Efficient Synthesis of Functionalized [7]Helicenes

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[7]Helicenebisquinones can be made easily and in quantity by reacting the silyl enol ethers of a 9,10-dialkoxy-, or better a 9,10-disiloxy-, 3,6-diacetylphenanthrene, with *p*-benzoquinone. If an ethyl enol ether is used in place of the silyl enol ether, the transformation proceeds in much lower yield. The [7]helicenes are efficiently resolved into their enantiomers, and absolute configurations are assigned.

In 1967, the synthesis of [7]helicene[1]—the first helicene made using the photocyclization of a stilbene[2] as the key step—was reported by Martin and co-workers. Prior to this report, the only carbohelicenes synthesized were [5]-[3] and [6]helicenes.[4] Because the stilbene precursors are easy to prepare and the photocyclizations are easy to carry out, within 8 years of Martin's initial report, this procedure had been used to prepare all of the parent helicenes between [6]- and [14]helicene.[5] It soon became possible to convert helicenes into materials with even more unusual structures and even more interesting optical properties.[6] However, stilbene photocyclizations have serious limitations. They must be carried out using solutions that are very dilute.[2a,7] For example, while irradiating a 1.67 mM solution of 4,4′-dimethylstilbene for 8 h produces 3,6-dimethylphenanthrene in 97% yield, increasing the concentration to 4.7 mM lowers the yield to 23%.[7,8] (A 59% yield of unreacted starting material is recovered.) Another limitation is that amino, nitro, and other functional groups that relax the singlet excited states of stilbenes inhibit photocyclizations.[2a] Thus, there is a need for procedures that are operationally as simple as photocyclizations, but that unlike photocyclizations produce helicenes in large quantity and with useful functional groups.

Although there are a number of syntheses of helicenes that do not use light, the majority produce either [5]-helicenes, which racemize at an appreciable rate at room temperature,[9] or heterohelicenes that are also likely to have low barriers to racemization.[10] The others[4,11] have given helicenes that are either unfunctionalized or functionalized only by methyls[11g,h,i] or a carboxylic acid.[11a] Recently, we showed that combining the enol ethers of 1,4-diacetylbenzene and 2,7-diacetylnaphthalene with *p*-benzoquinone produces derivatives of [5]- and [6]-helicene in large quantity.[12] Furthermore, the helicenes synthesized by this method contain a useful functionality—alkoxyl side-chains, which render the compounds soluble in a variety of organic solvents,[12] and quinones, which have rich chemistry[13]—and both these helicenes[6fg,14] and materials made from them[15] display interesting properties. For these reasons and because there is no nonphotochemical method for preparing [7]carbohelicenes, it would be significant if functionalized [7]helicenes could be made in quantity by an analogous method.

We report below that enol ethers of appropriate and easily accessible 3,6-diacetylphenanthrenes do indeed combine with *p*-benzoquinone to produce [7]helicenebisquinones. We show how such preparations can be carried out on a very large scale, and we show how the [7]-helicene derivatives can be obtained in nonracemic form.

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(5) See ref 2b, p 71.

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(8) The photodimerizations of stilbenes and the intermolecular reactions of stilbenes with phenanthrenes also complicate photocyclizations that are not performed at high dilution. See ref 2a.

(9) See refs 3f,g and: Goedicke, C.; Stegmeyer, H. *Tetrahedron Lett.* **1970**, 937.

(10) See footnotes 1 and 6 in ref 12.

(11) (a) Bogaert-Verhoogen, D.; Martin, R. H. *Tetrahedron Lett.* **1967**, 3045. (b) Teuber, H.-J.; Vogel, L. *Chem. Ber.* **1970**, *103*, 3319. (c) Rau, H.; Schuster, O. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 114. (d) Pereira, D. E.; Neelima; Leonard, N. J. *Tetrahedron* **1990**, *46*, 5895. (e) Staab, H. A.; Diehm, M.; Krieger, C. *Tetrahedron Lett.* **1994**, *35*, 8357. (f) Dore, A.; Fabbri, D.; Gladiali, S.; Valle, G. *Tetrahedron: Asymmetry* **1995**, *6*, 779. (g) Pischel, I.; Grimme, S.; Kotila, S.; Nieger, M.; Vögtle, F. *Tetrahedron: Asymmetry* **1996**, *7*, 109. (h) Larsen, J.; Bechgaard, K. *J. Org. Chem.* **1996**, *61*, 1151. (i) Tanaka, K.; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465.

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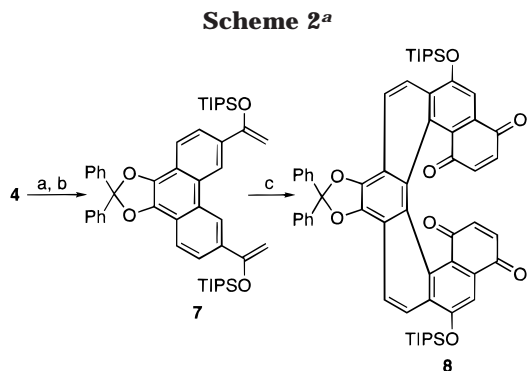(15) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274.

Scheme 1[a]
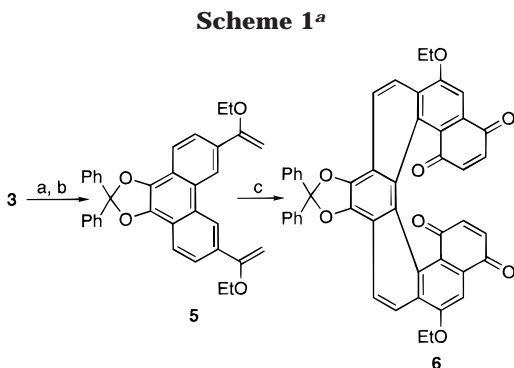
[a] Reagents and conditions: (a) diphenyldiazomethane, benzene (89% yield); (b) 1-ethoxyvinyltributylstannane, Pd(Ph₃P)₄, dioxane, reflux (72% yield); (c) *p*-benzoquinone, toluene, 100 °C, 48 h (10% yield).

Scheme 2[a]

[a] Reagents and conditions: (a) 1-ethoxyvinyltributylstannane, Pd(Ph₃P)₄, dioxane, reflux, 3 h; then H⁺ (62% yield); (b) triisopropylsilyl triflate, Et₃N, CH₂Cl₂, rt, 2h (92% yield); (c) *p*-benzoquinone, toluene, 103 °C, 63 h (20−22% yield).

