

# Synthesis and Aggregation of a Conjugated Helical Molecule

Colin Nuckolls,<sup>†</sup> Thomas J. Katz\*,<sup>†</sup> Gail Katz,<sup>†</sup> Peter J. Collings,<sup>‡</sup> and Louis Castellanos<sup>†</sup>

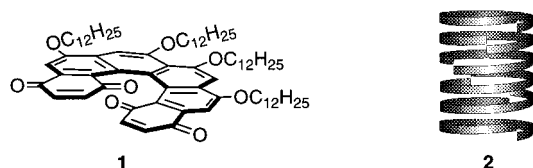
Contribution from The Department of Chemistry, Columbia University, New York, New York 10027, and The Department of Physics and Astronomy, Swarthmore College, Swarthmore, Pennsylvania 19081

Received September 10, 1998

**Abstract:** Described are an improved method to synthesize helicenebisquinone **1** and an efficient method to resolve its enantiomers and those of other helicenebisquinones by separating derived camphanate esters. The union of *p*-benzoquinone and the bis(triisopropylsilylenol ether) of a 2,7-diacetyl-4,5-dialkoxynaphthalene gives the helicene skeleton in 56% yield. Molecules of nonracemic **1** aggregate when their dodecane solutions are concentrated to  $5 \times 10^{-4}$  M or more. Chloroform dissociates the aggregates. Aggregation is characterized by enhanced circular dichroisms and *g* values, red-shifted UV–vis absorptions, increased specific rotations, increased light scattering at an absorption frequency, and, as reported previously, fluorescence emissions that shift to the red, <sup>1</sup>H NMR resonances that shift upfield, and organization of the pure material into fibers. The CD and UV–vis absorption spectra of spin-coated films are similar to those of concentrated solutions in dodecane, but the *g* values are higher. The specific rotation of a cast film,  $[\alpha]_D$ , is 158 000 (deg cm<sup>2</sup>)/10 g. Unlike the nonracemic material, the racemic in bulk does not form visible fibers and is too insoluble to give concentrated solutions in dodecane. Also nonracemic helicene **3** does not show the characteristics of aggregation either in solution or in bulk.

## Introduction

Nonracemic helicene **1** as the pure material,<sup>1,2</sup> in Langmuir–Blodgett films,<sup>3</sup> and when dissolved in saturated hydrocarbon solvents<sup>1,3</sup> assembles into helical columns, within which the molecules appear to be stacked along their helix axes as shown schematically in structure **2**.<sup>2</sup> In the pure material, the columnar



assemblies are further ordered into very long, micrometer-wide lamellar fibers.<sup>1,2</sup> Analyses of the fibers by electron and X-ray diffraction and by electron and polarized light microscopy show the columns to be ca. 42 Å in diameter and hexagonally packed collinearly with the fiber axes.<sup>2</sup> In Langmuir–Blodgett films, the organization in parallel columns can be seen directly by atomic force microscopy<sup>4</sup> and inferred from the similarity between the interlayer spacings of multilayers<sup>3</sup> and the diameters of the columns in the fibers of pure material,<sup>2</sup> both analyzed by X-ray diffraction. In dodecane solutions of sufficient concentration, the molecules aggregate,<sup>1</sup> and that they assemble into columns is implied by the CD and UV–vis absorption

spectra and specific rotations resembling those of the Langmuir–Blodgett films, but differing from those of solutions that are more dilute.<sup>3</sup>

Organizing into columns significantly alters **1**'s optical properties. Its second-harmonic-generating ability,<sup>4</sup> circular dichroisms, and optical rotations<sup>1,3</sup> increase greatly, and the UV–vis absorptions and fluorescence emissions shift.<sup>1,3</sup> More light at an absorption wavelength is scattered.<sup>5,6</sup> Not all helicenes surrounded by alkoxy chains behave in this way, and it appears that in structures similar to those of **1** the quinones are essential for the stacking to occur. Thus, a derivative of **1** that has only one of the termini reduced and acylated also aggregates into helical columns,<sup>7</sup> but none in which both quinones are reduced has been found by polarized light microscopy to form an anisotropic liquid phase.<sup>1,8</sup>

Because the optical and structural properties of **1** and its derivatives<sup>7</sup> are unique, it is unfortunate that the previously reported synthesis of **1** affords only very small amounts of material (<10 mg).<sup>1</sup> Accordingly, we tried to improve the synthesis, and in this paper, we show how to achieve such an improved preparation. In addition, the larger amounts available made it possible to more fully study the CD and UV–vis absorption spectra, optical rotation, light scattering, and thermal racemization of nonracemic **1**. The results of these studies are also recorded herein, as are similar studies of nonracemic **3**, which provide a standard to which the properties of **1** can be

<sup>†</sup> Columbia University.

<sup>‡</sup> Swarthmore College.

(1) Nuckolls, C.; Katz, T. J.; Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118*, 3767.

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

(3) Nuckolls, C.; Katz, T. J.; Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Kuball, H.-G.; Kiesewalter, S.; Lovinger, A. J.; Persoons, A. *J. Am. Chem. Soc.* **1998**, *120*, 8656.

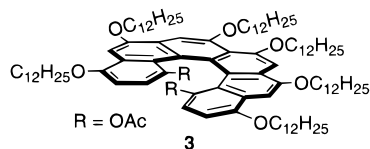
(4) Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913.

(5) This was first shown by Peter Collings (see ref 1).

(6) Pasternack, R. F.; Collings, P. J. *Science* **1995**, *269*, 935.

(7) A derivative of **1** was recently found to be the first core-chiral columnar liquid crystal: Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541.

(8) Besides **3**, the following, investigated preliminarily, appeared isotropic under the polarizing microscope: (a) analogues of **3** with pentyl, heptyl, nonyl, and heptadecyl side chains instead of dodecyls; (b) an analogue of **3** with methoxyls in place of acetates; (c) analogues of **14** with eight lauryls, 4-heptyloxybenzoyls, 3-cholesteryloxybenzoyls, and 1<sup>+</sup>pyr<sup>+</sup>(CH<sub>2</sub>)<sub>11</sub>CO groups in place of the acetyls, the last compound in water (Colin Nuckolls, Thomas J. Katz, and Louis Castellanos, unpublished results).



compared. Additionally, the new synthesis proceeds by way of *racemic* **1**, some of whose properties are compared with those of the enantiomerically pure material.

