First Friedel−Crafts Diacylation of a Phenanthrene as the Basis for an Efficient Synthesis of Nonracemic [7]Helicenes†

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Reported are the first examples of Friedel−Crafts reactions used to prepare 3,6-diacylphenanthrenes. 9,10-Dimethoxyphenanthrene gives its 3,6-diacetyl derivative in good yield and in large amounts. The ketone's triisopropylsilyl enol ether when combined with 1,4-benzoquinone forms a [7]helicenebisquinone. This bisquinone's reduction product, a bishydroquinone, when combined with methanolic HCl gives the [7]helicene whose peripheral side chains are all methoxyls but whose interior hydroxyls remain. The diastereomeric (1*S*)-(−)-camphanates can be separated by crystallization. Their structures, analyzed by X-ray diffraction, demonstrate that the camphanates' lactone functions point away from the ring system when the helicene has the (*P*) configuration and toward it when the helicene has the (*M*) configuration. This is because the camphanates' O=C−C−O dihedral angles are, as expected, close to 0° in the former and close to 180° in the latter. Other derivatives of 3,6-diacetylphenanthrene and of [7]helicenebisquinone are prepared, and the crystal structure of one of the latter is analyzed.

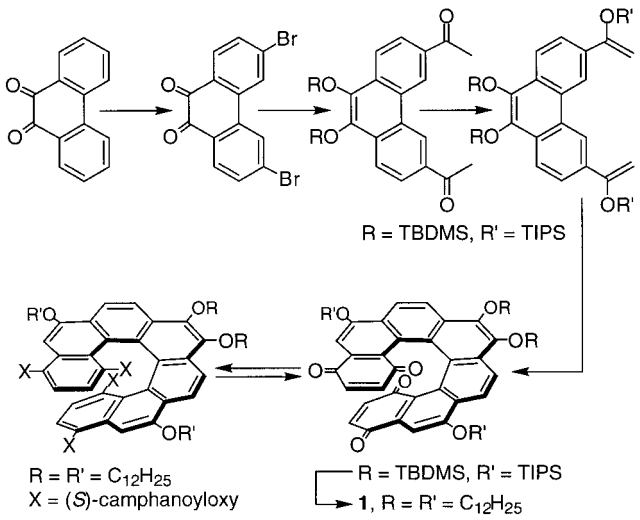
Introduction

Since the combination of enol ethers of bis(aryl methyl ketones) with 1,4-benzoquinone has recently made functionalized helicenes available in quantity,[1] and a general procedure that resolves them into their enantiomers has made them available in nonracemic form,[1] these helicenes have been used as the basis for materials that have novel structural and optical properties,[1d,2] that act as catalysts for enantioselective transformations,[3] and that serve as chiral derivatizing agents.[4] The reaction with 1,4-benzoquinone used to prepare these helicenes was applied first to make [5]- and [6]carbohelicenes,[1a,d,5,5] but, remarkably, it also is effective in giving [7]carbohelicenes[1b] and a variety of heterohelicenes.[1c,6]

The preparation of [7]helicene **1**, in abundance and nonracemic, is outlined in Scheme 1.[1b] It depends on threediscoveries: (1) a way to make 3,6-diacetylphenanthrenes and in large amounts; (2) the observation that, in the reaction with 1,4-benzoquinone, silyl enol ethers give higher yields than alkyl enol ethers;[7] and (3) the finding that the procedure previously applied to resolve a [6]carbohelicene also succeeds for the [7].[8]

Although other approaches to [7]helicenes are being developed, some of which[9] bypass the photocyclization of

Scheme 1



† Dedicated to Professor Jaroslav Jonas of Masaryk University, Brno, Czech Republic.

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(3) Dreher, S. D.; Katz, T. J.; Lam, K.-C.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 815.

(4) Weix, D. J.; Dreher, S. D.; Katz, T. J. *J. Am. Chem. Soc.* **2000**, *122*, in press.

(5) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1990**, *31*, 3983.

(6) Phillips, K. E. S.; Katz, T. J.; Jokusch, S.; Turro, N. J.; Lovinger, A. J. Manuscript in preparation.

(7) The discovery was subsequently applied successfully in a number of syntheses. See: refs 1a and 1c. Silyl enol ethers of aryl methyl ketones had been used as dienes prior to the work in refs 1a−c, but that they gave higher yields than other enol ethers had not been reported. See: (a) Willmore, N. D. Ph.D. Dissertation, Columbia University, New York, 1994. (b) Kita, Y.; Yasuda, H.; Tamura, O.; Tamura, Y. *Tetrahedron Lett.* **1984**, *25*, 1813. (c) Kita, Y.; Okunaka, R.; Honda, T.; Shindo, M.; Tamura, O. *Tetrahedron Lett.* **1989**, *30*, 3995.

(8) This discovery was also applied in many other syntheses. See: Thongpanchang, T.; Paruch, K.; Katz, T. J.; Rheingold, A. L.; Lam, K.-C.; Liable-Sands, L. *J. Org. Chem.* **2000**, *65*, 1850.

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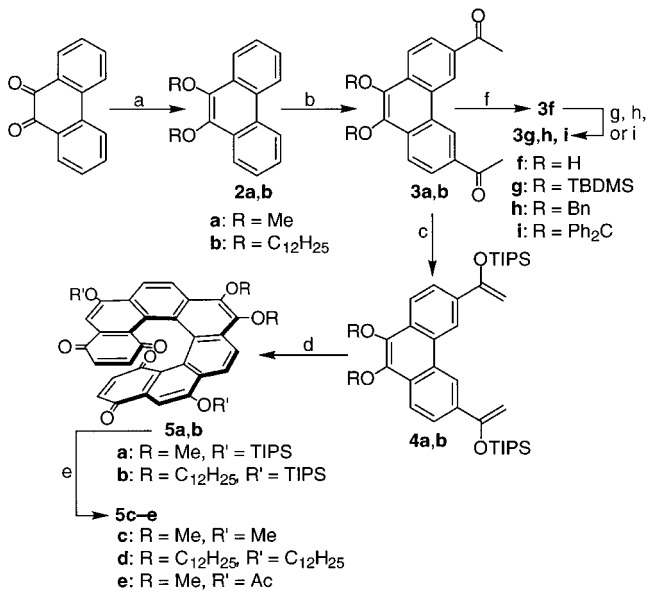
stilbenes,[10] the procedure in Scheme 1 is the only one reported to give a derivative of this structure on a practical scale. Because it could therefore be useful, and indeed it has already been used to prepare a helical phthalocyanine,[2d] we considered whether and how it might be improved and extended. The work described below resulted in two significant improvements. One is the discovery of an easier, cheaper, and less hazardous way to prepare derivatives of 3,6-diacetylphenanthrene. Two is the discovery of a way that, with the aid of the Russig−Laatsch reaction[11] and an appropriate choice of side chains, circumvents the need for chromatography to resolve [7]helicene enantiomers. The design of the procedure for resolution also resulted for the first time in the crystallization and X-ray diffraction analyses of both diastereomers of a 1-helicenol camphanate, and these analyses demonstrate more vividly than was previously possible the theory proposed to account for the effectiveness of camphanates as resolving agents.[8] The crystal structures also confirm the absolute stereochemistries previously assigned to [7]helicenes on the basis of their optical properties.[1b] The structure of a helicenebisquinone also has been analyzed, and it has been found to consist (for the racemic material) of layers in which (*M*)- and (*P*)-helicenes alternate, stacked with single enantiomers perfectly superimposed in individual columns.

