized absorption spectra in chloroform of **8** and **9** and, for comparison, of their shortened homologues **13** and **14**.

transition to an isotropic liquid phase could be observed up to our experimental limit of 375 °C.

This very wide temperature range of the columnar phase is in agreement with the evolution of liquid crystallinity as the core size increases in arene tetracarboxylates: the clarification temperature of the room-temperature liquid-crystalline pyrene, triphenylene, and coronene tetra(2-ethylhexyl) esters **11**, **12**, and **13** increases with core size from the pyrene (92 °C)[13] to the triphenylene (125 °C)[17] to the coronene ester (153 °C).[17] The perylene derivative **10b**[13] is an exception to the rule, as it has a higher clearing temperature (260 °C) than the coronene ester although it has four carbon atoms less, because stacking of rotated perylene moieties allows excellent space filling without interference from the out-of-plane carboxylate groups.[18]

In order that the LC-to-liquid transition occurred at an accessible temperature, we replaced half of the 2-ethylhexyl groups by using 2-decyltetracan-1-ol as well as 2-ethylhexyl bromide in the esterification. The resulting mixed ester (**8c** with one R group on each side being 2-ethylhexyl and the other 2-decyltetradecyl) shows a mesophase-to-liquid transition at 220 °C, and cooling through this temperature yields the typical six-petaled flowerlike domains of a hexagonal columnar phase growing in homeotropic alignment (that is, columns perpendicular to substrates; Figure 2).

To obtain a soluble ovalene derivative with only small non-absorbing alkyl substituents, we treated **5** with propanol and 1-bromopropane to yield the tetrapropyl ester **8a** (R = *n*-propyl). Ester **8a** melts above 375 °C and is highly soluble in common organic solvents (> 5 % in chloroform). Ovalene tetraesters **8** are dark brown in the solid state, and their orange solutions in chloroform show a main absorption maximum at 359 nm, which is shifted by 15 nm with respect to unsubstituted ovalene (**1**: maximum at 344 nm; Figure 3).

In the same manner as ovalene tetraesters **8** are formed from **5**, soluble benzobisanthene diesters **9** are obtained efficiently from **6** by reaction with 1-bromoalkane, 1-alkanol, and DBU. They are dark violet solids that give pinkish red solutions in chloroform with a main absorption maximum at the same wavelength as ovalene (359 nm) and strong long-wavelength absorptions at 539 and 501 nm. The identical wavelength of the main absorption peaks of **8** and **9** illustrate that the two chromophores are electronically related. No corresponding peak is found for solutions of bisanthene (**3**),[19] whereas coronene tetraester **13** and the corresponding benzo[ghi]perylene diester **14** show the same relationship (main absorption peak at 313 nm, shifted by 8 nm with respect to unsubstituted coronene; inset in Figure 3).

In summary, soluble ovalene and benzobisanthene dyes are readily accessible by an optimized approach from naphthadianthrone (**7**) and an efficient esterification procedure. Furthermore, the appropriate choice of the alkyl substituents leads to ovalene esters that undergo columnar self-assembly at room temperature over extremely large temperature ranges. Very few other mesogens, in particular, hexasubstituted hexabenzocoronenes[8,20] and octasubstituted phthalocyanines,[16,21] are known to self-assemble into columns over temperature ranges of over 350 °C.

Besides improving considerably their synthetic accessibility, we have thus dramatically increased the physical versatility of the ovalene and bisanthene chromophores by rendering them soluble and strongly self-organizing.