## Results and Discussion

**Helicene Syntheses.** Scheme 1 shows how a key step in the original synthesis (top equation) was improved (bottom equation).<sup>9</sup> The essential difference is that the diene component originally had the two phenols derivatized as pivalate esters, whereas in the newer synthesis they are derivatized as dodecyl ethers. Although a variety of ways were tried to improve the yield of helicene **5**,<sup>10</sup> the best that could be obtained was only 16%. Accompanying it as the major product seems to be the aromatized compound in which only one of the silyl enol ethers of **4** has combined with the *p*-benzoquinone and the other has converted into the methyl ketone.<sup>13</sup> Initially there was an additional difficulty because the silyl ether functions of helicene **5** were too labile to survive chromatography.<sup>14</sup> When they were removed, the phenolic product was rapidly destroyed, presumably by oxidation. While isolating **5** by chromatography was therefore precluded, the problem could be overcome, because everything in the reaction mixture *except* helicene **5** is soluble in acetone. This means that the desired product could be isolated, analytically pure, simply by filtering the acetone suspension.

Nevertheless, the reaction of **4** with *p*-benzoquinone gives **5** in yields that are dismal. However, when **6** was heated with an excess of *p*-benzoquinone, the only product the aromatic region of the <sup>1</sup>H NMR spectrum identified in the crude reaction mixture was the desired helicene.<sup>15</sup> Once again, the lability of the silyl ethers made it impossible to purify the product by chromatog-

(9) The reactions of bis(enol ether)s of arylmethyl ketones with *p*-benzoquinone have given a number of helicenebisquinones: (a) Willmore, N. D.; Liu, L.; Katz, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1093. (b) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054. (c) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456.

(10) The following attempts to improve the yield failed: changing the solvent to octane, benzene, or acetonitrile; running the reaction without solvent; adding trichloroacetic acid in catalytic<sup>11</sup> or stoichiometric amounts; adding more or adding less benzoquinone; purifying benzoquinone by recrystallizing it from acetone;<sup>12</sup> adding 2,6-di-*tert*-butylpyridine; adding pyridinium dichromate; adding bis(2,6-di-*tert*-butyl-4-hydroxyphenyl)-methane; adding Lewis acids (titanium tetraisopropoxide, *tert*-butyldimethylsilyl triflate, or europium tris(6,6,7,7,8,8,8)heptafluoro-2,2-dimethyl-3,5-octanedionate); adding 4 Å molecular sieves or K<sub>2</sub>CO<sub>3</sub>.

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

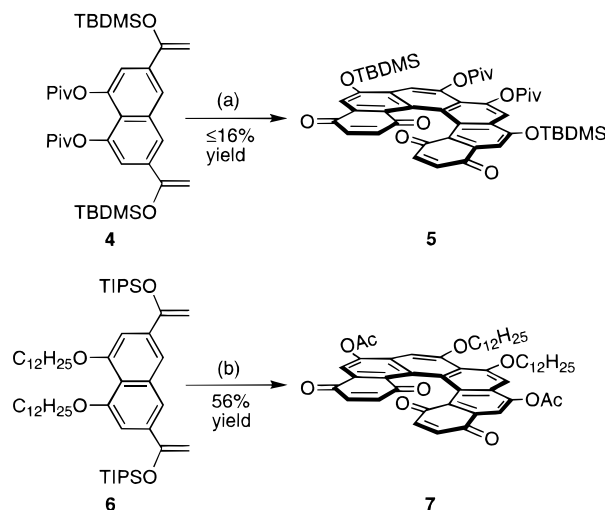
(12) Willmore, N. D. Ph.D. Dissertation, Columbia University, 1994.

(13) The evidence is the observation in the <sup>1</sup>H NMR spectrum of two meta-coupled aromatic hydrogens, one at very low fields, and the acetyl group. The spectrum (400 MHz) displays the former at δ 8.39 and 7.66 ppm (both 1 H, d, *J* = 1.6 Hz) and the latter at 2.67 ppm (3 H, s). In addition, there are the following resonances: two sharp singlets, at 7.76 and 7.57 ppm (both 1 H), expected from the other aromatic hydrogens; an AB quartet at 7.07 and 6.98 ppm (*J* = 10 Hz), attributable to the quinone hydrogens; a broad singlet at 1.48 ppm (18 H), attributable to the pivalates; and the two singlets expected from the TBDMS group, at 1.08 and 0.39 ppm (9 and 6 H, respectively).

(14) The adsorbents tried were silica gel, silica gel doped with triethylamine, basic alumina, neutral alumina, and florisil. The lability is presumed to be associated with conjugation between the siloxyls and the quinone's carbonyls. Other helical derivatives of 6-siloxy-1,4-naphthoquinone prepared in our lab proved less sensitive. They decomposed only slightly when chromatographed (ref 9b,c and S. Dreher, unpublished results).

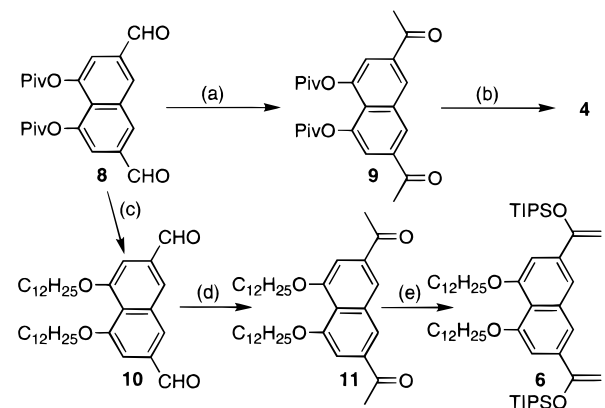
(15) The aromatic region of the <sup>1</sup>H NMR spectrum of the desired product is easily identified because it consists of two very sharp singlets and an AB quartet.

### Scheme 1<sup>a,b</sup>



<sup>a</sup> Abbreviations: TBDMS = *t*-BuMe<sub>2</sub>Si, TIPS = *i*-Pr<sub>3</sub>Si, Piv = Me<sub>3</sub>CCO. <sup>b</sup> Reagents and conditions: (a) *p*-benzoquinone, PhMe; (b) (i) *p*-benzoquinone, heptane; (ii) Ac<sub>2</sub>O, Et<sub>3</sub>N·3HF, Et<sub>3</sub>N.