The key to the synthesis is the discovery of a way to prepare 3,6-diacetylphenanthrenes by a Friedel−Crafts acylation. Surprisingly, there seems to be no previous report of a phenanthrene being transformed in useful and isolable amounts into a 3,6-disubstituted derivative, whether by acylation or by any electrophilic substitution. The Friedel−Crafts acetylation when applied to phenanthrene itself gives mixtures of 2-, 3-, and 9-acetylphenanthrenes.[12] Benzoylation gives 1-benzoylphenanthrene in up to 19% yield when the solvent is CS_2, and it gives a mixture consisting mainly of 3-benzoylphenanthrene, along with the 1- and 2-isomers, when the solvent is nitrobenzene.[12b,13] Of other possible electrophilic substitutions, the sulfonation of phenanthrene-3-sulfonic acid gives mainly (but not exclusively) the 3,6-disulfonic acid.[14] However, the starting phenanthrene-3-sulfonic acid can itself be obtained from the sulfonation product of phenanthrene in only ca. 25% yield and then only from a mixture including a comparable amount of the 2-sulfonic acid.[15] The major disulfonic acid formed by 9,10-dimethylphenanthrene is the 3,6 isomer, but it is mixed with much more of the 3- and 2-monosulfonic acids.[16] Nitration of 9,10-diacetoxyphenanthrene gives the 2,7-dinitro derivative.[17]

Scheme 2[a]



[a] Reaction conditions and yields: (a) $Na_2S_2O_4$, KOH or NaOH, Bu_4NBr, Me_2SO_4 or $C_{12}H_{25}Br$, H_2O, THF (yields: **2a**, 82%; **2b**, 80%). (b) AcCl, $AlCl_3$, CH_2Cl_2 (yields: **3a**, 81%; **3b**, 66%). (c) TIPSOTf, TEA, CH_2Cl_2 (yield: 100%). (d) 1,4-benzoquinone, heptane, reflux (yields: **5a**, 23%; **5b**, 20%). (e) R′I or AcCl (+DMAP), CsF, DMF (yields: **5c**, 97%; **5d**, 82%; **5e**, 96%). (f) $AlCl_3$, CH_2Cl_2 (yield: 78%). (g) TBDMSCl, imidazole, $(CH_2Cl)_2$, reflux (yield: 75%). (h) BnBr, K_2CO_3, acetone, reflux (yield: 54%). (i) Ph_2CCl_2, 180 °C (yield: 74%).

Results

As Scheme 2 summarizes, 3,6-diacetylphenanthrenes can be prepared easily if the Friedel−Crafts acetylation is applied to 9,10-dialkoxyphenanthrenes (in our case the 9,10-dimethoxy and 9,10-didodecyloxy derivatives), compounds that themselves can be made in good yields from 9,10-phenanthrenequinone by reduction and alkylation. These methyl ketones can then be transformed quantitatively by reaction with triisopropylsilyl triflate (TIPS triflate) into their bis(TIPS enol ethers), which with 1,4-benzoquinone give the [7]helicenebisquinones **5a** and **5b**.

The TIPS substituents in these helicenes can be replaced in one step by alkyl or acyl groups (methyl and dodecyl were the alkyls studied, and acetyl was the acyl studied) when the helicenes are combined with CsF and either alkyl iodide or acyl chloride in DMF[18] to which, in the case of the acyl chloride, DMAP has been added.[19] Also, the methyls of **3a**'s ethers can be replaced by other

(9) A method that uses the acetylene trimerization to give hydro derivatives is described in the following: (a) Stará, I. G.; Starý, I.; Kollárovič, A.; Teplý, F.; Vyskočil, Š.; Šaman, D. *Tetrahedron Lett.* **1999**, *40*, 1993. (b) Stará, I. G.; Starý, I.; Kollárovič, A.; Teplý, F.; Šaman, D.; Tichý, M. *J. Org. Chem.* **1998**, *63*, 4046. One that cyclizes a 3,3′-dimethyl-4,4′-biphenanthryl is described in the following: (c) Gingras, M.; Dubois, F. *Tetrahedron Lett.* **1999**, *40*, 1309.

(10) For uses and deficits of photocylization procedures in syntheses of [7]helicenes, see: (a) Mallory, F. B.; Mallory, C. W. *Organic Reactions*; Wiley: New York, 1984; Vol. 30, p 1. (b) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63. (c) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.* **1986**, *27*, 2231. (d) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769. (e) Owens, L.; Thilgen, C.; Diederich, F.; Knobler, C. B. *Helv. Chim. Acta* **1993**, *76*, 2757. (f) Howarth, J.; Finnegan, J. *Synth. Commun.* **1997**, *27*, 3663.

(11) See: ref 3 and Dreher, S. D.; Paruch, K.; Katz, T. J. *J. Org. Chem.* **2000**, *65*, 806 and references therein.

(12) (a) Mosettig, E.; van de Kamp, J. *J. Am. Chem. Soc.* **1930**, *52*, 3704. (b) Gore, P. H. *J. Org. Chem.* **1957**, *22*, 135. (c) Blin, P.; Bunel, C.; Maréchal, E. *J. Chem. Res., Synop.* **1978**, 206. (d) Fernández, F.; Gómez, G.; López, C.; Santos, A. *J. Prakt. Chem.* (*Leipzig*) **1989**, *331*, 15.

(13) Clar and Kelly, in a report that differs greatly from those in ref 12, asserted that phthalic anhydride and aluminum chloride diacylate phenanthrene in the 3 and 6 positions and that benzoyl chloride plus $AlCl_3$ without solvent give a pure dibenzoylphenanthrene. See: Clar, E.; Kelly, W. *J. Am. Chem. Soc.* **1954**, *76*, 3502.

(14) Fieser, L. F. *J. Am. Chem. Soc.* **1929**, *51*, 2471.

(15) Fieser, L. F. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 482.

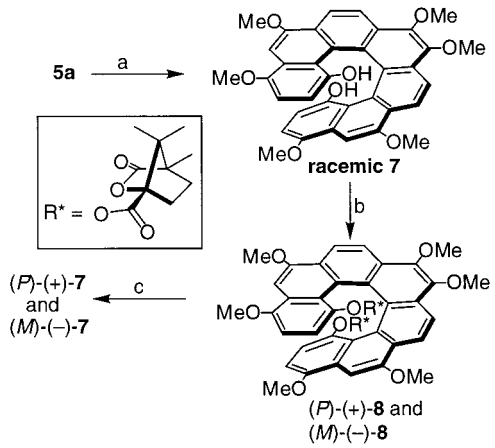
(16) Cerfontain, H.; Koeberg-Telder, A.; Laali, K.; Lambrechts, H. J. A. *J. Org. Chem.* **1982**, *47*, 4069.

(17) Schmidt, J.; Schairer, O. *Chem. Ber.* **1923**, *56*, 1331.

(18) For similar replacements by alkyl groups, see ref 1b and footnote 27 therein.

(19) Hassner, A. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 3, p 2022.

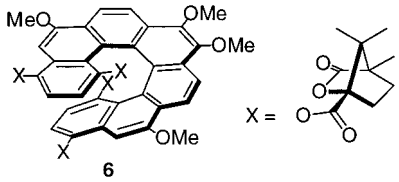
Scheme 3[a]



[a] Reaction conditions and yields: (a) $Na_2S_2O_4$, Bu_4NBr, EtOAc, CH_2Cl_2, H_2O, then HCl, MeOH, 60 °C (yield: 84%). (b) (1*S*)-camphanoyl chloride, DMAP, TEA, $(CH_2Cl)_2$, reflux (yields: (*P*)-**8**, 92%; (*M*)-**8**, 88%). (c) BuLi, THF, −78 °C, then aqueous NH_4Cl (yields:(*P*)-**7**, 96%; (*M*)-**7**, 97%).

alkyl or silyl groups, but it requires two steps. In the first, aluminum chloride in methylene chloride removed the methyls,[20] giving diol **3f**, which in a second step was alkylated with benzyl bromide or dichlorodiphenylmethane or silylated with *tert*-butyldimethylsilyl chloride. These last replacements are significant because when the benzyl or silyl groups were introduced earlier in the synthesis, as the ethers in **2**, they did not survive the Friedel−Crafts acylation. Yet, the silyl derivative **3g** is the one[1b] among **3a**, **3b**, **3g**, and **3i** that gives the [7]helicene skeleton in highest yield, and the diphenylmethylene derivative **3i** is one whose protecting group, after **3i** is transformed into the helicene, can be removed selectively, a property that was used in a synthesis of a helical phthalocyanine.[2d] (The benzyl derivative **3h** might be used in the same way.)