Results and Discussion

As precursors we chose the enol ethers not of 3,6-diacetylphenanthrene itself but of its 9,10-dialkoxy derivatives (**1**) because these would lead to more highly functionalized helicenebisquinones (**2**), because the additional electron-donating substituents should facilitate the Diels−Alder reactions in eq 1 and because, as shown

$$(1)$$
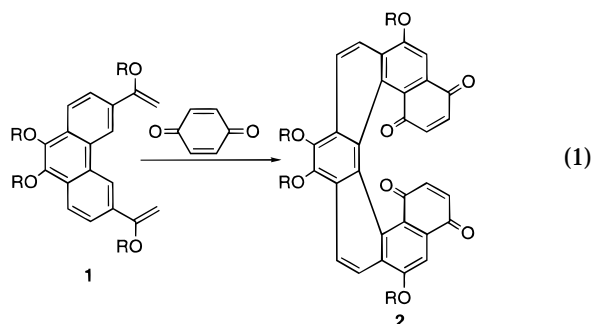
below, these, unlike the parent 3,6-diacetylphenanthrene, could be synthesized easily. Compounds of structure **1** should be preparable from suitably functionalized 9,10-phenanthrenequinones. Initially, 3,6-dibromo-,[16] 3,6-dicyano-,[16] 3,6-dimethyl-,[17] and 3,6-diacetoxyphenanthrene[18] were considered as potential precursors. However, to synthesize these requires several steps, and to introduce the phenanthrenequinone functionality requires more yet. In contrast, 3,6-dibromo-9,10-phenanthrenequinone[19] (**3**) can be prepared by brominating commercially available 9,10-phenanthrenequinone in nitrobenzene, a process we used to make 185 g of **3** in the course of 1 day. This makes **3** an excellent precursor for the synthesis of [7]helicenes. Indeed, as summarized in Scheme 1, **3** reacts with diphenyldiazomethane to give 3,6-dibromo-9,10-(diphenylmethylenedioxy)phenanthrene, **4**,[20] a compound that with 1-ethoxyvinyltributylstannane[21,22] undergoes Stille coupling to give bis-enol ether **5** in 72% yield. Reaction of **5** with *p*-benzoquinone then gives [7]helicenebisquinone **6**. The brevity of the sequence and the significant functionality that helicene

6 possesses are notable. Unfortunately, the yield in the reaction that produces **6** is only 10%, and our efforts to improve it were unsuccessful. A typical reaction started with 1 g of **5** and gave only 140 mg of **6**. Thus, Scheme 1 offers, in terms of scale, no great advantage over the photochemical methods previously used to make [7]-helicenebisquinones.[6f,23]

We therefore sought ways to improve the yield of the Diels−Alder reaction in Scheme 1. Since in some cases, Diels−Alder reactions of siloxy dienes proceed in high yields when those of alkoxy dienes fail,[24] presumably because the electron-donating abilities of siloxyls are greater than those of alkoxyls,[25] the bis(triisopropylsilyl) enol ether **7** was prepared (Scheme 2) and combined with *p*-benzoquinone. In the latter reaction, the yield of helicenebisquinone **8** was 20−22%, twice that in the preparation of **6**. More importantly, it proved possible to prepare **8** in quantities (ca. 1 g) that are large when compared to the amounts of helicenebisquinones preparable by photochemical methods.[23]

In view of this improvement, we prepared tetrasiloxy-phenanthrene derivative **11** to see whether it reacted even more efficiently with *p*-benzoquinone. The synthesis of **12** was accomplished as outlined in Scheme 3. Thus, 3,6-dibromo-9,10-phenanthrenequinone **3** with zinc and TMEDA in the presence of *tert*-butyldimethylsilyl chloride gave **9**,[26] which when subjected to Stille coupling with 1-ethoxyvinyltributylstannane and hydrolysis gave **10**. Reaction with triisopropylsilyl triflate and Et₃N gave
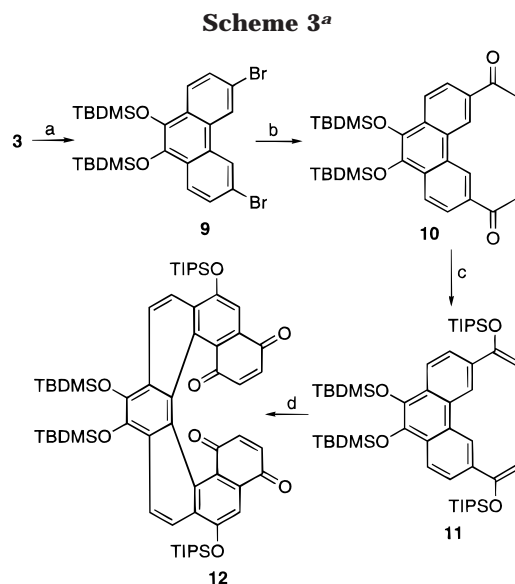
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(19) Schmidt, J.; Eitel, M. *J. Prakt. Chem.* **1932**, *134*, 167.
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(21) 1-Ethoxyvinyltributylstannane can be purchased from Aldrich chemical company or prepared as described in: (a) Gadwood, R. C.; Rubino, M. R.; Nagarajan, S. C.; Michel, S. T. *J. Org. Chem.* **1985**, *50*, 3255. (b) Soderquist, J. A.; Hsu, G. J.-H. *Organometallics* **1982**, *1*, 830. For its use in the conversion of arylbromides to arylmethylketones, see: (c) Kosugi, M.; Sumiya, T.; Obara, Y.; Suzuki, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 767.
(22) 1-Ethoxyvinyltributylstannane had previously been used in our lab to produce a bis-ethyl enol ether, which was used to synthesize a [6]helicenebisquinone. Nuckolls, C. Unpublished results.
(23) The photocyclization shown in Scheme 2 of ref 6f produced, after a solution in 400 mL of benzene had been irradiated for 8 h, 120 mg of 1,18-dimethoxy[7]helicene, a compound that was converted in 39% yield to 1,4,15,18-tetrahydro-1,4,15,18-tetraoxo[7]helicene: Yang, B. V. Ph.D. Dissertation, Columbia University, 1987.
(24) (a) Semmelhack, M. F.; Tomoda, S.; Hurst, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 7567. (b) Savard, J.; Brassard, P. *Tetrahedron Lett.* **1979**, 4911.
(25) (a) Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. (b) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400.
(26) For a related procedure in which *p*-benzoquinones are reduced by Zn in the presence of TMSCl but in the absence of an amine, see: Rasmussen, J. K.; Krepski, L. R.; Heilmann, S. M.; Smith, H. K.; Tumey, M. L. *Synthesis* **1983**, 457.

Scheme 3[a]

[a] Reagents and conditions: (a) Zn, *tert*-butyldimethylsilyl chloride, TMEDA, CH_2Cl_2, 16 h, rt (79% yield); (b) 1-ethoxyvinyltributylstannane, $Pd(Ph_3P)_4$, dioxane, reflux, 7 h; then H^+ (72% yield); (c) triisopropylsilyl triflate, Et_3N, CH_2Cl_2, rt, 1.5 h (94% yield); (d) *p*-benzoquinone, toluene, 100 °C, 86 h (37% yield).

Scheme 4[a]
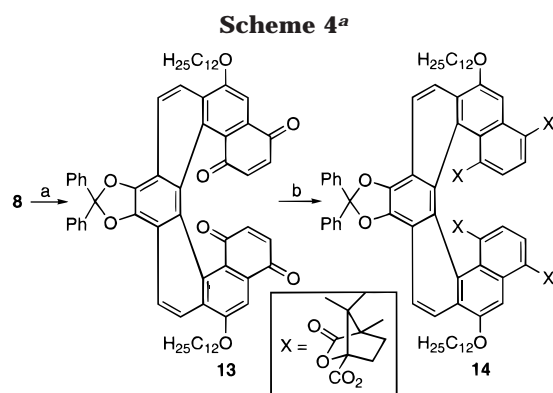
[a] Reagents and conditions: (a) CsF, $C_{12}H_{25}I$, DMF, 70 °C, 2.5 h (88% yield); (b) Zn, TMEDA, (*S*)-(−)-camphanoyl chloride, toluene 1 h, reflux (99% yield).

11. Enol ether **11** does indeed react even more efficiently than **9** with *p*-benzoquinone, producing [7]helicenebisquinone **12** in 37% yield. The consequence is that 30 g of helicene **12** can be prepared in a single 1 L round-bottomed flask.