### Scheme 2<sup>a,b</sup>



<sup>a</sup> Abbreviations: TBDMS = *t*-BuMe<sub>2</sub>Si, TIPS = *i*-Pr<sub>3</sub>Si, Piv = *t*-BuCO. <sup>b</sup> Reagents and conditions: (a) (i) MeMgBr, THF; (ii) pyridinium dichromate, CH<sub>2</sub>Cl<sub>2</sub>, 73% yield. (b) TBDMSOTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 100% yield. (c) (i) KOH, EtOH, 97% yield; (ii) C<sub>12</sub>H<sub>25</sub>I, K<sub>2</sub>CO<sub>3</sub>, DMF, 98% yield. (d) (i) MeLi, THF, 96% yield; (ii) tetrapropylammonium perruthenate, *N*-methylmorpholine *N*-oxide, CH<sub>2</sub>Cl<sub>2</sub>, 4 Å molecular sieves, 85% yield. (e) TIPSOTf, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 95% yield.

raphy, and since the helicene formed in this reaction, unlike **5**, is soluble in acetone, the silyl ethers were converted into acetate esters,<sup>16</sup> which allowed **7** to be obtained from **6** in a remarkable 56% yield. The important point is that when the substituents meta to the enol ethers are *ethers* rather than *esters*, the yields of helicenebisquinone are very high. We suppose that the ethers exert their effect by donating electrons, thereby increasing either the reactivity of the diene or the rate at which the diene–benzoquinone adduct oxidizes.

As summarized in Scheme 2, both **4** and **6** were synthesized from dipivaloxydialdehyde **8**,<sup>17</sup> itself prepared on a multigram scale from the known 3,6-dimethyl-1,8-naphthalenediol.<sup>18</sup> Thus,

(16) We could not find a previous example in which Ac<sub>2</sub>O, Et<sub>3</sub>N·3HF, and Et<sub>3</sub>N had been used to replace a silyl ether by an acetate, but similar combinations have been used, such as ZnCl<sub>2</sub>–AcCl (Kim, S.; Lee, W. J. *Synth. Commun.* **1986**, *16*, 659) and FeCl<sub>3</sub>–Ac<sub>2</sub>O (Ganem, B.; Small, V. R., Jr. *J. Org. Chem.* **1974**, *39*, 3928).

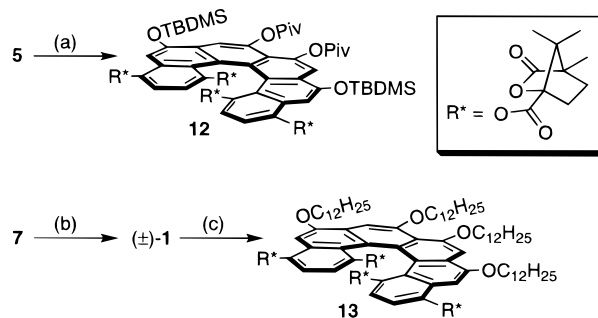
(17) The three-step synthesis is described in the Supporting Information to ref 1.

(18) Synthesized in three steps from dehydroacetic acid: (a) Bethell, J. R.; Maitland, P. J. *Chem. Soc.* **1962**, 3751. (b) Overeem, J. C.; Van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1005.

methylmagnesium bromide adds selectively to **8**'s aldehyde groups, oxidation with pyridinium dichromate then gives diacetylnaphthalene **9**,<sup>19</sup> and this, on reaction with *tert*-butyldimethylsilyl triflate and triethylamine, converts into enol ether **4**.<sup>20</sup> The yield of **4** from **8** was 73%. For the last transformation in this series and a number of similar ones, we found that silyl triflates give higher yields and more easily purified products than other reagents that convert ketones into silyl enol ethers.<sup>21</sup> To synthesize **6**, the esters of **8** were saponified and the resulting phenols then alkylated. Addition of methyllithium and oxidation by Ley's method, using tetrapropylammonium perruthenate plus *N*-methylmorpholine *N*-oxide,<sup>22</sup> gave very clean diacetylnaphthalene **11**. Once again, it was reaction with the silyl triflate (triisopropylsilyl triflate in this case) that gave the corresponding enol ether, **6**.<sup>23</sup>

**Resolution of Helicene Enantiomers.** Prior to this work, a compound similar to **1**, but with only two alkoxy groups, had been resolved into its enantiomers by a reduction and esterification that produced a separable mixture of two diastereomeric tetra-*N*-toluenesulfonyl-L-proline esters, which were then each reconverted into the bisquinone, now optically active.<sup>9b</sup> Also previously resolved into their enantiomers by way of diesters of a nonracemic acid, in this case (–)-menthoxyacetic acid,<sup>24</sup> were some helicenediols that were subsequently transformed into [6]- and [7]helicenebisquinones.<sup>25</sup> However, for the resolution of helicenebisquinones derived from those synthesized according to Scheme 1, tetraesters, formed by reduction and esterification with *N*-toluenesulfonyl-L-proline, (–)-menthoxyacetic acid, and a variety of other nonracemic acids,<sup>26</sup> all proved unsatisfactory. What does work superbly, *not only for these examples, but also for 10 other helicenequinones synthesized subsequently in the course of this and related studies*,<sup>27</sup> is reduction and esterification with (1*S*)-(–)-camphanoyl chloride.<sup>28</sup>

But before (±)-**1** could be resolved, it had to be prepared from **7**, and as Scheme 3 shows, this was done in a way that avoided the isolation of the phenolic quinone. The combination of potassium carbonate and dodecyl iodide in warm DMF transformed the acetates into dodecyl ethers in a yield of 93%. The resolution was then effected in the following way. Sodium dithionite<sup>29</sup> reduced helicenequinones **5** and (±)-**1** to the bishydroquinones, which, because they were easily oxidized in the air, were esterified directly with (1*S*)-(–)-camphanoyl chloride and triethylamine. An alternative was to use Fox's modification<sup>9c</sup> of Willmore's procedure,<sup>9b</sup> using Zn, TMEDA,

Scheme 3<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) (i) Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, H<sub>2</sub>O, THF; (ii) (1*S*)-(–)-camphanoyl chloride, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>. Yields: 76%, (–)-diastereomer; 96%, (+)-diastereomer. (b) C<sub>12</sub>H<sub>25</sub>I, K<sub>2</sub>CO<sub>3</sub>, DMF, 93% yield. (c) (i) Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, H<sub>2</sub>O, THF; (ii) (1*S*)-(–)-camphanoyl chloride, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>. Yields: 85%, (–)-diastereomer; 82%, (+)-diastereomer.

and (1*S*)-(–)-camphanoyl chloride in boiling toluene, but it gave yields that were slightly lower: a 78% yield of the (–)-diastereomer and an 86% yield of the (+)-diastereomer. Chromatography on an ordinary silica gel column easily separates the diastereomers of **12** and **13** in yields of 76–96%. In both cases the separation is excellent. In the case of **13** the difference in *R<sub>f</sub>* values was measured to be 0.3, which is large,<sup>30</sup> and the separation was carried out on a gram scale. In fact, the separations are so good that, according to <sup>1</sup>H NMR, <sup>13</sup>C NMR, and thin layer chromatographic analysis, no contamination by diastereomeric material could be detected in any of the four samples. The ratio of the signal to noise in the <sup>1</sup>H NMR spectra was such that the diastereomeric purities of the samples prepared from **12** were ≥98% and from **13** ≥99.5%.