To obtain nonracemic helicenes, **5c** was transformed into a mixture of tetracamphanates **6** by the action of



zinc, (1*S*)-(−)-camphanoyl chloride, and TMEDA in boiling toluene.[1b] However, attempts to separate these diastereomers by means of either chromatography or crystallization failed. In contrast, an alternative method (Scheme 3) that had proven to be the simplest to resolve other helicene enantiomers[3,11] was successful. That method employs the Russig−Laatsch reaction.[3,11] Thus, when **5a** is reduced with aqueous sodium dithionite and then warmed to 60 °C with methanolic HCl, it gives **7**, a molecule with methyls attached to all of the oxygens on the periphery, including those that had been attached to triisopropylsilyl groups. However, there are no methyls attached to the oxygens on the inside of the ring system. The yield is 84%. The remaining hydroxyls can then be

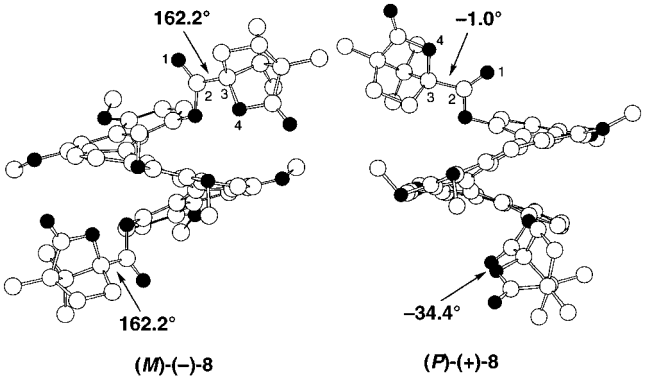


Figure 1. Structures of (*M*)-(−)-**8** and (*P*)-(+)-**8** according to X-ray diffraction analyses. The O=C−C−O dihedral angles are shown. Oxygen atoms are shown in black and carbons in white. Hydrogens have been omitted for clarity.

esterified by reaction with (1*S*)-(−)-camphanoyl chloride. The dextrorotatory dicamphanate crystallizes from a mixture of toluene and cyclohexane, and the levorotatory diastereomer can be recovered from the mother liquor. The yields are high, 92% for the (+) isomer and 88% for the (−).

It was possible to grow single crystals of these diastereomers, allowing the structures of both to be analyzed by X-ray diffraction. These structures, displayed in Figure 1, identify the absolute stereochemistries of the diastereomers, for the absolute stereochemistries of their camphanate moieties are known to be those shown.[21] They also provide striking evidence for a theory about the conformations of camphanate groups with respect to helicene ring systems.[8] In accord with the theory, the dihedral angles of the camphanates' O=C−C−O groups (labeled in half of the molecule as atoms 1, 2, 3, and 4) are large when the helicene has the (*M*) configuration (the angles are 162.2° for both its camphanates) and small (−1.0 and −34.4°) when the helicene has the (*P*) configuration.

Single crystals of racemic **5e** also were grown and analyzed by X-ray diffraction. Their structure exhibits interesting features. It confirms the assigned connectivity, but more interestingly (Figure 2), it shows that the individual molecules are arrayed in layers, each layer consisting of one enantiomer, the opposite of that in the adjacent layer. Moreover, the helix axes of molecules of each enantiomeric configuration are perfectly superimposed, which means that helices twisting in the same direction are stacked in parallel long columns. The distance between identical molecules in one column is 11.67 Å.

One experiment that failed was to convert the enantiomers of **7** into enantiomerically pure samples of **5c**. The analogous transformation works well when all of the side chains are dodecyls,[11] but when they are methyls, oxidation with cerric ammonium nitrate gives a complex mixture from which **5c** could be isolated in only 10−21% yield. When the oxidant was bis(trifluoroacetoxy)iodobenzene, the results were similar. DDQ in either pure MeOH or a mixture of MeOH and CH_2Cl_2 gave only a trace of **5c**, and air in the presence of $CuCl_2$ gave none at all.

(20) (a) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 30 and 31. (b) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.

(21) Buckingham, J.; Hill, R. A. *Atlas of Stereochemistry, Absolute Configurations of Organic Molecules*, 2nd ed., supplement; Chapman and Hall: New York, 1986; p 62.

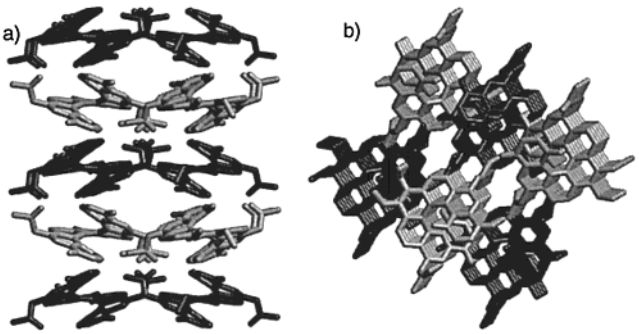


Figure 2. Structure of crystals of racemic **5e** according to X-ray diffraction analysis. The (*P*) enantiomers are shown dark; the (*M*) enantiomers are shown light. Only three of the molecules in each layer are displayed in these pictures. (a) Horizontal view of five layers. (b) Vertical view of five layers, each consisting of three molecules of the (*M*) enantiomer, interleaved with five layers, each consisting of three molecules of the (*P*) enantiomer. To show depth, the latter view is from a point displaced from the perpendicular to the layers.

Discussion

Considering how easy it is to obtain the 3,6-diacetyl derivatives **3a** and **3b** from the 9,10-dialkoxyphenanthrenes **2a** and **2b**, it is surprising that previously not only was there no clean Friedel−Crafts acylation of a phenanthrene, but neither was there any electrophilic substitution of 9,10-dialkoxyphenanthrene. The reason is that almost no 9,10-dialkoxy derivatives of phenanthrene had previously been prepared, and of those few that had, the amounts were either small or not stated.[22] Perhaps the reason for the dearth of 9,10-dialkoxyphenanthrenes is that the procedure used here for the alkylation, employing a two-phase system and a phase-transfer catalyst, is critical to the success of the transformation, and it was unknown in the early years of the last century. In any case, the availability of 9,10-dialkoxyphenanthrenes and the discovery that 9,10-dimethoxy- and 9,10-didodecyloxyphenanthrene can be acetylated easily to 3,6-diacetyl derivatives suggest that 3,6-diacylated 9,10-dialkoxyphenanthrenes in general will be easy to obtain. Moreover, because they are available so simply, it is likely that other uses will be found for them.

The only previous synthesis for such derivatives was the one in Scheme 1, developed by Fox.[1b] It works well and can be used to make significant quantities of material. However, the Stille coupling it employs is less practical than the Friedel−Crafts reaction used here because the reagents are more expensive, tin compounds are toxic, and the removal of side products, mainly Bu_3SnBr, requires chromatography. For the preparation reported here, no chromatographic purification is required.

The absolute configurations were previously assigned to related [7]helicenes on the basis of correlations between their circular dichroism spectra and those of helicenes, whose absolute configurations are known.[1b] The structures determined by X-ray diffraction of (+)- and (−)-**8** (Figure 1) confirm these assignments.