Resolution of [7]Helicenebisquinones. As outlined in Scheme 4, treating **8** with CsF and $C_{12}H_{25}I$ in DMF converted its siloxy groups into alkoxyls.[27] Subsequent reduction with zinc and TMEDA[28] in the presence of (*S*)-(−)-camphanoyl chloride—a reagent previously used to resolve [6]helicenebisquinones[14a]—converted bisdodecyloxyhelicene **13** into diastereomeric helicene tetracamphanates **14**, which column chromatography separated in high optical purity (de ≥ 98%). The UV−vis absorption and CD spectra of the dextrorotatory diastereomer,
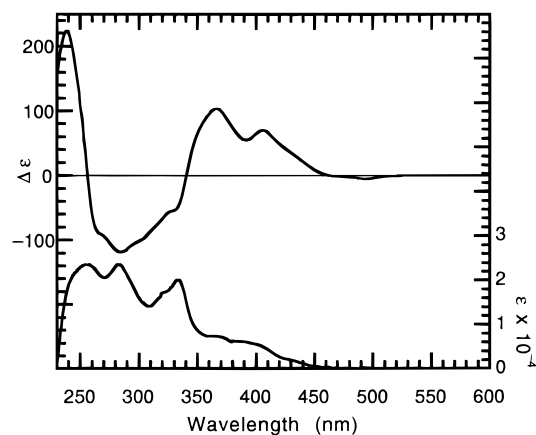
(27) For a related procedure that uses MeI or BnBr and KF in DMF to convert *tert*-butyldimethylsilylaryl ethers into methyl- or benzylaryl ethers, see: Sinhababu, A. K.; Kawase, M.; Borchardt, R. T. *Tetrahedron Lett.* **1987**, *28*, 4139.

(28) The previous procedure[14a] employs $Na_2S_2O_4$ as the reducing agent. For the [7]helicenebisquinones studied here Zn/TMEDA in toluene generally effected cleaner conversion.

Figure 1. CD (upper curve, ordinate on left) and UV−vis (lower curve, ordinate on right) of a 2.0×10^{-5} M solution of (+)-**14** in CH_2Cl_2.

(+)-**14**, in CH_2Cl_2 are displayed in Figure 1. Those of (−)-**14** are shown in the Supporting Information.

The absolute configurations of (+)- and (−)-**14** were assigned by comparing their CD spectra and specific rotations with those of other helicenes. The CD spectra of helicenes possess two intense long-wavelength $\pi-\pi^*$ transitions: the p-band and the higher energy β-band.[29,30] For helicenes with the *P*-configuration, the circular dichroisms of the p- and β-bands are positive, and for helicenes with the *M*-configuration they are negative. At wavelengths longer than their lowest energy absorptions,[29c] helicenes with the *P*-configuration have dextrorotatory-specific rotations, and those with the *M*-configuration have levorotatory rotations.

The CD spectrum of (+)-**14** (Figure 1) includes two intense positively dichroic maxima at 405 ($\Delta\epsilon = 69$) and 367 nm ($\Delta\epsilon = 103$), which were assigned to the p- and β-bands, respectively. Accordingly, (+)-**14** was assigned the *P*-configuration. Similarly, (−)-**14**, which is diastereomeric with (+)-**14**, was assigned the *M*-configuration. The peaks in its CD spectrum at 402 ($\Delta\epsilon = -73$) and 365 nm ($\Delta\epsilon = -95$), assigned to the p- and β-bands, respectively, are negatively dichroic.

Steps similar to those applied above to **8** were applied to tetrasiloxybisquinone **12**. Thus (Scheme 5), CsF/dodecyl iodide converted **12** into tetraalkoxybisquinone **15**, which when reduced with zinc in the presence of (*S*)-(−)-camphanoyl chloride gave a mixture of diastereomeric helicenes **16** that could be separated by chromatography into materials with de ≥ 98%. The UV−vis absorption and CD spectra of the dextrorotatory diastereomer, (+)-**16**, are displayed in Figure 2. Those of (−)-**16** are shown in the Supporting Information.
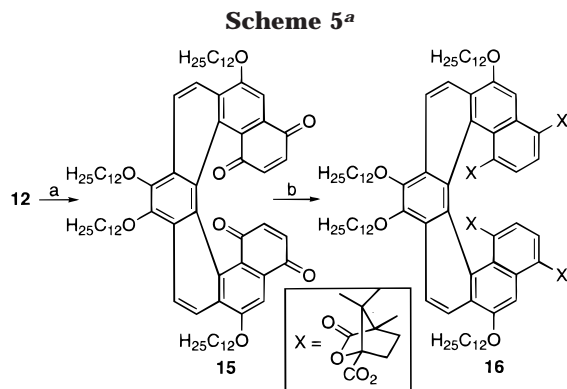
The maxima at 401 ($\Delta\epsilon = 67$) and 366 nm ($\Delta\epsilon = 94$) in the CD spectrum of (+)-**16** were assigned to the p- and β-bands, respectively, and therefore, (+)-**16** was assigned

(29) (a) Brown, A.; Kemp, C. M.; Mason, S. F. *J. Chem. Soc. (A)* **1971**, 751. (b) Newman, M. S.; Darlak, R. S.; Tsai, L. *J. Am. Chem. Soc.* **1967**, *89*, 6191. (c) Brickell, W. S.; Brown, A.; Kemp, C. M.; Mason, S. F. *J. Chem. Soc. (A)* **1971**, 756. (d) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 343. (e) Groen, M. B.; Wynberg, H. *J. Am. Chem. Soc.* **1971**, *93*, 2968.

(30) In addition, the CD spectra of [6]helicenes[29b] and thiahelicenes[29e] possess an additional, low-intensity transition at longer wavelength—the α-band—but this transition cannot be distinguished from the p-band in the CD spectra of [7]-, [8]-, and [9]helicenes,[29d] nor can it be recognized in the CD of (+)- and (−)-**14** and **16**.

Scheme 5[a]

[a] Reagents and conditions: (a) CsF, $C_{12}H_{25}I$, DMF, 65 °C, 2.5 h (78% yield); (b) Zn, TMEDA, (S)-(−)-camphanoyl chloride, toluene 1 h, reflux (75% yield).
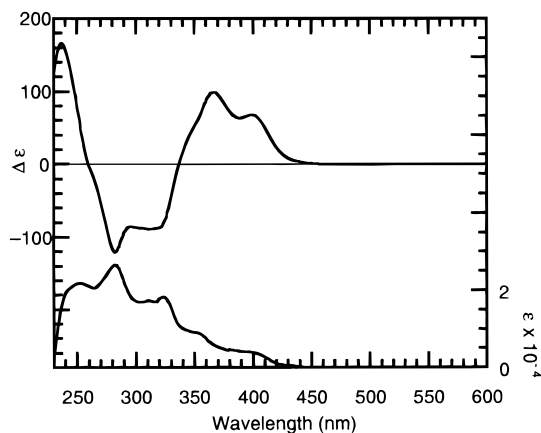

Figure 2. CD (upper curve, ordinate on left) and UV−vis (lower curve, ordinate on right) of a 2.0×10^{-5} M solution of (+)-**16** in CH_2Cl_2.

the *P*-configuration. The *M*-configuration was assigned to (−)-**16**. The corresponding peaks are at 398 ($\Delta\epsilon = -87$) and 364 nm ($\Delta\epsilon = -109$).

Each of the nonracemic tetracamphanates **14** and **16** was combined with *n*-BuLi to give a bis-hydroquinone, which after workup was oxidized by chloranil to give nonracemic bisquinones **13** and **15** in yields, for the two steps, of 74−89%. The UV−vis absorption and CD spectra of the resulting (*P*)-**13** and (*P*)-**15** are displayed in Figure 3.