**Conversion of 12 and 13 into Nonracemic 1.** To complete the synthesis of nonracemic **1**, the camphanates of the separated diastereomers of **12** and **13** had to be removed and the resulting helicenes oxidized. In addition, for the synthesis from **12**, the silyl ethers and pivalate esters had to be converted into long-chain ethers. Notably, when combined with methyllithium in 1,2-dimethoxyethane and then acetic anhydride, the silyl, pivalate, and camphanate groups of **12** were all replaced by acetates in only one step. The yield of **14** was 95%.

A strategy that had been used to convert only some of the ester groups of hexaacetoxytriphenylenes into ethers, heating with potassium carbonate, 18-crown-6, and dodecyl iodide in isobutyl methyl ketone,<sup>31</sup> removed the six least hindered esters of octaacetate **14**, replacing them with dodecyls in 30% yield.<sup>32</sup> The structure **3** was assigned to the product on the basis of the NMR chemical shift of the acetate protons. Of the acetate resonances of **14**, at δ 1.22, 2.48, 2.50, and 2.53 ppm, the ones that are absent in **3** are the latter three, those at the normal position for aryl acetate NMRs.<sup>33</sup> The one that remains (in **3** it resonates at δ 1.12 ppm), like the related resonances of previously synthesized helicenes that have acetoxy groups occupying the positions assigned to those in **3**,<sup>9b,12,34</sup> is at ca. 1.5 ppm higher field than normal. In addition, the structure is

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

(31) (a) Kranig, W.; Hüser, B.; Spiess, H. W.; Kreuder, W.; Ringsdorf, H.; Zimmermann, H. *Adv. Mater.* **1990**, *2*, 36. (b) Kreuder, W.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 807.

(32) Also formed in this reaction was a triacetate, presumably a material with the two acetoxy groups of **3** and one other.

(33) 2-Naphthyl acetate and phenyl acetate have resonances for the acetate methyls at 2.31 and 2.27 ppm, respectively, Pouchert, C. J.; Behnke, J. *The Aldrich Library of <sup>13</sup>C and <sup>1</sup>H FT-NMR Spectra, Edition 1, Vol. 2*; Aldrich Chemical Co.: Milwaukee, 1993; pp 1298C and 1285B.

(34) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274. In addition, this reference shows a similar effect applies to isobutyrate esters.

(19) The method of Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

(20) The method of Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1984**, *25*, 5953.

(21) (a) TBDMSCl, NaI, Et<sub>3</sub>N: see ref 9b. (b) TBDMSCl and KH: Orban, J.; Turner, J. V.; Twitchin, B. *Tetrahedron Lett.* **1984**, *25*, 5099.

(22) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.

(23) By the method of Corey, E. J.; Cho, H.; Rücker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

(24) Yang, B. V. Ph.D. Dissertation, Columbia University, 1987.

(25) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993.

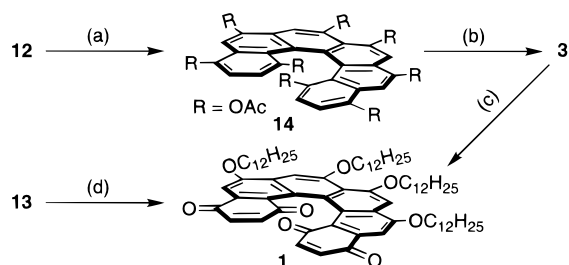
(26) (–)-Menthyl carbonic, cholesteryl carbonic, (R)-(–)-*O*-acetylmandelic, and camphorsulfonic. Either the yields of the diastereomers were poor or the diastereomers could not be separated.

(27) Reference 9c and unpublished results by a number of co-workers in our lab.

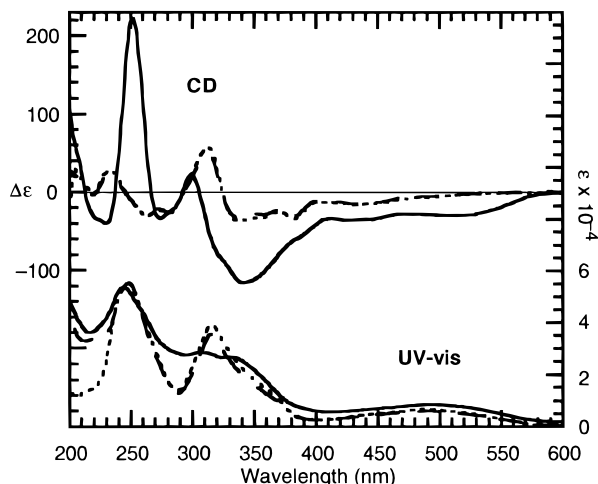
(28) Commercially available and easily prepared (Gerlach, H.; Kappes, D.; Boeckman, R. K., Jr.; Maw, G. N. *Organic Syntheses*; Wiley: New York, 1998; Collect. Vol. IX, p 151).

(29) (a) Ulrich, H.; Richter, R. In *Methoden der Organischen Chemie (Houben-Weyl)*; Grundmann, C., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. VII/3a, pp 649–650. (b) Liu, L. Ph.D. Dissertation, Columbia University, 1991, applied sodium dithionite to reduce helicene bisquinones.



Scheme 4<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) (i) MeLi, DME; (ii) Ac<sub>2</sub>O, 95% yield. (b) C<sub>12</sub>H<sub>25</sub>I, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, *i*-BuCOMe, 30% yield. (c) (i) KOEt, THF; (ii) (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>, H<sub>2</sub>O, dioxane, 94% yield. (d) (i) MeLi, THF; (ii) chloranil, 95% yield.