The structures also provide the strongest evidence for the theory proposed to account for why camphanates are excellent resolving agents for helicen-1-ols.[8] According to that theory, the O=C−C−C−O dihedral angles of the camphanate groups should, as indicated in Figure 1, be ca. 180° when the helicene has the (*M*) configuration and ca. 0° when the helicene has the (*P*) configuration. Previously, this theory was supported by analyses of a number of structurally different helicenol camphanates of both helicities by X-ray diffraction and by ROESY NMR supplemented by molecular mechanics calculations. However, until now, it has not been possible to use X-ray diffraction analyses to compare the molecular structures of two stereoisomers, molecules that differ *only* in stereochemistry. Figure 1 does, and by showing that the dihedral angles are approximately those theorized, it provides the clearest evidence for the hypothesis that the reason (1*S*)-camphanates of (*P*)-helicen-1-ols move much more slowly upon silica gel chromatography than the corresponding camphanates of (*M*)-helicen-1-ols is that the lactone groups in the former point away from the helicene and in the latter point toward the helicene. Figure 1 should also make this clear.

Also worth noting is that the diastereomers of **8** crystallize. Previously, a number of diastereomeric helicene camphanates have been separated, but when the molecules have many long aliphatic side chains, the separations could be achieved only by means of chromatography. That the diastereomers can be separated by crystallization when the side chains are methyls was demonstrated in two cases.[3,11] The example of **8** is the third. As expected on the basis of the conformational analysis described, the (*P*) diastereomer of **8** is less soluble than the (*M*) in a mixture of toluene and cyclohexane, and its R_f is lower.

The observation that the diastereomers of tetracamphanates **6** could not be separated, while those of dicamphanate **8** could be easily separated, accords with the proposition that it is only the camphanates on the insides of the helicene structures that change conformation when the direction in which the helicene twists changes.[8]

Except for one analysis in a dissertation,[24] the structure displayed in Figure 2 is the first of a helicenebisquinone to be analyzed in detail, although two possibly liquid-crystalline examples of nonracemic helicenebisquinones have been shown by X-ray and electron diffraction to be organized in hexagonally packed columns of closely stacked molecules whose helix axes are superimposed.[6,25]

Conclusion

9,10-Phenanthrenequinone can be sequentially reduced, alkylated, and acetylated, giving good yields of 3,6-

(22) The best reported yield of 9,10-dimethoxyphenanthrene is, after two chromatographies, 51%, and the amount prepared was 880 mg.[23a] The reductant for the phenanthrenequinone was sodium in diglyme, and dimethyl sulfate was the alkylating agent. Methyl iodide gave a 2.6% yield of noncrystalline product.[23b] A cathodic reduction of the quinone, followed by methyl iodide, was said to give a 49% yield, but no amounts or details were specified.[23c] Other reported syntheses of 9,10-dimethoxyphenanthrene do not state yields.[23d,e] The only other reported alkylations of phenanthrene-9,10-diol are by 1-chloro-2-diethylaminoethane, in 10% yield,[23f] and by 1,2-di(bromomethyl)-benzene, in 22% yield.[23g]

(23) (a) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1972**, 822. (b) Dannenberg, H.; Keller, H.-H. *Chem. Ber.* **1967**, *100*, 23. (c) Adams, C.; Kamkar, N. M.; Utley, J. H. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1767. (d) Sucharda-Sobczyk, A.; Syper, L. *Rocz. Chem.* **1975**, *49*, 749. (e) Santamaria, J.; Ouchabane, R. *Tetrahedron* **1986**, *42*, 5559. (f) Goldschmidt, S.; Schmidt, W. *Chem. Ber.* **1922**, *55*, 3197. (g) Fourneau, E.; Matti, J. *Bull. Soc. Chim. Fr.* **1942**, 633. (h) Kurebayashi, H.; Mine, T.; Harada, K.; Usui, S.; Okajima, T.; Fukazawa, Y. *Tetrahedron* **1998**, *54*, 13495.

(24) Willmore, N. D. Ph.D. Dissertation, Columbia University, New York, 1994. The structure Willmore describes, of racemic [5]helicenebisquinone, like that of racemic **5e**, consists of interleaved columns of single enantiomers.

(25) Lovinger, A. J.; Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 264.

diacetyl-9,10-dialkoxyphenanthrenes. These are expeditiously transformed into [7]helicenebisquinones and then into easily resolved helicenyl camphanates. X-ray diffraction analyses confirm a theory explaining why camphanates are excellent resolving agents.

Experimental Section

THF and heptane were distilled from Na/Ph_2CO, and CH_2Cl_2 and Et_3N from CaH_2. DMF (anhydrous), $Na_2S_2O_4$ (tech, 85%), $AlCl_3$ (98%), AcCl (98%), 1-bromododecane (97%), and 1-iododododecane were purchased from Aldrich; phenanthrenequinone (95%) and CsF (99%) from Acros; and TIPSOTf (97%) from GFS Chemicals. 1,4-Benzoquinone (98%, Aldrich) was purified by slurrying it in CH_2Cl_2 with 2 times its weight of basic alumina, filtering it through Celite, and drying it under a vacuum. (1*S*)-(−)-Camphanoyl chloride was synthesized.[26] The term "chromatography" refers to flash chromatography on silica gel.[27]

3,6-Diacetyl-9,10-dimethoxyphenanthrene (3a). A mixture of 9,10-phenanthrenequinone (52.0 g, 0.250 mol), Bu_4NBr (25.8 g, 0.080 mol), $Na_2S_2O_4$ (130 g, 0.75 mol), THF (0.5 L), and H_2O (0.5 L) in a 4 L separatory funnel was shaken for 5 min, and then dimethyl sulfate (123 mL, 1.30 mol) was added, followed by aqueous sodium hydroxide (128 g, 3.20 mol, in 250 mL of H_2O). The mixture was shaken for 15 min, during which, after 3 min, 300 g of ice was added to keep the mixture at ambient temperature. The aqueous layer was separated and extracted with EtOAc (3 × 200 mL). The combined organics were washed with water (300 mL), 14% aqueous NH_3 (2 × 200 mL), and brine (100 mL); dried over Na_2SO_4; and filtered. Removal of the solvents and drying in a vacuum gave crude 9,10-dimethoxyphenanthrene (**2a**) as a thick brown oil (48.7 g, 82%), which was used for the next step.

The oil, dissolved in CH_2Cl_2 (250 mL) plus acetyl chloride (250 mL) in a 3 L three-necked flask fitted with an HCl trap, was stirred and cooled by means of an ice bath. The cooling bath was removed, and over a period of 5 min, $AlCl_3$ (90 g, 0.67 mol) was added in portions to the stirred solution. The mixture was then stirred for 15 min at 25 °C and then carefully poured onto 2 L of crushed ice. The aqueous layer was extracted with CH_2Cl_2 (3 × 250 mL), and the combined organics were washed with water (250 mL) and aqueous 5% Na_2CO_3 (250 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residual solid was dried in a vacuum at 100 °C, shaken with MeOH (250 mL), filtered, and washed with 150 mL of MeOH. Drying overnight in a vacuum at 100 °C afforded 52.9 g (66% based on phenanthrenequinone) of a pale yellow solid. Mp: 161−162 °C, after recrystallization from MeOH. IR (CCl_4): 2939, 1687, 1611, 1318, 1059 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.31 (d, J = 1.3 Hz, 2H), 8.32 (d, J = 8.5 Hz, 2H), 8.20 (dd, J = 8.5, 1.3 Hz, 2H), 4.13 (s, 6H), 2.82 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 198.0, 145.5, 134.7, 132.6, 128.5, 126.3, 123.6, 122.8, 61.1, 27.0 ppm. UV−vis (CH_3CN, $c = 1.81 \times 10^{-4}$ M): λ_{max} (log ϵ) 266 (4.05), 325 nm (4.06). Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.52, H; 5.66.