In Table 1 and Figure 3, the peaks in the CD spectra of these bisquinones are compared to that of (+)-[6]-helicenebisquinone (**17**), which is known to have the *P*-configuration.[12] The sign of the specific rotation of **13** can be changed by changing the solvent (see the Experimental Section), and accordingly the structures of **13** and **15** displayed in Figure 3 are referred to in Table 1 as (*P*)-**13** and (*P*)-**15**. All three of the CD spectra summarized in the table have positive dichroisms at ca. 265 and 360 nm and a negative dichroism at ca. 300 nm. These similarities verify that **13** and **15** have *P*-helicity.

The n−π* transition in the UV−vis spectrum of **15** is assigned to the peak at 450 nm,[31] and like that in the CD spectrum of **17**,[12] it gives rise to a positive dichroism.

(31) n−π* transitions in the UV−vis spectra of *p*-quinones generally occur at 420−460 nm. See: Berger, S.; Rieker, A. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley: London, 1974; Chapter 4.
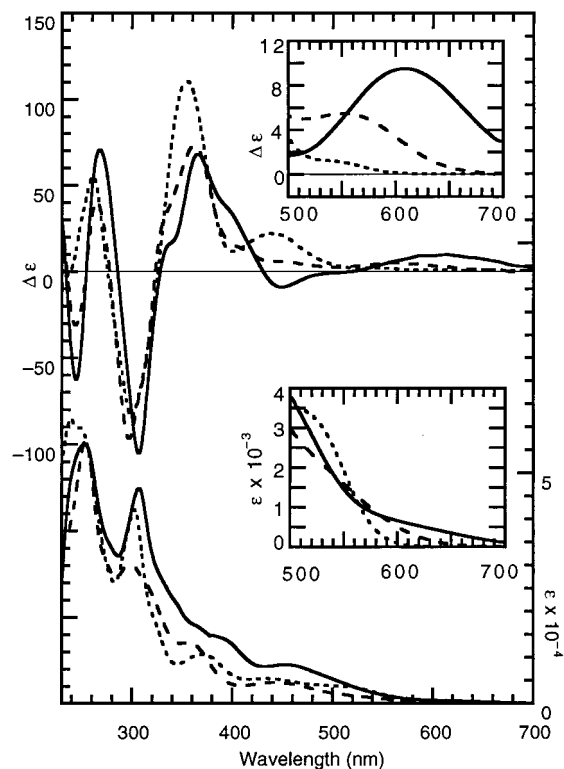

Figure 3. CD (upper curves, scale at left) and UV−vis (lower curves, scale at right) of CH_2Cl_2 solutions of (*P*)-**13** (−, 2.0×10^{-5} M), (*P*)-**15** (- - -, 2.1×10^{-5} M), and (*P*)-**17** (···, 2.2×10^{-5} M). The insets show long-wavelength dichroisms and absorptions in the CD (upper right) and UV−vis (lower right) spectra of CH_2Cl_2 solutions of (*P*)-**13** (−, 8.7×10^{-4} M), (*P*)-**15** (- - -, 8.7×10^{-4} M), and (*P*)-**17** (···, 8.7×10^{-4} M).

Table 1. Peaks in the CD Spectra of (*P*)-13, (*P*)-15, and (*P*)-17[a]

(*P*)-**13**	(*P*)-**15**	(*P*)-**17**[12]
264 (42)	267 (71)	259 (40)
296 (−98)	305 (−106)	296 (−80)
363 (74)	366 (69)	351 (90)
450 (−9)	450 (6)	440 (15)
483 (−2)	570 (5)	
602 (10)		

[a] The positions of peaks are given in nm, $\Delta\epsilon$ in parentheses.

The n−π* transtion of **13** is assigned similarly to a peak in the UV−vis spectrum at 460 nm, but it is difficult to locate in the CD spectrum because a negative dichroism falls just to the blue, at 450 nm. A notable observation is that **13** and **15** each display a CD peak at even longer wavelengths, observed neither in the spectrum of **17** nor in the spectra of the parent [5]-, [6]-, [7]-, and [8]-helicenebisquinones.[6f,32,33] The dichroisms are weak and positive and maximize at 602 and 570 nm, respectively. Possibly they arise from charge transfer between the second and seventh rings.

Conclusions

[7]Helicenes can be synthesized by nonphotochemical methods in only five steps from 9,10-phenanthrene-

(32) (a) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1990**, *31*, 3983. (b) Yang, B. V. Dissertation, Columbia University, 1987. (c) Liu, L. Ph.D. Dissertation, Columbia University, 1991.

(33) The peaks at longest wavelengths (λ, nm) in the CD spectra of the (+)- or (−)-[*n*]-helicenebisquinones are as follows [*n*, λ ($\Delta\epsilon$)]: (+)-**5**, 495 (2.8); (−)-**6**, 440 (−20); (−)-**7**, 430 (−3); (−)-**8**, 450 (−15).[32b,c]

17

R = (CH₂)₂OC₄H₉
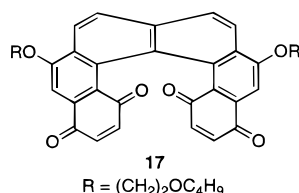
quinone. Large quantities can be produced, the structures are usefully functionalized, and resolutions into optically active materials are easy to carry out. The absolute configurations have been assigned.

Experimental Section

THF and toluene were distilled from Na/benzophenone; CH₂Cl₂ and Et₃N, from CaH₂. TMEDA (Aldrich, anhydrous, 99.5+%) was used without purification. DMF (Aldrich, anhydrous, 99.8%) was boiled and cooled under N₂ to free it of oxygen. Zn dust (Aldrich, <10 μm, 98+%) was activated prior to use.[34] 1,4-Benzoquinone (Aldrich, 98%) was purified by slurrying it in CH₂Cl₂ with 4 times its weight of basic alumina, filtering through Celite, and drying under vacuum. Manipulations involving stannanes were performed in a fume hood. Glassware was flame-dried under vacuum and cooled under N₂. Reactions were run under N₂. Additions by syringe were through rubber septa. "Chromatography" refers to "flash chromatography".[35] FAB was used for high-resolution mass spectra.

3,6-Bis(1-(triisopropylsiloxy)ethenyl)-9,10-(diphenyl-methylenedioxy)phenanthrene (7). Pd(Ph₃P)₄ (1.0 g, 0.87 mmol) was added to a solution of 3,6-dibromo-9,10-(diphenyl-methylenedioxy)phenanthrene **4**[20] (7.80 g, 14.7 mmol) and 1-ethoxyvinyltributylstannane[21] (11.65 g, 32 mmol) in 80 mL of dioxane. After the mixture had refluxed for 3 h, it was cooled to room temperature and the solvent was stripped. Acetone (20 mL), H₂O (1 mL), and acetic acid (1 mL) were then added, and the mixture was heated for 20 min at 60 °C, cooled to room temperature, and partitioned between CH₂Cl₂ and H₂O. The organic layer was washed with saturated aqueous NaHCO₃ and dried (Na₂SO₄), and the solvent was removed under reduced pressure. Hexane was added, and the hexane-soluble portion was loaded onto a short column of silica gel. The column was washed with hexane to remove the majority of the (C₄H₉)₃SnCl. The eluent was changed to CH₂Cl₂ until fluorescent material was near the bottom of the column and then to EtOAc. The eluted material was combined with the material that had not dissolved in hexane, and this was dissolved in CH₂Cl₂, filtered, and chromatographed (5% EtOAc/hexane), giving 4.14 g (62%) of 3,6-diacetyl-9,10-(diphenylmethylenedioxy)phenanthrene, an off-white solid, mp > 225 °C. IR (CCl₄): 3070, 1685, 1653, 1612 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 9.38 (d, 2H, J = 1.4 Hz), 8.24 (dd, 2H, J = 8.5, 1.4 Hz), 8.17 (d, 2H, J = 8.4 Hz), 7.73 (m, 4H), 7.42 (m, 6H), 2.82 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 197.7, 139.7, 139.4, 133.6, 129.5, 128.4, 127.4, 126.5, 126.4, 124.4, 124.0, 120.9, 119.0, 26.9 ppm. HRMS calcd for C₃₁H₂₂O₄: 458.1518, found 458.1535.