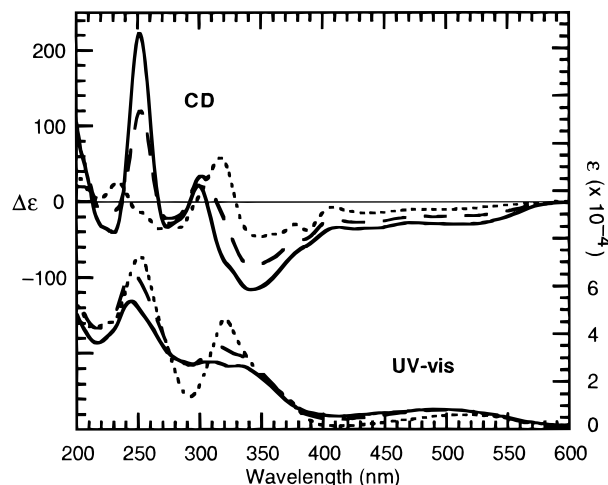
**Figure 1.** (a, top) CD spectra (ordinate on the left, displaying molar circular dichroism) and (b, bottom) UV-vis absorption spectra (ordinate on the right, displaying molar extinction coefficient) of (–)-**1** in dodecane: (–) when the concentration is  $2.5 \times 10^{-2}$  M and the path length is  $10 \mu\text{m}$ ; (– – –) when the concentration is  $1.0 \times 10^{-4}$  M and the path length is 2 mm; (- · - ·) when the concentration is  $1.0 \times 10^{-5}$  M and the path length is 1 cm.

supported by the demonstration that removing the acetates of **3** and then oxidizing gives **1**. Thus, (Scheme 4) treatment with potassium ethoxide in THF and then with ceric ammonium nitrate<sup>35</sup> gives the helicenebisquinone in 94% yield.

It is because yields are so poor in the Diels–Alder oxidation step producing **5** (Scheme 1) and in the reaction converting octaacetate **14** into the hexaether diacetate **3** that only small amounts of **1** could be obtained following the procedure reported originally.<sup>1</sup> The synthesis that proceeds by way of **13** does not have these shortcomings. Not only is the yield good in the reaction that gives **7**, but, as seen in Scheme 4, the removal of the camphanate esters of **13**, by treatment with methyllithium, followed by the immediate oxidation of the resulting bishydroquinone, by treatment with chloranil,<sup>36</sup> gives **1** in 95% yield.

**Aggregation of Nonracemic 1 in Solution.** When solutions of nonracemic **1** in dodecane are concentrated, a number of their properties change.

**(a) CD and UV-Vis Absorption Spectra and Specific Rotations.** Figure 1 shows that while the CD spectra of  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  M solutions of (–)-**1** in dodecane are essentially identical, when the concentration is increased to  $2.5$



**Figure 2.** (a, top) CD spectra (ordinate on the left, displaying molar circular dichroism) and (b, bottom) UV-vis absorption spectra (ordinate on the right, displaying molar extinction coefficient) of  $2.5 \times 10^{-2}$  M solutions of (–)-**1**: (–) in dodecane; (– – –) in 10% CHCl<sub>3</sub>–90% dodecane; (- · - ·) in 50% CHCl<sub>3</sub>–50% dodecane. The path lengths are all  $10 \mu\text{m}$ .

$\times 10^{-2}$  M, circular dichroisms at ca. 251, 342, and 511 nm increase greatly. In particular, the circular dichroism at 251 nm becomes very large, whereas in the dilute solutions it is tiny. These changes are one indication that the molecules of nonracemic **1**, which at  $1.0 \times 10^{-5}$  M behave independently of one another, aggregate when their solutions in dodecane are concentrated. Similar changes in CD spectra are seen when a related helicene that organizes into a columnar mesophase is dissolved in dodecane and similarly concentrated<sup>7</sup> and when planar chromophores aggregate that have chiral groups attached.<sup>37</sup> Figure 1 also shows that in the most concentrated solution in dodecane (the one that is  $2.5 \times 10^{-2}$  M), the UV absorption maximum at 315 nm decreases in intensity and an additional maximum appears at 332 nm.

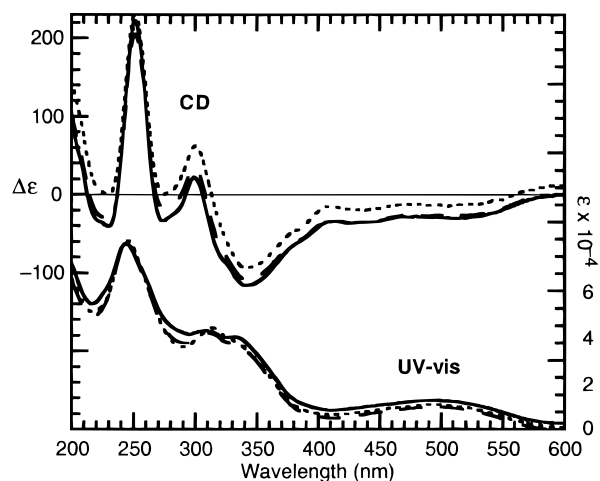
Figure 2 shows that when chloroform is added to the dodecane, the CD and UV-vis absorption spectra of a  $2.5 \times 10^{-2}$  M solution of (–)-**1**, which in the absence of chloroform are those attributed to the aggregates, change to those attributed to the unassociated molecules.<sup>38</sup> The spectra of a solution in 1:1 CHCl<sub>3</sub>–dodecane are essentially those of the  $1.0 \times 10^{-5}$  M solution in dodecane displayed in Figure 1. When the solvent is 10% CHCl<sub>3</sub>–90% dodecane, the spectra are partway between the two extremes.