3,6-Diacetyl-9,10-dihydroxyphenanthrene (3f). A solution of **3a** (6.44 g, 20.0 mmol) in CH_2Cl_2 (30 mL) was added under N_2 to a stirred mixture of $AlCl_3$ (11.2 g, 0.084 mol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at 0 °C for 5 min and at 25 °C for 24 h and then poured onto a slush of ice and concentrated HCl (4:1, 500 mL). The solid was filtered, washed on the filter with 1 M HCl (200 mL), and dissolved in acetone (200 mL). The acetone solution was filtered and dried (Na_2SO_4, 20 g), and the solvent was evaporated. The remaining solid was suspended in CH_2Cl_2 (500 mL), filtered, and washed on the filter with CH_2Cl_2 (100 mL). Drying in a vacuum at 100 °C gave 4.60 g (78%) of a green solid. Mp: >250 °C. IR (KBr): 3391, 3167, 1676, 1592, 1357, 1236, 1030 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 9.71 (s, 2H), 9.32 (s, 2H), 8.28 (d, J = 8.6 Hz, 2H), 8.15 (d, J = 8.6 Hz, 2H), 2.8 (s, 6H). ^{13}C NMR (DMSO-d_6, 75 MHz): 197.9, 136.8, 132.9, 130.47, 125.6, 125.5, 123.9, 122.0, 27.1 ppm. HRMS (FAB): m/z calcd for $C_{18}H_{14}O_4$, 294.0892; found, 294.0885.

3,6-Diacetyl-9,10-bis(*tert*-butyldimethylsiloxy)phenanthrene (3g). A mixture of **3f** (150 mg, 0.510 mmol), *t*-$BuMe_2$-SiCl (230 mg, 1.53 mmol), and imidazole (173 mg, 2.55 mmol) in 1,2-dichloroethane (5 mL) was stirred and refluxed under N_2 by heating in an oil bath at 100 °C for 2 days. The mixture was cooled to 25 °C, CH_2Cl_2 (10 mL) was added, and the mixture was washed with 1 M HCl (2 × 30 mL). The aqueous washings were reextracted with CH_2Cl_2 (5 mL), and the combined organics were washed with saturated aqueous $NaHCO_3$ (30 mL) and dried over Na_2SO_4. Filtration, evaporation of the solvent, and drying in a vacuum gave a cream-colored solid (200 mg, 75%) whose ^1H and ^{13}C NMR spectra were identical to those published.[1b]

3,6-Diacetyl-9,10-bis(benzyloxy)phenanthrene (3h). A solution of benzyl bromide (0.242 mL, 2.04 mmol) in acetone (3 mL), added under N_2 to a mixture of **3f** (150 mg, 0.51 mmol) and K_2CO_3 (282 mg, 2.04 mmol), was stirred and refluxed under N_2 for 2 days. CH_2Cl_2 (10 mL) was added, and the mixture was filtered through a pad of Celite. The solvents were evaporated, hexane (20 mL) and sand (2 g) were added to the residue, and the mixture was shaken for 15 min. The solid was filtered, washed with hexane (20 mL), and dissolved in CH_2Cl_2 (20 mL). The solution was filtered, the solvent was evaporated, and the residue was dried in a vacuum, boiled with MeOH (5 mL), and, after cooling to 25 °C, filtered and washed on the filter with MeOH (5 mL). Drying in a vacuum afforded 130 mg (54%) of **3h**, a pale yellow solid. Mp: 165−167 °C. IR (CCl_4): 2927, 1688, 1610, 1431, 1357, 1316, 1046 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.31 (s, 2H), 8.33 (d, J = 8.6 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 6.5 Hz, 4H), 7.39 (m, 6H), 5.32 (s, 4H), 2.81 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 197.9, 145.0, 136.8, 134.7, 132.7, 128.7, 128.4, 126.3, 123.6, 123.2, 75.6, 27.0 ppm. UV−vis (CH_3CN, $c = 1.03 \times 10^{-4}$ M): λ_{max} (log ϵ) 206 (4.27), 262 (4.28), 283 (sh, 4.24), 337 nm (4.17). HRMS (FAB): m/z + H calcd for $C_{32}H_{26}O_4$, 474.1829; found, 474.1851.

3,6-Diacetyl-9,10-(diphenylmethylenedioxy)phenanthrene (3i). A mixture of **3f** (100 mg, 0.34 mmol) and Ph_2-CCl_2 (0.50 mL, 2.61 mmol) was stirred under N_2 at 180 °C for 10 min. The resulting brown solution was cooled to 25 °C and then mixed with hexane (10 mL). The solid was filtered, washed on the filter with hexane (10 mL), dissolved in a minimal amount of CH_2Cl_2, and loaded onto a column (1 in. × 5 in.) of neutral alumina. Chromatography with CH_2Cl_2 afforded 115 mg (74%) of a pale yellow solid whose ^1H and ^{13}C NMR spectra were identical to those published.[1b]

9,10-Didodecyloxyphenanthrene (2b). A mixture of phenanthrenequinone (10.0 g, 0.048 mol), Bu_4NBr (10.0 g, 0.031 mol), and $Na_2S_2O_4$ (48.0 g, 0.276 mol) in H_2O (200 mL) and THF (200 mL) was shaken for 5 min. Dodecyl bromide (35.9 g, 0.144 mol) was added, followed by aqueous KOH (40.0 g, 0.713 mol, in 200 mL of H_2O). The mixture was shaken for 2 days, poured into H_2O (1.5 L), and extracted with EtOAc (2 × 200 mL and 1 × 100 mL). The extracts were washed with H_2O (2 × 1 L) and brine (100 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was shaken for 15 min with 500 mL of 100% EtOH. The solid was filtered and washed with EtOH (2 × 100 mL). Drying in a vacuum afforded a pale-rose-colored solid (20.9 g, 80%), which was used directly for the next step. An analytically pure sample (a white solid, mp 49−50 °C) was obtained by column chromatography (silica gel, 5:1 hexane/EtOAc). IR (CCl_4): 2928, 2856, 1327, 1113 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.63 (m, 2H), 8.24 (m, 2H), 7.60 (m, 4H), 4.21 (t, J = 6.7 Hz, 4H), 1.91 (m, 4H), 1.57 (m, 4H), 1.40−1.27 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 143.2, 129.6, 128.6, 126.7, 126.0, 122.6, 122.3, 73.6, 31.9, 30.5, 29.7, 29.6, 29.4, 26.3, 22.7, 14.1 ppm. UV−vis (CH_2Cl_2, $c = 1.05 \times 10^{-4}$ M): λ_{max} (log ϵ) 247 (4.27), 258 (4.21), 281 (4.01), 293 (4.04), 328 (2.97), 345 nm (3.00). Anal. Calcd for $C_{38}H_{58}O_2$: C, 83.46; H, 10.69. Found: C, 83.33; H, 10.68.

(26) Gerlach, H.; Kappes, D.; Boeckman, R. K., Jr.; Maw, G. N. *Org. Synth.* **1993**, *71*, 48.