Triisopropylsilyl triflate (3.37 g, 11.0 mmol, 2.92 mL) was added to a solution of the above diacetyl compound (2.40 g, 5.25 mmol) in CH₂Cl₂ (36 mL) and Et₃N (6.8 mL), cooled in an ice bath, and the mixture was then warmed to room temperature and stirred for 2 h. Additional CH₂Cl₂ was added, and after the solution had been washed with saturated aqueous NaHCO₃ and dried (Na₂SO₄), the solvents were removed and the residue was dissolved in CH₂Cl₂ (25 mL). MeOH (50 mL) was added. Solvents were then removed under reduced pressure until the total volume was ca. 20 mL. Additional MeOH (50 mL) was added, and the solvents were

again stripped until the total volume was ca. 20 mL. The flask was cooled briefly in a dry ice/acetone bath, and the precipitated pasty solid was filtered on a bed of Celite and washed with additional cold MeOH. Washing the filter cake with CH₂Cl₂ and stripping the solvent gave 3.72 g (92%) of **7**, a sticky, pale yellow solid. IR(CCl₄): 2946, 2868, 1685, 1656 cm⁻¹. ¹H NMR (C₆D₆, 400 MHz): δ 9.30 (d, 2H, J = 1.3 Hz), 8.10 (d, 2H, J = 8.5 Hz), 7.97 (dd, 2H, J = 1.5, 8.5 Hz), 7.81 (m, 4H), 7.08 (m, 6H), 5.11 (d, 2H, J = 1.8 Hz), 4.65 (d, 2H, J = 1.8 Hz), 1.31 (m, 6H), 1.20 (m, 36H) ppm. ¹³C NMR (C₆D₆, 75 MHz): δ 157.1, 141.0, 138.2, 134.8, 129.3, 128.5, 127.0, 124.9, 121.8, 120.7, 120.5, 118.6, 91.0, 18.1, 12.9 ppm.

6,13-Bis(triisopropylsiloxy)-9,10-(diphenylmethylene-dioxy)[7]helicenebisquinone (8). A flask containing **7** (3.72 g, 4.84 mmol) and *p*-benzoquinone (10.45 g, 96.7 mmol) and fitted with a reflux condenser was evacuated and filled with N₂ three times. Toluene (24 mL) was syringed in, and the mixture was heated in an oil bath at 103 °C for 63 h. The reaction mixture was then cooled, and the toluene was stripped. Excess *p*-benzoquinone was removed into a trap by vacuum sublimation at 100 °C. The residue was chromatographed on silica (4:1 CH₂Cl₂/hexanes), giving 0.94 g (20%) of **8**, a brown-red solid, mp > 225 °C. A similar reaction starting from 1.51 g of **7** gave 0.42 g (22%) of **8**. IR(CCl₄): 2948, 2869, 1663, 1613 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 8.39 (d, 2H, J = 8.8 Hz); 8.25 (d, 2H, 8.8 Hz); 7.76 (m, 4H); 7.43 (m, 6H); 7.34 (s, 2H); 6.47 (d, 2H, J = 10.1 Hz); 5.94 (d, 2H, J = 10.1 Hz); 1.51 (m, 6H); 1.25 (s, 9H); 1.23 (s, 9H); 1.21 (s, 9H); 1.19 (s, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 184.6, 183.3, 157.6, 140.7, 140.1, 140.0, 133.9, 133.2, 129.5, 129.3, 128.7, 128.3, 126.5, 124.6, 124.4, 122.0, 121.4, 120.7, 119.3, 107.7, 18.0, 13.0 ppm. HRMS calcd for C₆₁H₆₃O₈Si₂: (M + 1) 979.4062, found 979.4106.

6,13-Bis(dodecyloxy)-9,10-(diphenylmethylenedioxy)-[7]helicenebisquinone (13). DMF (50 mL) and dodecyl iodide (4.54 g, 15.3 mmol, 3.78 mL) were sequentially syringed into a flask containing **8** (0.500 g, 0.511 mmol) and CsF (0.466 g, 3.07 mmol). After 2 h at 70 °C, the mixture was cooled to room temperature and partitioned between CH₂Cl₂ and H₂O. The organic layer was dried (Na₂SO₄), and the solvent was stripped. The residue, loaded onto a chromatography column with ca. 10% CH₂Cl₂/hexane, was washed with excess hexane and then eluted with CH₂Cl₂. Further purification by trituration with MeOH gave 0.453 g (88%) of **13**, a red-brown solid, mp 161–162 °C. IR(CCl₄): 2928, 2856, 1662, 1612 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz): δ 8.39 (d, 2H, J = 8.8 Hz), 8.22 (d, 2H, J = 8.8 Hz), 7.78 (m, 4H), 7.41 (m, 6H), 7.37 (s, 2H), 6.47 (d, 2H, J = 10.1 Hz); 5.96 (d, 2H, J = 10.1 Hz); 4.36 (m, 2H), 4.26 (m, 2H), 2.01 (m, 4H), 1.61 (m, 4H), 1.5–1.2 (m, 32H), 0.87 (t, 6H, J = 7.0 Hz) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 184.9, 183.3, 159.7, 141.0, 140.1, 140.0, 133.8, 133.5, 129.4, 128.3, 128.1, 127.5, 126.6, 124.4, 124.2, 122.0, 120.9, 120.8, 119.4, 100.7, 69.5, 31.9, 29.7, 29.65, 29.60, 29.57, 29.38, 29.35, 29.0, 26.2, 22.7, 14.1 ppm. HRMS calcd for C₆₇H₇₂O₈: (M + 2)[36] 1004.5227, found 1004.5226.

Resolution of 13. Toluene (23 mL) and TMEDA (5.80 g, 50 mmol, 7.53 mL) were sequentially syringed into a flask containing **13** (0.533 g, 0.53 mmol), Zn (0.533 g, 8.2 mmol), and (S)-(−)-camphanoyl chloride (1.70 g, 7.9 mmol). The mixture was refluxed for 1 h, cooled to room temperature, and filtered. CH₂Cl₂ was added, and after it had been washed with HCl (1 M) and saturated aqueous NaHCO₃ and dried (Na₂SO₄), the solvent was stripped and the residue was combined with the crude product from a similar reaction that had started with 0.092 g of **13**. Chromatography on silica gel, eluting first with CH₂Cl₂, then with 3% EtOAc in CH₂Cl₂, and finally with 5% EtOAc in CH₂Cl₂, gave the levorotatory diastereomer, (M)-**14** (0.530 g, 99%), mp 92–94 °C, followed by the dextrorotatory diastereomer, (P)-**14** (0.534 g, 99%), mp 108–110 °C. The latter was further purified by chromatography (10% EtOAc/benzene). Both diastereomers are yellow solids.