(37) For examples in which the CDs of aggregating molecules are enhanced by concentration see footnote 4 in ref 1 and (a) Gottarelli, G.; Mezzina, E.; Spada, G. P.; Carsughi, F.; Di Nicola, G.; Mariani, P.; Sabatucci, A.; Bonazzi, S. *Helv. Chim. Acta* **1996**, *79*, 220 and references therein. For examples in which solvents and temperature are the agents of change, see: (b) Palmans, A. R. A.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2648. (c) Matile, S.; Berova, N.; Nakanishi, K. *Chem. Biol.* **1996**, *3*, 379. (d) Huang, D.; Matile, S.; Berova, N.; Nakanishi, K. *Heterocycles* **1996**, *42*, 723 and references therein. (e) Schnur, J. M.; Ratna, B. R.; Selinger, J. V.; Singh, A.; Jyothi, G.; Easwaran, K. R. K. *Science* **1994**, *264*, 945. For examples in which organization in films results in enhanced CD spectra, see ref 37b. Also see: (f) van Nostrum, C. F.; Bosman, A. W.; Gelinck, G. H.; Schouten, P. G.; Warman, J. M.; Kentgens, A. P. M.; Devillers, M. A. C.; Meijerink, A.; Picken, S. J.; Soehling, U.; Schouten, A.-J.; Nolte, R. J. M. *Chem. Eur. J.* **1995**, *1*, 171. (g) Barberá, J.; Iglesias, R.; Serrano, J. L.; Sierra, T.; de la Fuente, M. R.; Palacios, B.; Pérez-Jubindo, M. A.; Vázquez, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 2908.

(38) Similar effects of CHCl<sub>3</sub> on aggregates of other molecules are in ref 37b. For those of ClCH<sub>2</sub>CH<sub>2</sub>Cl see: (a) Markovitsi, D.; Bengs, H.; Ringsdorf, H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1275. (b) Gallivan, J. P.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 2423.

(35) By the method of Brimble et al. and Jacob et al.: (a) Brimble, M. A.; Hodges, R.; Stuart, S. J. *Tetrahedron Lett.* **1988**, *29*, 5987. (b) Jacob, P., III; Callery, P. S.; Shulgin, A. T.; Castagnoli, N., Jr. *J. Org. Chem.* **1976**, *41*, 3627.

(36) By the method described in ref 9b.



**Figure 3.** (a, top) CD spectra (ordinate on the left, displaying molar circular dichroism) and (b, bottom) UV-vis absorption spectra (ordinate on the right, displaying molar extinction coefficient) of (–)-**1** in dodecane: (–) when the concentration is  $2.5 \times 10^{-2}$  M and the path length is  $10 \mu\text{m}$ ; (– –) when the concentration is  $1.0 \times 10^{-3}$  M and the path length  $105 \mu\text{m}$ ; (– – –) when the concentration is  $5.0 \times 10^{-4}$  M and the path length is 1 mm.

**Table 1.** Specific Rotation and  $g$  Values ( $\Delta\epsilon/\epsilon$ ) at Three Wavelengths of (–)-**1** in Dodecane and Neat

concn (M)	$g \times 10^3$			$[\alpha]_D \times 10^3$ <sup>a</sup>
	252 nm	350 nm	530 nm	
$1 \times 10^{-5}$	–0.19	–1.7	–0.36	–0.60
$5 \times 10^{-4}$	4.5	–4.5	–2.2	–5.4
$2.5 \times 10^{-2}$	4.5	–5.2	–4.1	–7.1
$1.0 \times 10^{-1}$				–16
neat <sup>b</sup>	12	–9.8	–8.1	–160

<sup>a</sup> (deg cm<sup>2</sup>)/10 g. <sup>b</sup> The  $g$  values were measured using a film on a quartz plate that had been spin coated from a  $1 \times 10^{-3}$  M octane solution. To determine the  $[\alpha]_D$  of such a film, the thickness ( $0.41 \mu\text{m}$ ) was measured by comparing the absorbance with that of a sample of known thickness ( $2 \mu\text{m}$ ). The density was assumed to be 0.85 g/mL.

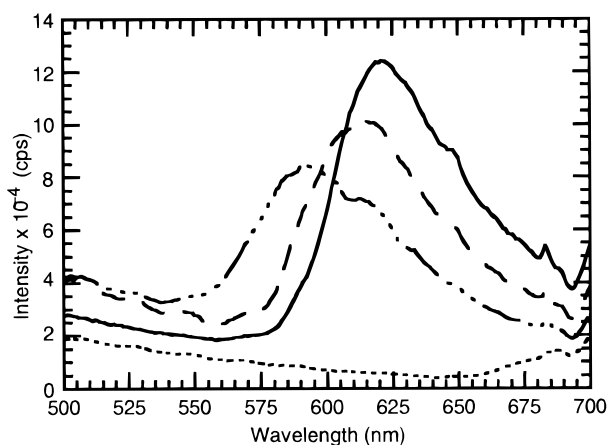
Figure 3 shows that concentrations much less than  $2.5 \times 10^{-2}$  M are sufficient for aggregation to be recognizable in the electronic spectra. Thus, even a solution in dodecane as dilute as  $5.0 \times 10^{-4}$  M displays CD and UV-vis absorption spectra essentially identical to those of a  $2.5 \times 10^{-2}$  M solution in dodecane. Measures of the aggregation are the values of  $\Delta\epsilon/\epsilon$ , Kuhn's dissymmetry factors  $g$ ,<sup>39</sup> which Table 1 summarizes at three wavelengths for the dodecane solutions of varying concentration.

The table also displays how the specific rotations of the samples vary with concentration. It shows that the  $g$  values are larger for the more concentrated solutions than for the one that is most dilute and that the  $[\alpha]_D$  values rise from  $-600$  (deg cm<sup>2</sup>)/10 g when the sample is most dilute, to  $-5400$  (deg cm<sup>2</sup>)/10 g when aggregation is first detected spectroscopically (at  $5.0 \times 10^{-4}$  M), to  $-16\,000$  (deg cm<sup>2</sup>)/10 g when the solution is 0.1 M.<sup>40</sup> The  $g$  values suggest that more concentrated samples have higher specific rotations because the aggregates they contain are larger.

**(b) Light Scattering and Viscosity.** Evidence that aggregation increases when the solutions are concentrated is provided

(39) (a) Kuhn, W. *Trans. Faraday Soc.* **1930**, *26*, 293. (b) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; Chapter 13.

(40) There was no sign of anisotropy. The specific rotations did not change when the samples were rotated about the light beam, and no features were seen when the samples, sandwiched between crossed polarizers, were observed with a microscope.



**Figure 4.** Light scattering from solutions of (–)-**1**: (–) in dodecane at a concentration of  $2.0 \times 10^{-2}$  M; (– –) in dodecane at a concentration of  $5.0 \times 10^{-3}$  M; (– – –) in dodecane at a concentration of  $1.0 \times 10^{-3}$  M; (· · ·) in 50% CHCl<sub>3</sub>–50% dodecane at a concentration of  $2.0 \times 10^{-2}$  M. The solutions were in 2 mm path length cells.