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

3,6-Diacetyl-9,10-didodecyloxyphenanthrene (3b). $AlCl_3$ (18.6 g, 140 mmol) was added in portions during 1 min to a solution of 9,10-didodecyloxyphenanthrene (20.5 g, 37.6 mmol) in CH_2Cl_2 (95 mL) and CH_3COCl (130 mL) that was cooled to 5 °C. The mixture was stirred for 8 min at 25 °C and then poured slowly onto 800 mL of crushed ice. Brine (50 mL) was added, the organic layer was separated, and the aqueous part was extracted with CH_2Cl_2 (2 × 200 mL). The combined organics were washed with water (2 × 500 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (100 mL); dried over Na_2SO_4; and filtered. After the solvent had been evaporated, the residue was dried in a vacuum at 25 °C, suspended in MeOH (300 mL), and shaken for 45 min. The solid was filtered, washed with MeOH (150 mL), and dried on the filter. Drying in a vacuum afforded 15.7 g (66%) of a white solid. Mp: 86−88 °C. IR (CCl_4): 2928, 1686, 1609, 1357, 1316 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.29 (d, J = 1.3 Hz, 2H), 8.31 (d, J = 8.6 Hz, 2H), 8.17 (dd, J = 8.6, 1.4 Hz, 2H), 4.24 (t, J = 6.7 Hz, 4H), 2.80 (s, 6H), 1.92 (m, 4H), 1.57 (m, 4H), 1.41−1.27 (m, 32 H), 0.88 (t, J = 6.8 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 197.8, 144.9, 134.5, 133.0, 128.4, 126.1, 123.5, 122.9, 73.8, 31.9, 30.4, 29.6, 29.5, 29.3, 26.9, 26.2, 22.7, 14.1 ppm. UV−vis (CH_2Cl_2, c = 7.78 × 10^{-5} M): λ_{max} (log ϵ) 215 (4.20), 253 (4.40), 274 (sh, 4.29), 330 nm (4.24). Anal. Calcd for $C_{42}H_{62}O_4$: C, 79.95; H, 9.91. Found: C, 79.82; H, 9.76.

3,6-Bis(1-(triisopropylsiloxy)ethenyl)-9,10-dimethoxyphenanthrene (4a). Triisopropylsilyl triflate (28.2 mL, 0.105 mol) was added under N_2 to a solution of **3a** (16.1 g, 0.050 mol) in CH_2Cl_2 (160 mL) plus Et_3N (55.8 mL) that was cooled in an ice bath. The mixture was stirred at 0 °C for 15 min and then at 25 °C for 1 h, and after hexane (0.5 L) had been added, it was washed with 10% aqueous KOH (1 × 300 mL and 2 × 100 mL), dried over K_2CO_3, and filtered. The solvent was evaporated, and the oily residue was dried overnight in a vacuum at 100 °C. The resulting slightly brown oil (32.0 g, 101%) was used directly for the next step. IR (CCl_4): 2946, 2868, 1607, 1464, 1322, 1292, 1113, 1015 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.96 (d, J = 1.5 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2H), 7.90 (dd, J = 8.6, 1.6 Hz, 2H), 5.06 (d, J = 1.8 Hz, 2H), 4.57 (d, J = 1.8 Hz, 2H), 4.11 (s, 6H), 1.35 (m, 6H), 1.18 (d, J = 7.3 Hz, 36H). ^{13}C NMR ($CDCl_3$, 75 MHz): 156.4, 144.1, 135.4, 129.1, 128.6, 124.3, 122.0, 119.5, 90.8, 61.0, 18.2, 12.8 ppm.

6,13-Bis(triisopropylsiloxy)-9,10-dimethoxy[7]helicenebisquinone (5a). Heptane (250 mL) was added under N_2 to **4a** (32.0 g, 50.4 mmol) and *p*-benzoquinone (81 g, 0.75 mol) in a 1 L round-bottomed flask that was fitted with a reflux condenser. The mixture was stirred and heated in an oil bath at 120 °C for 3 days. Then it was cooled to 25 °C, CH_2Cl_2 (50 mL) was added, the solid was broken into small pieces, and the mixture was shaken for 15 min. The supernatant liquid was decanted, and the residue was extracted with 1:1 hexane/CH_2Cl_2 (6 × 200 mL). The combined solutions were filtered through a pad of Celite, the solvents were evaporated, and the residual benzoquinone was sublimed away in a vacuum at 100 °C. The residue was suspended in MeOH (250 mL) and shaken until the solid became finely suspended (ca. 30 min). Water (50 mL) was added; the mixture was shaken for 10 min; and the solid was filtered, washed on the filter with 5:1 MeOH/H_2O, and dried in a vacuum at 100 °C. The resulting powder was loaded onto a plug of silica gel (5 in. wide × 3 in. high), impurities were eluted with 1:1 hexane/CH_2Cl_2, and the product was eluted with 1:3 hexane/CH_2Cl_2. Evaporation of the solvent and drying in a vacuum at 100 °C gave 9.47 g (23% based on **3a**) of a dark red solid. Mp: >250 °C. IR (CCl_4): 2948, 2870, 1665, 1610, 1573, 1471, 1385, 1295, 1096 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, J = 8.9 Hz, 2H), 8.40 (d, J = 8.9 Hz, 2H), 7.38 (s, 2H), 6.48 (d, J = 10.1 Hz, 2H), 5.92 (d, J = 10.1 Hz, 2H), 4.21 (s, 6H), 1.51 (m, 6H), 1.24 (d, J = 7.5 Hz, 18H), 1.20 (d, J = 7.5 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): 184.6, 183.6, 157.4, 145.3, 140.4, 134.1, 133.0, 129.9, 129.6, 128.0, 126.1, 125.0, 123.3, 121.1, 107.7, 61.2, 18.1, 13.0 ppm. UV−vis (CH_3CN, c = 5.50 × 10^{-5} M): λ_{max} (log ϵ) 241 (4.54), 285 (4.48), 342 (4.18), 417 nm (3.76). Anal. Calcd for $C_{50}H_{58}O_8Si_2$: C, 71.22; H, 6.93. Found: C, 70.99; H, 6.87.

6,9,10,13-Tetramethoxy[7]helicenebisquinone (5c). DMF (11 mL) and MeI (1.60 mL, 25.7 mmol) were added under N_2 to a mixture of **5a** (0.90 g, 1.07 mmol) and CsF (0.63 g, 4.15 mmol). The mixture was stirred at 60 °C for 18 h, poured into H_2O (80 mL) plus brine (10 mL), and extracted with CH_2Cl_2 (5 × 10 mL). The organic part was washed with H_2O (5 × 50 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was suspended in MeOH (20 mL), filtered, washed on the filter with MeOH (20 mL), and dried in a vacuum at 100 °C. The yield of a brick-red solid (mp >250 °C) was 580 mg (97%). IR (CCl_4): 2939, 1662, 1607, 1462, 1384, 1296, 1103 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, J = 8.9 Hz, 2H), 8.39 (d, J = 8.9 Hz, 2H), 7.40 (s, 2H), 6.49 (d, J = 10.1 Hz, 2H), 5.93 (d, J = 10.1 Hz, 2H), 4.22 (s, 6H), 4.18 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 184.8, 183.5, 160.0, 145.2, 140.6, 134.0, 133.2, 129.7, 127.7, 127.4, 125.8, 125.0, 123.4, 120.5, 100.1, 61.2, 56.5 ppm. UV−vis (CH_3CN, c = 7.58 × 10^{-5} M): λ_{max} (log ϵ) 205 (4.41), 258 (4.41), 296 (4.38), 351 (4.14), 429 nm (3.69). Anal. Calcd for $C_{34}H_{22}O_8$: C, 73.11; H, 3.97. Found: C, 73.06; H, 3.95.

6,13-Diacetoxy-9,10-dimethoxy[7]helicenebisquinone (5e). AcCl (0.339 mL, 4.75 mmol) and DMF (3.5 mL) were added under N_2 to a mixture of **5a** (200 mg, 0.24 mmol), CsF (144 mg, 0.95 mmol), and DMAP (58 mg, 0.48 mmol). The reaction mixture was stirred vigorously for 13 h, poured into 1 M HCl (50 mL), and extracted with CH_2Cl_2 (1 × 10 mL and 2 × 5 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the solvent was evaporated. The residue was chromatographed with 5:1 CH_2Cl_2/EtOAc, giving 140 mg (96%) of an orange solid, mp >250 °C. Crystals for X-ray diffraction analysis were grown from a solution in 2:1 $PhCH_3/CH_2Cl_2$ that was allowed to evaporate slowly at room temperature. Purple crystals formed. IR (KBr): 2939, 1773, 1664, 1609, 1385, 1190, 1069 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.48 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 8.9 Hz, 2H), 7.80 (s, 2H), 6.53 (d, J = 10.2 Hz, 2H), 6.23 (d, J = 10.2 Hz, 2H), 4.22 (s, 6H), 2.56 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 184.6, 183.5, 168.8, 150.8, 145.6, 140.5, 134.6, 131.9, 129.6, 129.5, 129.3, 127.5, 125.5, 124.8, 119.7, 115.2, 61.3, 21.0 ppm. UV−vis (CH_3CN, c = 5.77 × 10^{-5} M): λ_{max} (log ϵ) 251 (4.52), 285 (sh, 4.42), 327 (4.28), 425 nm (sh, 3.52). Anal. Calcd for $C_{36}H_{22}O_{10}$: C, 70.36; H, 3.61. Found: C, 70.31; H, 3.38.