Experimental Section

8b: Four portions of zinc powder (4 × 6 g) and 80% acetic acid (4 × 10 mL) were added in 30-minute intervals to a refluxing suspension of **7** (2 g) in pyridine (200 mL). The yellow suspension became green, then brown. After 5 h, the solution was cooled to room temperature, the zinc powder filtered off, and water (1 L) added. The precipitate thus formed was filtered off and dried under vacuum to yield 1.6 g of a yellow insoluble solid (crude, partially hydrogenated **3**). This solid was heated at reflux for 12 h with maleic anhydride (5 g) in nitrobenzene (60 mL). A color change from greenish yellow via blue and violet to brown was observed during warming and the first 30 minutes at reflux. Chloroform was added to the cooled solution, and the insoluble solid filtered off, washed with chloroform, and dried under vacuum to yield crude dianhydride **5** (2.9 g). The dianhydride was suspended in acetonitrile (150 mL), then 2-ethylhexyl bromide (0.1 mol, 19.3 g), 2-ethylhexanol (0.1 mol, 13.0 g), and DBU (80 mmol, 12.2 g) added, and the mixture refluxed for 16 h. The solvent was evaporated, and methanol added to precipitate the product, which was purified by column chromatography (silica gel, dichloromethane) and reprecipitation from butanol. Yield: 2.79 g of a brown (dark orange-red) waxy solid (52% with respect to naphthodianthrone). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.59$ (d, $J = 9$ Hz, 4H, ArH), 8.01 (d, $J = 9$ Hz, 4H, ArH), 7.98 (s, 2H, ArH), 4.90–4.77 (m, 8H, CH_2O), 2.22–2.13 (m, 4H, CH), 1.91–1.48 (m, 32H, CH_2), 1.25 (t, $J = 7$ Hz, 12H, CH_3), 1.07 ppm (t, $J = 7$ Hz, 12H, CH_3); ^{13}C NMR (400 MHz, APT, $CDCl_3$): $\delta = 169.2$ (CO_2), 127.8 ($C_{Ar}H$), 126.8 (C_{Ar}), 126.1 (C_{Ar}), 123.8 ($C_{Ar}H$), 123.5 (C_{Ar}), 123.0 ($C_{Ar}H$), 118.8 (C_{Ar}), 116.3 (C_{Ar}), 115.6 (C_{Ar}), 69.2 (CH_2O), 39.3 (CH), 30.8 (CH_2), 29.3 (CH_2), 24.2 (CH_2), 23.4 (CH_2), 14.4 (CH_3), 11.3 ppm (CH_3). Elemental analysis calcd for $C_{68}H_{78}O_8$: C 79.81, H 7.68%; found: C 79.99, H 7.82%

9a (R = *n*-propyl): In the same way as described above, crude monoanhydride **6** (2.5 g) was obtained if the reflux with maleic anhydride in nitrobenzene was stopped after 15 min. The anhydride was esterified with propyl bromide, propanol, and DBU as above and purified by column chromatography (silica gel, dichloromethane) and recrystallization from butanol. Yield: 1.29 g of dark red/violet crystals (45% with respect to naphthodianthrone). M.p. 315 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8$ Hz, 2H, ArH), 7.82 (d, $J = 9$ Hz, 2H, ArH), 7.51 (d, $J = 8$ Hz, 2H, ArH), 7.45 (s, 2H, ArH), 7.40 (t, $J = 8$ Hz, 2H, ArH), 7.36 (d, $J = 9$ Hz, 2H, ArH), 4.59 (t, $J = 7$ Hz, 4H, CH_2O), 2.01 (sext, $J = 7$ Hz, 4H, CH_2), 1.19 ppm (t, $J = 7$ Hz, 6H, CH_3); ^{13}C NMR (400 MHz, APT, $CDCl_3$): $\delta = 168.8$ (CO_2), 128.8 (C_{Ar}), 128.0 ($C_{Ar}H$), 127.8 (C_{Ar}), 127.3 (C_{Ar}), 125.4 ($C_{Ar}H$), 124.9 (C_{Ar}), 124.8 (C_{Ar}), 124.4 ($C_{Ar}H$), 123.5 ($C_{Ar}H$), 122.8 ($C_{Ar}H$), 121.0 (C_{Ar}), 120.7 (C_{Ar}), 119.8 (C_{Ar}), 118.3 ($C_{Ar}H$), 118.0 (C_{Ar}), 67.6 (OCH_2), 22.3 (CH_2), 10.9 ppm (CH_3). Elemental analysis calcd for $C_{38}H_{26}O_4$: C 83.50, H 4.79%; found: C 83.88, H 5.06%.

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