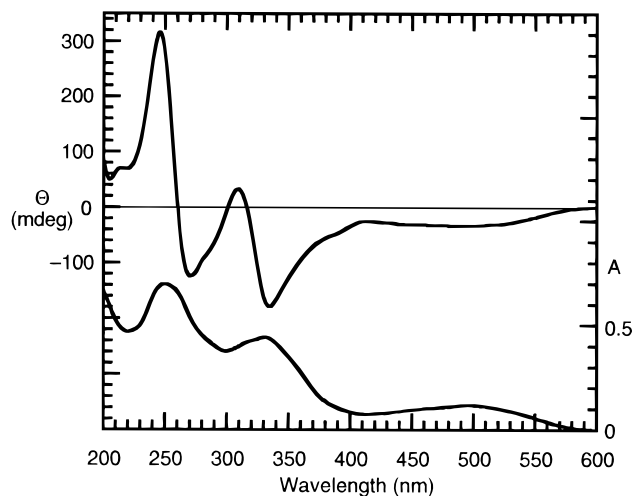
by light scattering data (Figure 4). There are two significant observations. One is that while a  $2.5 \times 10^{-2}$  M solution of (–)-**1** in 1:1 CHCl<sub>3</sub>–dodecane, in which the helicene molecules appear to be unassociated (Figure 2), scatters no amount of measurable light between 500 and 700 nm, a solution in dodecane that is  $1 \times 10^{-3}$  M does scatter detectable amounts of light, maximally at ca. 590 nm. The second is that, as the concentration in dodecane increases, the scattered light increases in intensity.<sup>6,41</sup> Enhanced light scattering is expected near absorption bands of aggregates whose chromophores couple, an effect called resonance light scattering,<sup>6</sup> and as illustrated by the curves in Figure 4, the scattering can be perturbed by intense absorption.<sup>42</sup> The peaks are at wavelengths much greater than those of the lowest energy absorption bands (ca. 490 nm, Figures 1 and 3), presumably because strong absorption of light at lower wavelengths shifts the observed scattering peaks to higher wavelengths. Moreover, it shifts the peaks further when the concentration, and therefore the absorption, increases. However, the telling observation is that, at wavelengths above 625 nm, the intensity of scattered light overcomes the effects of absorption. It increases with the sample's concentration. This is possible only if the aggregates increase appreciably in size.

There is a more evident manifestation of aggregation. Just like solutions of other molecules that aggregate, those of nonracemic **1** in dodecane, which are not notably viscous when their concentrations are  $\leq 1 \times 10^{-3}$  M, are highly viscous when the concentration is  $2.5 \times 10^{-2}$  M.<sup>43</sup> In sum, the increasing  $g$

(41) (a) Pasternack, R. F.; Bustamante, C.; Collings, P. J.; Gianetto, A.; Gibbs, E. J. *J. Am. Chem. Soc.* **1993**, *115*, 5393. (b) Pasternack, R. F.; Schaefer, K. F. *Inorg. Chem.* **1994**, *33*, 2062. (c) de Paula, J. C.; Robblee, J. H.; Pasternack, R. F. *Biophys. J.* **1995**, *68*, 335. (d) Parkash, J.; Robblee, J. H.; Agnew, J.; Gibbs, E.; Collings, P.; Pasternack, R. F.; de Paula, J. C. *Biophys. J.* **1998**, *74*, 2089. (e) Purrello, R.; Scolaro, L. M.; Bellacchio, E.; Gurrieri, S.; Romeo, A. *Inorg. Chem.* **1998**, *37*, 3647.

(42) (a) Pasternack, R. F.; Goldsmith, J. I.; Szép, S.; Gibbs, E. J. *Biophys. J.* **1998**, *75*, 1024. (b) Collings, P. J.; Gibbs, E. J.; Pasternack, R. F. unpublished results.

(43) Molecules whose solutions are either viscous or gel include, besides many that hydrogen-bond to one another, a number that are united by  $\pi$ -stacking forces: (a) Scheibe, G. *Kolloid-Z.* **1938**, *82*, 1. (b) Lin, Y.; Kachar, B.; Weiss, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 5542. (c) Snijder, C. S.; de Jong, J. C.; van Bolhuis, F.; Feringa, B. L. *Chem. Eur. J.* **1995**, *1*, 594. (d) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957. (e) Brotin, T.; Utermöhlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J.-P. *J. Chem. Soc., Chem. Commun.* **1991**, 416.



**Figure 5.** (a, top) CD spectra (ordinate on the left, displaying ellipticity in mdeg) and (b, bottom) UV-vis absorption spectra (ordinate on the right, displaying absorbance) of a spin-coated film of (–)-**1**.

values, specific rotations, and light scattering all imply that as the concentrations of nonracemic **1** in dodecane increase, so do the sizes of the aggregates the molecules form.

**Chiroptical Properties of Thin Film and Solvent-Free Samples of Nonracemic 1.** Displayed in Figure 5 are the CD and UV-vis absorption spectra of a thin film that was prepared by spin coating from a  $1 \times 10^{-3}$  M solution of (–)-**1** in octane onto a quartz slide. The CD spectrum did not change appreciably when the sample was rotated in the plane perpendicular to the beam of light,<sup>44</sup> but to eliminate any effects of linear birefringence and linear dichroism, a spectrum was measured each time the sample had been rotated through six successive  $30^\circ$  increments.<sup>45</sup> Figure 5 is the average of these spectra. The significant observation is that the film has essentially the same CD and UV-vis absorption spectra as the solutions of aggregated **1** (that is the  $2.5 \times 10^{-2}$  M solution in Figure 1), with one important difference. The  $g$  values (Table 1) are larger for the film than for the solutions (e.g., at 252 nm, 3 times larger). They are similar to one of the highest recorded, that of an optically active polythiophene.<sup>46</sup> That the value of  $g$  is larger for the film than for the most concentrated solution (Table 1) suggests that the aggregates in the bulk material are larger too. This notion is supported by the organization of the molecules in the pure material into very long fibers that are ca.  $3 \mu\text{m}$  wide.<sup>1,2</sup>

The spectra of the spin-coated films are similar to those of previously prepared Langmuir–Blodgett (LB) films.<sup>3</sup> Both are characteristic of the aggregates in dodecane solution. Notable differences are that the spectra of the spin-coated sample are sharper and their  $g$  values are higher ( $g = 1.2 \times 10^{-2}$  at 252 nm, compared to  $g = 7.5 \times 10^{-3}$  at 240 nm for the LB film).<sup>3</sup> Possibly the differences originate from the LB film having been spread from  $\text{CHCl}_3$  and the spin-coated film from octane, in which, according to Figures 1 and 2 (if octane is like dodecane), the molecules should be more organized than in  $\text{CHCl}_3$ .<sup>47</sup>

(44) The beam was ca.  $200 \text{ mm}^2$  in area.