3,6-Bis(1-(triisopropylsiloxy)ethenyl)-9,10-didodecyloxyphenanthrene (4b). Triisopropylsilyl triflate (1.99 mL, 7.40 mmol) was added to a solution of **3b** (2.28 g, 3.62 mmol) in CH_2Cl_2 (20 mL) and Et_3N (5.0 mL) that was cooled in an ice bath. The mixture was stirred at 0 °C for 15 min and then at 25 °C for 1 h. Hexane (60 mL) was added, and the mixture was washed with 10% aqueous KOH (30 mL, 2 × 10 mL), dried over K_2CO_3, and filtered. The solvent was evaporated, and the oily residue in a vacuum was dried overnight at 100 °C. The resulting colorless oil (3.37 g, 99%) was used directly for the next step. IR (CCl_4): 2927.2, 2867, 1605, 1465, 1321, 1015 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.95 (d, J = 1.3 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2 H), 7.88 (dd, J = 8.6, 1.3 Hz, 2H), 5.05 (d, J = 1.7 Hz, 2H), 4.56 (d, J = 1.7 Hz, 2H), 4.20 (t, J = 6.7 Hz, 4H), 1.90 (m, 4H), 1.56 (m, 4H), 1.40−1.22 (m, 38 H), 1.18 (d, J = 7.4 Hz, 36H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 156.5, 143.4, 135.2, 129.6, 128.5, 124.2, 122.1, 119.4, 90.7, 73.7, 32.0, 30.5, 29.7, 29.6, 29.4, 26.3, 22.7, 18.2, 14.1, 12.8 ppm.

6,13-Bis(triisopropylsiloxy)-9,10-didodecyloxy[7]helicenebisquinone (5b). A mixture of **4b** (3.37 g, 3.58 mmol) and *p*-benzoquinone (5.82 g, 53.8 mmol) in heptane (50 mL) was stirred under N_2 and heated at reflux in an oil bath at 120 °C for 4 days. The mixture was cooled to 25 °C and filtered through a pad of Celite, and the filter cake was washed with hexane (ca. 200 mL) until the filtrate was colorless. The solvent was evaporated, and the residue was chromatographed, eluting with 1:2 CH_2Cl_2/hexane. The yield of a dark red solid (mp 116−118 °C) was 0.82 g (20%). IR (CCl_4): 2928, 2870, 1665, 1608, 1573, 1461, 1351, 1295, 1098 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, J = 8.9 Hz, 2H), 8.38 (d, J = 8.9 Hz, 2H), 7.38 (s, 2H), 6.47 (d, J = 10.1 Hz, 2H), 5.92 (d, J = 10.1 Hz, 2H), 4.45 (m, 2H), 4.20 (m, 2H), 1.98 (m, 4H), 1.62−

1.20 (m, 78H), 0.89 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 184.7, 183.6, 157.3, 144.8, 140.4, 134.0, 132.9, 130.0, 129.8, 128.0, 126.0, 125.1, 123.5, 121.0, 107.6, 74.0, 31.9, 30.5, 29.7, 29.6, 29.4, 26.2, 22.7, 18.1, 14.1, 13.0 ppm. UV−vis (CH_2Cl_2, c = 5.98 × 10^{-5} M): λ_{max} (log ϵ) 246 (4.51), 288 (4.49), 345 (4.21), 425 nm (3.78). Anal. Calcd for $C_{72}H_{102}O_8Si_2$: C, 75.08; H, 8.93. Found: C, 75.17; H, 8.91.

6,9,10,13-Tetradodecyloxy[7]helicenebisquinone (5d). DMF (20 mL) and 1-iodododecane (1.70 mL, 6.9 mmol) were added to a mixture of **5b** (0.36 g, 0.31 mmol) and CsF (0.211 g, 1.39 mmol) under N_2. The mixture was stirred at 60 °C for 14 h, poured into H_2O (300 mL), and extracted with CH_2Cl_2 (5 × 30 mL). The combined extracts were washed with H_2O (4 × 300 mL), dried over Na_2SO_4, and filtered. The residue was dissolved in hexane (20 mL) and filtered through a plug (1 in. wide × 2 in. high) of silica gel, which was washed with hexane (100 mL) and 3:1 hexane/CH_2Cl_2 (50 mL). The product was eluted with CH_2Cl_2 and, after removal of the solvent and drying in a vacuum, triturated with MeOH (30 mL). The solid was filtered, washed with MeOH (2 × 30 mL), and dried in a vacuum. The yield of a red solid was 300 mg (82%). The ^{1}H and ^{13}C NMR spectra were identical to those published.[3]

Preparation of Racemic 7. All operations were performed in the absence of direct light. A solution of **5a** (8.00 g, 9.50 mmol) in 3:1 EtOAc/CH_2Cl_2 (480 mL) was added to a solution of $Na_2S_2O_4$ (41.3 g, 237 mmol) and Bu_4NBr (160 mg) in H_2O (640 mL). The mixture, in a 2 L separatory funnel, was shaken until it became yellow (ca. 10 min) and then for 5 min more. Brine (30 mL) was added, and the organic layer was separated, washed with brine (2 × 150 mL), briefly dried over Na_2SO_4, and filtered. The solvent was evaporated, and the resulting yellow solid was dried in a vacuum at 25 °C. A saturated solution of HCl gas in MeOH (40 mL) plus additional MeOH (152 mL) were added to the solid, and the mixture, at 60 °C, was stirred under N_2 for 5 h. It was then poured into H_2O (1 L) and extracted with EtOAc (300 mL). The organic part was washed with brine (100 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue, dissolved in CH_2Cl_2 (200 mL), was loaded onto a plug of silica gel (4 in. wide × 3 in. high) that was soaked with CH_2Cl_2. Impurities were eluted with CH_2Cl_2 (ca. 0.5 L), and then the product was eluted with 15:1 CH_2Cl_2/EtOAc. The yellow fractions, which contained the product, were collected, and the solvent was evaporated. The solid was dried in a vacuum, suspended in pentane (2 × 100 mL), and filtered. Drying in a vacuum at 100 °C gave 4.70 g (84%) of pure **7**, a bright yellow solid. Mp: >240 °C. IR (CCl_4): 3607, 3567, 2940, 1604, 1374, 1289, 1234, 1110, 1087 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.48 (d, J = 8.6 Hz, 2H), 8.42 (d, J = 8.6 Hz, 2H), 7.12 (s, 2H), 6.33 (d, J = 8.4 Hz, 2H), 5.89 (d, J = 8.4 Hz, 2H), 4.25 (s, 6H), 4.10 (s, 6H), 3.85 (s, 6H), 3.45 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): 152.8, 148.0, 144.4, 143.5, 127.6, 126.1, 124.0, 123.9, 122.5, 121.3, 120.1, 117.8, 109.3, 105.2, 97.5, 61.4, 55.9, 55.7 ppm. HRMS (FAB) m/z calcd for $C_{36}H_{30}O_8$, 590.1941; found, 590.1959.