(34) Shriner, R. L.; Neumann, F. W. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. 3, p 73.

(35) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(36) M + 2 peaks are often seen in the mass spectra of quinones. See: Zeller, K.-P. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley: London, 1974; Chapter 5.

(**P**)-**14:** [α]$_D$ +723 (*c* 0.066, CH$_2$Cl$_2$); IR (CCl$_4$) 2960, 2929, 2873, 1799, 1750 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.38 (d, 2H, *J* = 8.5 Hz); 8.18 (d, 2H, *J* = 8.5 Hz); 7.74 (m, 4H); 7.42 (m, 6H); 7.04 (d, 2H, *J* = 8.4 Hz); 6.84 (s, 2H); 5.99 (d, 2H, *J* = 8.4 Hz); 4.29 (m, 2H); 4.13 (m, 2H); 2.64 (m, 2H); 2.24 (m, 2H); 2.1−1.9 (m, 6H); 1.82 (m, 2H); 1.64−1.50 (m, 8H); 1.48−1.11 (m, 54H); 0.89 (m, 12H); 0.63 (s, 6H); 0.40 (s, 6H) ppm; ^{13}C NMR (CDCl$_3$, 75 MHz) δ 178.0, 177.0, 165.1, 165.0, 154.5, 143.1, 142.3, 140.0, 138.4, 129.5, 128.4, 126.9, 126.5, 126.3, 123.7, 123.4, 122.8, 121.7, 120.2, 120.0, 118.9, 116.6, 115.5, 96.2, 91.2, 90.2, 68.8, 55.0, 54.5, 54.3, 54.0, 31.9, 31.0, 29.7 (m), 29.5, 29.4, 29.2, 28.9, 28.7, 26.4, 22.7, 17.0, 16.8, 16.7, 16.3, 14.1, 9.8, 9.4 ppm; HRMS calcd for C$_{107}$H$_{122}$O$_{20}$ 1727.8564, found 1727.8605.

(**M**)-**14:** [α]$_D$ −801 (*c* 0.073, CH$_2$Cl$_2$); IR (CCl$_4$) 2961, 2930, 2856, 1799, 1798, 1750 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.46 (d, 2H, *J* = 8.5 Hz); 8.29 (d, 2H, *J* = 8.5 Hz); 7.82 (m, 4H); 7.4−7.3 (m, 6H); 7.06 (d, 2H, *J* = 8.4 Hz); 6.80 (s, 2H); 6.12 (d, 2H, *J* = 8.4 Hz); 4.32 (m, 2H); 4.03 (m, 2H); 2.65 (m, 2H); 2.33 (m, 2H); 2.1−1.9 (m, 6H); 1.83 (m, 2H); 1.59 (m, 4H); 1.5−1.0 (m, 54H); 0.89 (t, 6H, *J* = 7.0 Hz); 0.84 (s, 6H); 0.82 (m, 2H); 0.69 (m, 2H); 0.52 (s, 6H); 0.30 (s, 6H) ppm; ^{13}C NMR (CDCl$_3$, 75 MHz) δ 178.5, 178.1, 165.5, 165.4, 155.0, 143.2, 142.4, 141.6, 138.5, 129.4, 128.7, 127.2, 126.5, 126.1, 124.0, 123.6, 122.3, 122.2, 121.5, 120.4, 118.5, 116.5, 115.3, 96.5, 91.7, 89.9, 69.3, 55.4, 54.8, 54.7, 54.5, 32.4, 31.5, 30.1 (m), 29.9, 29.8, 29.6, 29.5, 28.6, 26.7, 23.1, 17.5, 17.3, 16.6, 16.3, 14.6, 10.2, 9.9 ppm; HRMS calcd for C$_{107}$H$_{122}$O$_{20}$ 1727.8564, found 1727.8601.

Preparation of Nonracemic Helicenes 13 from Tetraesters 14. *n*-BuLi (2.64 mL of a 2.5 M solution in hexane, 6.6 mmol) was added to a solution of (*M*)-**14** (0.456 g, 0.264 mmol) in THF (20 mL) that had been cooled in a dry ice/acetone bath. After the mixture had stirred for 20 min at −78 °C, the reaction was quenched at this temperature with saturated aqueous NH$_4$Cl, and ca. 20 mL of HCl (1 M) and CH$_2$Cl$_2$ were added. After a wash with HCl (0.5 M) and two washes with H$_2$O, the organics were dried (Na$_2$SO$_4$). Chloranil (0.200 g, 0.81 mmol) was added, whereupon the solution turned brown-red. After standing for 15 min, the solution was filtered, washed twice with saturated aqueous NaHCO$_3$, and dried (Na$_2$SO$_4$). The solvent was stripped, and the residue was chromatographed (2:1 CH$_2$Cl$_2$/hexanes), giving after trituration with a small amount of MeOH 0.220 g (83%) of (*M*)-**13**, mp 112−113 °C. The ^{1}H NMR spectrum was identical to that of the racemic material. [α]$_D$: +260 (*c* 0.070, CH$_2$Cl$_2$).[37] UV−vis (CH$_2$Cl$_2$, *c* = 1.8 × 10^{-5} M): λ$_{max (nm)}$ (log ε) 250 (4.79), 306 (4.65), 365 (4.16), 395 (4.09), 454 (3.81), 600 (2.71). CD (*c* = 1.8 × 10^{-5} M): nm ([θ]), 243 (2.44 × 10^{-5}), 267 (−2.24 × 10^{-5}), 306 (3.73 × 10^{-5}), −332 (3.63 × 10^{-4}), 365 (−2.18 × 10^{-5}), 397 (−1.06 × 10^{-5}), 448 (3.3 × 10^{-4}), 480 (3.3 × 10^{-3}), 602 (−2.64 × 10^{-4}). The same reaction conditions applied to the other diastereomer, (*P*)-**14**, gave (*P*)-**13** in 76% yield. [α]$_D$: −260 (*c* 0.077, CH$_2$Cl$_2$); +340° (*c* 0.070, THF); −170° (*c* 0.070, benzene); +280° (*c* 0.070, hexanes).[37]

3,6-Dibromo-9,10-bis(*tert*-butyldimethylsiloxy)phenanthrene (9). Zn (268 g, 4.12 mol), TMEDA (200 mL, 154 g, 1.33 mol), and *tert*-butyldimethylsilyl chloride (168 g, 1.12 mol) were sequentially added to a three-necked 2 L round-bottomed flask containing 3,6-dibromo-9,10-phenanthrenequinone[19] (100 g, 0.273 mol) in CH$_2$Cl$_2$ (1 L). After the mixture had been stirred mechanically for 16 h at room temperature, it was filtered on Celite, which was rinsed exhaustively with hot CHCl$_3$ to recover any product that had precipitated from solution. After they had been washed with HCl (1 M) and H$_2$O, the organics were dried over Na$_2$SO$_4$ and solid NaHCO$_3$ and filtered. The solvent was stripped, and CH$_2$Cl$_2$ (ca. 0.75 L)

was added to the residue. A large crop of white crystals of pure **9** that did not dissolve was removed by filtration, and the filtrate was directly loaded onto a large plug of silica gel (6 in. × 6 in.). Elution with hexane was continued until TLC indicated that the eluant contained no more product. The solvents were then stripped, and the residual solid was slurried with 1:1 CH$_2$Cl$_2$/hexane. The precipitate plus the crystals obtained earlier amounted to 129 g (79%) of pure **9**, a white crystalline solid, mp 224−226 °C. IR (CCl$_4$): 2959, 2932, 2860, 1589 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.61 (d, 2H, *J* = 1.8 Hz); 8.04 (d, 2H, *J* = 8.8 Hz); 7.67 (dd, 2H, *J* = 1.8, 8.8); 1.12 (s, 18H); 0.07 (s, 12 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 137.6, 129.8, 129.4, 128.0, 125.2, 124.8, 119.5, 26.4, 18.7, −3.7 ppm. Anal. Calcd for C$_{26}$H$_{36}$Br$_2$Si$_2$O$_2$: C, 52.3; H, 6.1. Found: C, 52.5; H, 6.2.

3,6-Diacetyl-9,10-bis(*tert*-butyldimethylsiloxy)phenanthrene (10). A solution of **9** (71 g, 0.12 mol), 1-ethoxyvinyltributylstannane (95 g, 0.26 mol), and Pd(PPh$_3$)$_4$ (5.0 g, 4.3 mmol) in 600 mL of dioxane was refluxed for 4 h. Additional Pd(PPh$_3$)$_4$ (1.0 g, 0.87 mmol) was added as a solution in dioxane, and after it had refluxed for another 3 h, the mixture was cooled to room temperature. Acetic acid (5 mL) and H$_2$O (10 mL) were added, and the mixture was stirred for 1 h. The solvent was then stripped, and the residue was added to a large column of silica gel (6 in. × 8 in.), which, to remove the majority of the (C$_4$H$_9$)$_3$SnCl, was washed first with hexanes and then with ca. 1 L of 20% EtOAc in hexane (TLC monitoring!). Elution with pure EtOAc, followed by 20% EtOAc in CH$_2$-Cl$_2$, removed the product from the column. Trituration with hexanes gave 44.6 g (72%) of **10**, an off-white solid, mp > 225 °C. IR (CCl$_4$): 2960, 2932, 2861, 1686, 1600 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.31 (d, 2H, *J* = 1.4 Hz); 8.29 (d, 2H, *J* = 8.6 Hz); 8.17 (dd, 2H, *J* = 1.5, 8.6 Hz); 2.82 (s; 6H); 1.14 (s, 18H); 0.09 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 198.0, 139.8, 133.9, 133.6, 127.5, 125.5, 123.6 (2 peaks), 27.0, 26.4, 18.7, −3.5 ppm. Anal. Calcd for C$_{30}$H$_{42}$Si$_2$O$_4$: C, 68.9; H, 8.1. Found: C, 68.9; H, 8.1.

3,6-Bis(1-(triisopropylsiloxy)ethenyl)-9,10-bis(*tert*-butyldimethylsiloxy)phenanthrene (11). Triisopropylsilyl triflate (54.9 g, 0.179 mol, 48.1 mL) was added to an ice-bath-cooled solution of **10** (44.6 g, 0.085 mol) in 400 mL of CH$_2$Cl$_2$ and 71 mL of Et$_3$N. The ice bath was then removed, and after the mixture had stirred for 1.5 h, it was washed three times with saturated aqueous NaHCO$_3$ and dried (Na$_2$SO$_4$). Solvent was then removed under reduced pressure until product began to precipitate. MeOH (ca. 300 mL) was added, and the solvents were again concentrated under reduced pressure until the total volume was ca. 100 mL. More MeOH was added, and the volume was once again reduced to ca. 100 mL. The solid that had precipitated was filtered and rinsed with cold MeOH, dissolved in hexane, washed with saturated aqueous NaHCO$_3$, and dried (Na$_2$SO$_4$). The solution was filtered into a 2 L flask. Removal of solvents and drying in vacuo gave 66.6 g (94%) of **11**, a white, fibrous material, mp 119−121 °C. IR (CCl$_4$): 2947, 2867, 1599, 1472 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 9.45 (s, 2H); 8.57 (d, 2H, *J* = 8.6 Hz); 8.16 (d, 2H, *J* = 8.7 Hz); 5.25 (d, 2H, *J* = 1.6 Hz); 4.76 (d, 2H, *J* = 1.5 Hz); 1.5−1.2 (m, 60H); 0.22 (s, 12H) ppm. ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ 157.1, 138.4, 135.3, 130.9, 128.4, 124.1, 123.4, 120.1, 90.9, 26.6, 18.9, 18.3, 13.1, −3.4 ppm.

6,13-Bis(triisopropylsiloxy)-9,10-bis(*tert*-butyldimethylsiloxy)[7]helicenebisquinone (12). A 1 L round-bottomed flask that contained **11** (66.6 g, 0.080 mol) and *p*-benzoquinone (173 g, 1.60 mol) was fitted with a reflux condenser and evacuated and filled with N$_2$ three times. Toluene (400 mL) was added (via cannula), and the mixture was heated in an oil bath at 100 °C for 86 h. The reaction mixture was then cooled to room temperature and the solvent stripped. Excess *p*-benzoquinone was removed to a trap by vacuum sublimation at 100 °C. The residue, dissolved in CH$_2$Cl$_2$, was loaded onto a large plug of silica gel (5 in. × 6 in.) and sequentially eluted with 1:1 CH$_2$Cl$_2$/hexane, CH$_2$Cl$_2$, and 25% EtOAc/CH$_2$Cl$_2$. After the solvents had been removed, the material was divided into three parts, each of which was chromatographed (1:1 CH$_2$-Cl$_2$/hexane). The yield of **12**, a red-brown solid, mp > 225 °C,

(37) The small value of **14**'s [α]$_D$ and the solvent dependence of its sign are probably a consequence of the CD spectrum peaking at the wavelength of the sodium D-line (589 nm). A Cotton effect in the ORD spectrum is expected to coincide with the λ$_{max}$ of an isolated transition in the CD spectrum. See: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; Chapter 13.

was 30.5 g (37%). IR (CCl₄): 2950, 2932, 2868, 1665 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 8.37 (d, 2H, *J* = 9.0 Hz); 8.33 (d, 2H, *J* = 9.0 Hz); 7.34 (s, 2H); 6.44 (d, 2H, *J* = 10.1 Hz); 5.94 (d, 2H, *J* = 10.1 Hz); 1.52 (m, 6H); 1.25−1.23 (m, 18H); 1.20−1.18 (m, 36H); 0.32 (s, 6H); 0.13 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 184.7, 184.1, 157.2, 140.3, 139.9, 134.0, 132.8, 130.2, 129.3, 127.9, 125.6, 125.0, 123.8, 120.4, 107.3, 26.4, 18.7, 18.1, 13.0, −3.1, −4.1 ppm. Anal. Calcd for C₆₀H₈₂Si₄O₄: C, 69.1; H, 7.9. Found: C, 69.0; H, 8.0.