(*P*)-(+)- and (*M*)-(−)-8. 1,2-Dichloroethane (150 mL) and Et_3N (30 mL) were added under N_2 to a mixture of **7** (4.70 g, 7.97 mmol), (1*S*)-(−)-camphanoyl chloride (5.18 g, 23.9 mmol), and DMAP (1.95 g, 16.0 mmol). The mixture was stirred and refluxed under N_2 for 3 h, cooled to 25 °C, poured into 1 M HCl (0.5 L), and extracted with EtOAc (0.5 L). The organic layer was washed with 1 M HCl (0.5 L), 2:1 saturated aqueous $NaHCO_3$/brine (2 × 300 mL), and brine (100 mL); dried over Na_2SO_4; and filtered. The solvent was evaporated, MeOH (50 mL) was added to the solid, and the solvent was again evaporated. The solid residue in a vacuum was dried at 60 °C and then mixed with MeOH (200 mL) and sand (20 g), and the mixture was shaken for 30 min. The finely suspended yellow solid was filtered on Celite, washed with MeOH (2 × 100 mL), and dissolved in CH_2Cl_2. The solution was filtered, and the solvent was evaporated. Drying in a vacuum at 60 °C afforded 7.26 g of a clean mixture of the two diastereomers. The solid was boiled in 150 mL of $PhCH_3$ for 5 min. Cyclohexane (34 mL) was added, and the mixture was cooled to 25 °C and then allowed to stand overnight in a refrigerator at 4 °C. The precipitated solid was filtered and washed on the filter with $PhCH_3$ (3 × 30 mL). Drying in a vacuum gave 3.50 g (92%) of (*P*)-(+)-**8** (a yellow solid, mp 237−239 °C). Crystals for X-ray diffraction analysis were grown from a saturated solution in acetone that was allowed to evaporate slowly at room temperature. $[\alpha]_D$: +1646 (c = 0.019, CH_3CN). IR (CCl_4): 2938, 1798, 1774, 1602, 1284, 1236, 1110 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 4H), 7.07 (s, 2H), 6.36 (d, J = 8.4 Hz, 2H), 5.91 (d, J = 8.4 Hz, 2H), 4.17 (s, 6H), 4.08 (s, 6H), 3.92 (s, 6H), 1.73 (m, 2H), 1.43 (m, 2H), 1.31 (m, 2H), 1.06 (m, 2H), 0.97 (s, 6H), 0.70 (s, 6H), 0.50 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 177.5, 165.6, 153.9, 152.2, 144.2, 138.5, 128.0, 126.7, 125.0, 124.3, 123.2, 122.0, 121.0 (2 peaks), 115.7, 103.5, 97.1, 90.4, 61.2, 56.1, 55.5, 54.4, 54.1, 28.7 (2 peaks), 16.7, 16.5, 9.5 ppm. UV−vis (CH_3CN, c = 1.59 × 10^{-5} M): λ_{max} (log ϵ) 208 (4.80), 253 (3.66), 285 (4.59), 325 (sh, 4.35), 349 nm (sh, 3.74). CD (c = 1.59 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$): 237 (178), 288 (−103), 372 (101), 399 (sh, 63).

The solvent was removed from the filtrate from which (*P*)-(+)-**8** had been separated. The residue was dissolved in 10:1 $PhCH_3$/THF (50 mL) and loaded onto a plug of silica gel (2.5 in. wide × 4 in. high). The diastereomer with higher R_f eluted with 10:1 $PhCH_3$/THF. The yield of (*M*)-(−)-**8** (a yellow solid, mp 202−204 °C) was 3.33 g (88%). Crystals for X-ray diffraction analysis were grown by allowing a solution in 4:1 EtOAc/MeOH to evaporate slowly at room temperature. The crystals were yellow. $[\alpha]_D$: −1799 (c = 0.018, CH_3CN). IR (CCl_4): 2938, 1794, 1747, 1603, 1284, 1236, 1090 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (s, 4H), 7.04 (s, 2H), 6.34 (d, J = 8.4 Hz, 2H), 5.96 (d, J = 8.4 Hz, 2H), 4.17 (s, 6H), 4.08 (s, 6H), 3.92 (s, 6H), 1.52 (m, 2H), 1.33 (m, 4H), 0.94 (m, 2H), 0.93 (s, 6H), 0.59 (s, 6H), 0.43 ppm (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): 177.9, 165.9, 154.1, 152.2, 143.9, 138.4, 127.6, 126.8, 125.1, 123.9, 122.4, 122.1, 121.5, 120.8, 115.0, 103.1, 96.7, 89.6, 61.0, 56.0, 55.4, 54.2, 29.7, 28.5, 16.2, 16.1, 9.5 ppm. UV−vis (CH_3CN, c = 2.11 × 10^{-5} M): λ_{max} (log ϵ) 208 (4.77), 252 (4.63), 284 (4.62), 320 (sh, 4.39), 373 (sh, 3.83), 392 nm (sh, 3.74). CD (c = 2.11 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$): 206 (62), 236 (−202), 285 (133), 320 (sh, 65), 374 (−111), 393 (sh, −80). Anal. Calcd for $C_{56}H_{54}O_{14}$: C, 70.72; H, 5.72. Found: C, 70.44; H, 5.72.

(*P*)-(+)- and (*M*)-(−)-7. *n*-BuLi in hexanes (16.0 mL, 2.5 M, 40 mmol) was added slowly under N_2 to a stirred solution of (*P*)-(+)-**8** (1.90 g, 2.00 mmol) in dry THF (50 mL) that was cooled to −78 °C. The mixture was stirred for 20 min at −78 °C, quenched with 5 M HCl (10 mL), and then stirred for 5 min at 25 °C. The yellow solution was poured into 1 M HCl (150 mL) and extracted with EtOAc (30 mL). The organic part was washed with H_2O (100 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated, and the residue was loaded onto a short column of silica gel (1.5 in. wide and 5.5 in. high). The yellow product was eluted with 1:1 hexane/EtOAc. Evaporation of the solvent and drying in a vacuum gave 1.13 g (96%) of (*P*)-(+)-**7**. Mp: >240 °C. $[\alpha]_D$: +2563 (c = 0.018, CH_3CN). The ^{1}H and ^{13}C NMR spectra were identical to those of the racemic material. UV−vis (CH_3CN, c = 3.60 × 10^{-5} M): λ_{max} (log ϵ) 249 (4.66), 301 (4.56), 362 nm (sh, 4.04). CD (c = 3.60 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$): 233 (109), 249 (sh, 42), 272 (−105), 301 (−88), 361 (78). The same procedure, when applied to (M)-(−)-**8**, gave 1.14 g (97%) of (M)-(−)-**7**. $[\alpha]_D$: −2581 (c = 0.015, CH_3CN). UV−vis (CH_3CN, c = 3.98 × 10^{-5} M): λ_{max} (log ϵ) 249 (4.68), 301 (4.58), 362 nm (sh, 4.04). CD (c = 3.98 × 10^{-5} M, CH_3CN), nm ($\Delta\epsilon$): 233 (−110), 249 (sh, −42), 273 (106), 301 (sh, 90), 361 (−78).

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Supporting Information Available: ^{1}H and ^{13}C NMR and IR spectra of **2b**, **3a**,**b**,**f**,**h**, **4a**,**b**, **5a**−**c**,**e**, **7**, (+)-**8**, and (−)-**8**. UV spectra of **2b**, **3a**,**b**,**h**, **5a**−**c**,**e**, (+)-**7**, (−)-**7**, (+)-**8**, and (−)-**8**. CD spectra of (+)-**7**, (−)-**7**, (+)-**8**, and (−)-**8**. Details of the X-ray diffraction analyses of (*P*)−(+)-**8**, (*M*)−(−)-**8**, and **5e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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