6,9,10,13-Tetrakis(dodecyloxy)[7]helicenebisquinone (15). DMF (24 mL) and dodecyl iodide (7.2 g, 24 mmol, 6.0 mL) were sequentially syringed into a flask containing **12** (0.500 g, 0.48 mmol) and CsF (0.58 g, 3.84 mmol), and the mixture was heated in an oil bath at 65 °C for 2.5 h. After cooling the mixture to room temperature, CH₂Cl₂ was added. This was washed with H₂O, dried (Na₂SO₄), and stripped, and the residue was loaded onto a chromatography column, which was washed first with hexane. The product was then eluted with 4:1 CH₂Cl₂/hexane, triturated with MeOH, and then dissolved in a minimum amount of CH₂Cl₂. MeOH (ca. 30 mL) was then added, and the solvent was stripped until the total volume was ca. 10 mL. Again, MeOH (ca. 30 mL) was added, and the volume was again reduced to ca. 10 mL. The precipitated solid was then filtered and washed with excess cold MeOH, yielding 0.440 g (78%) of **15**, a red solid, mp 77−78 °C. IR (CCl₄): 2928, 2856, 1663, 1608 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 8.46 (d, 2H, *J* = 9.0 Hz); 8.40 (2H, d, *J* = 9.0 Hz); 7.36 (s, 2H); 6.46 (d, 2H, *J* = 10.1 Hz); 5.92 (d, 2H, *J* = 10.1 Hz); 4.43 (m, 4H); 4.25 (m, 4H); 1.99 (m, 8H); 1.60 (m, 8H); 1.29 (m, 64 H); 0.89 (m, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ 184.8, 183.5, 159.5, 144.6, 140.6, 133.8, 133.2, 130.0, 127.7, 127.4, 125.7, 124.7, 123.5, 120.3, 100.5, 74.0, 69.3, 31.9, 30.5, 29.6 (m), 29.4, 29.0, 26.2, 26.1, 22.7, 14.1 ppm. HRMS calcd for C₇₈H₁₁₁O₈: (M + 1) 1175.8279, found 1175.8269.

Resolution of 15. Toluene (16 mL) and TMEDA (4.40 g, 37.9 mmol, 5.71 mL) were syringed into a flask containing **15** (0.445 g, 0.379 mmol), Zn (0.382 g, 5.87 mmol), and (−)-camphanoyl chloride (1.23 g, 5.68 mmol). The mixture was refluxed for 2 h, cooled to room temperature, washed with HCl (1 M) and then saturated aq NaHCO₃, dried (Na₂SO₄), and chromatographed (5% EtOAc/CH₂Cl₂). The levorotatory diastereomer (*M*)-**16** (0.275 g, 76%, mp 51−53 °C) eluted first. The dextrorotatory diastereomer (*P*)-**16** eluted second and was rechromatographed (25% EtOAc in hexane). The yield was 0.271 g (75%), mp 90−92 °C.

(*P*)-16: [α]_D +715 (*c* 0.057, CH₂Cl₂); IR (CCl₄) 2928, 2856, 1798, 1750 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.38 (d, 2H, *J* = 8.7 Hz); 8.36 (d, 2H, *J* = 8.7 Hz); 7.03 (d, 2H, *J* = 8.4 Hz); 6.86 (s, 2H); 6.05 (d, 2H, *J* = 8.4 Hz); 4.37−4.28 (m, 4H); 4.20−4.12 (m, 4H); 2.67 (m, 2H); 2.25 (m, 2H); 2.11−1.95 (m, 10H); 1.83 (m, 2H); 1.74 (m, 2H); 1.63 (m, 8H); 1.5−1.2 (m, 88H); 0.98 (s, 6H); 0.90 (m, 12 H); 0.72 (s, 6H); 0.52 (s, 6H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 178.0, 177.1, 165.0, 164.8, 154.3, 143.9, 142.9, 142.3, 128.9, 127.4, 126.2, 124.7, 123.3, 122.7, 122.0, 121.1, 116.5, 115.2, 96.2, 91.2, 90.3, 74.1, 68.7, 55.0, 54.41, 54.37, 54.25, 31.9, 31.0, 30.7, 29.7 (m), 29.5, 29.3, 29.2,

28.8, 28.7, 26.4, 26.3, 22.7, 17.0, 16.8, 16.7, 16.5, 14.1, 9.8, 9.5 ppm; HRMS calcd for C₁₁₈H₁₆₂O₂₀ 1899.1659, found 1899.1586.

(*M*)-16: [α]_D −790 (*c* 0.090, CH₂Cl₂); IR (CCl₄) 2928, 2856, 1798, 1750 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.44 (m, 4H); 7.06 (d, 2H, *J* = 8.5 Hz); 6.81 (s, 2H); 6.11 (d, 2H, *J* = 8.4 Hz); 4.40−4.28 (m, 4H); 4.15 (m, 2H); 4.04 (m, 2H); 2.66 (m, 2H); 2.34 (m, 2H); 2.1−1.94 (m, 12H); 1.84 (m, 2H); 1.59 (m, 8H); 1.5−1.1 (m, 88H); 0.94−0.86 (m, 18H); 0.60 (s, 6H); 0.44 (s, 6H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ 178.1, 177.6, 165.2, 165.0, 154.6, 143.7, 142.8, 142.0, 128.4, 127.5, 125.6, 124.8, 123.1, 122.4, 122.1, 121.1, 115.8, 114.5, 96.0, 91.2, 89.4, 74.0, 68.7, 55.0, 54.4 (2 peaks), 54.3, 31.9, 31.0, 30.7, 29.7 (m), 29.5, 29.3, 29.2, 29.0, 28.5, 26.3, 22.7, 17.0, 16.8, 16.2, 16.0, 14.1, 9.8, 9.5 ppm; HRMS calcd for C₁₁₈H₁₆₂O₂₀ 1900.1694, found 1900.1702.

Preparation of Nonracemic Helicenes 15 from Tetraesters 16. *n*-BuLi (1.24 mL of a 2.5 M solution in hexane, 3.1 mmol) was added to a solution of (*P*)-**16** (0.236 g, 0.124 mmol) in THF (10 mL) that had been cooled in a dry ice/acetone bath. After this had stirred for 25 min at −78 °C, the reaction was quenched at this temperature by the addition of saturated aqueous NH₄Cl, and ca. 20 mL of HCl (1 M) and CH₂Cl₂ were added. After a wash with HCl (0.5 M) and two washes with H₂O, the organics were dried (Na₂SO₄). Chloranil (0.100 g, 0.40 mmol) was then added, whereupon the solution turned brown-red. After 15 min, the solution was filtered, washed twice with saturated aqueous NaHCO₃, and dried (Na₂-SO₄). The solvent was removed under reduced pressure, and the residue chromatographed (4:1 CH₂Cl₂/hexanes), giving after trituration with MeOH 0.130 g (89%) of (*P*)-**15**, mp 65−67 °C. The ¹H NMR spectrum was identical to that of the racemic material. [α]_D: +1480 (*c* 0.050, CH₂Cl₂). The same reaction conditions applied to the other diastereomer, (*M*)-**16**, gave (*M*)-**15** in 74% yield. [α]_D: −1480 (*c* 0.050, CH₂Cl₂). UV−vis (CH₂Cl₂, *c* = 2.0 × 10⁻⁵ M): λ_max (nm) (log ε) 252 (4.79), 300 (4.51), 358 (4.17), 445 (3.69), 570 (2.85). CD (*c* = 2.0 × 10⁻⁵ M): nm ([θ]), 243 (1.42 × 10⁻⁵), 264 (−1.25 × 10⁻⁵), 295 (3.53 × 10⁻⁵), 328 (−1.02 × 10⁻⁴), 360 (−2.57 × 10⁻⁵), 454 (−2.9 × 10⁻⁴), 571 (−1.65 × 10⁻⁴).

Supporting Information Available: Graphs showing the ¹H and ¹³C NMR and IR spectra of 3,6-diacetyl-9,10-(diphenylmethylenedioxy)phenanthrene, **7**−**13**, (*P*)-(+)-**14**, (*M*)-(−)-**14**, **15**, (*P*)-(+)-**16**, and (*M*)-(−)-**16**, and the UV−vis and CD spectra of (*M*)-**13**, (*M*)-(−)-**14**, (*M*)-**15**, and (*M*)-(−)-**16**. (43 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.