(45) (a) Kuball, H.-G.; Schönhofer, A. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R., Eds.; VCH: New York, 1994; Chapter 4. (b) Schönhofer, A.; Kuball, H.-G. *Chem. Phys.* **1987**, *115*, 159. (c) Nördén, B. *Acta Chem. Scand.* **1972**, *26*, 1763. (d) Tunis-Schneider, M. J. B.; Maestre, M. F. *J. Mol. Biol.* **1970**, *52*, 521. (e) Cornell, D. G. *J. Colloid Interface Sci.* **1979**, *70*, 167.

(46) For optically active polythiophenes in dodecanol  $g$  values are said to be typically  $2 \times 10^{-2}$  (Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 4908).

The films of nonracemic **1** have unparalleled ability to rotate the plane of polarization of plane-polarized light. Initially we reported<sup>1</sup> that  $10 \mu\text{m}$  thick samples rotated plane-polarized light at 589 nm (the sodium D-line) by  $1400^\circ/\text{mm}$ , which corresponds to  $[\alpha]_D$  170 000 ( $\text{deg cm}^2$ )/10 g.<sup>48</sup> After further study, we found that 633 nm light from a low-power HeNe laser was appreciably scattered by these films. We therefore experimented with making films that are thinner and found that, by casting solutions in octane onto quartz plates, we could prepare thin films that scattered less. The thickness of one such film was determined to be  $0.41 \mu\text{m}$  by comparing its absorbance of 550 nm light with that of a film known to be  $2 \mu\text{m}$  thick.<sup>49</sup> The specific rotation of 589 nm light was measured each time this film, perpendicular to the light beam, was rotated about the beam through six successive  $30^\circ$  increments. The values diverged little and averaged to  $0.534 \pm 0.03^\circ$ . This means that  $\alpha = -1300 \text{ deg/mm}$  and  $[\alpha]_D -158 000 (\text{deg cm}^2)/10 \text{ g}$ .<sup>50</sup>

The specific rotation of **1** appears to be the highest recorded. Other materials with high specific rotations include a metal-locene oligomer ( $[\alpha]_D$  34 000 ( $\text{deg cm}^2$ )/10 g)<sup>51</sup> and a ferroelectric liquid crystal ( $\alpha = 100^\circ/\text{mm}$ ).<sup>52</sup> Cholesteric liquid crystals exhibit comparable rotations, but only for light at the reflecting wavelength (which is the product of their pitch and refractive index).<sup>53</sup>

**Properties of Racemic 1.** *Racemic 1* is much less soluble than nonracemic **1** in dodecane. Accordingly, its UV-vis absorption spectra in this solvent could be determined only if the concentration was less than ca.  $5.4 \times 10^{-4}$  M. These spectra were the same as those of the most dilute solutions of the nonracemic material. Unlike the nonracemic material, racemic **1** does *not* form fibers visible under the microscope when it is treated in the same way as the nonracemic material, that is, when it is heated to a temperature (ca.  $210^\circ\text{C}$ ) at which it flows freely and then is cooled. This accords with the observation that AFM images of Langmuir–Blodgett films of the racemic material do *not* show the long columnar structures that are seen in comparable films of the nonracemic material.<sup>4</sup> The implication is that long columns form and assemble into large fibrous structures only if the molecules have the same handedness.<sup>2</sup>

**Properties of Nonracemic 3.** To provide a reference to which the properties of nonracemic **1** could be compared, the optical properties of (+)-**3** were examined. The thought was that the cores of **1** and **3** have the same number of rings, the side chains projecting from the cores are similar, and **3** even has two more dodecyl side chains than **1**, which might make stacking more favorable. Yet as Figure 6 shows, the CD, UV-vis absorption, and fluorescence emission spectra of solutions of nonracemic **3** in dodecane are essentially the same when the concentration

(47) Similar effects of solvents on the films of phthalocyanines have been attributed to the formation of a lyotropic phase (Fujiki, M.; Tabei, H.; Kurihara, T. *Langmuir* **1988**, *4*, 1123).

(48) In the initial communication,<sup>1</sup> the units of the specific rotations were stated incorrectly as ( $\text{deg cm}^2$ )/g instead of ( $\text{deg cm}^2$ )/10 g. The  $[\alpha]_D$  for pure nonracemic **1** should have been listed as 170 000 ( $\text{deg cm}^2$ )/10 g instead of 170 000 ( $\text{deg cm}^2$ )/g.

(49) This sample was made by sandwiching **1** between quartz plates that were separated by a  $2 \mu\text{m}$  aluminum spacer from The Goodfellow Corp., Berwyn, PA.

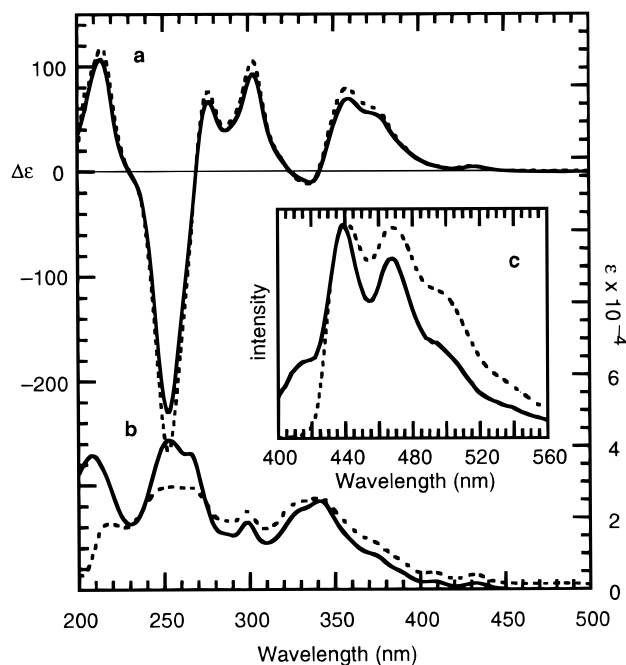
(50) The density was assumed, as previously,<sup>1</sup> to be 0.85 g/mL.

(51) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182.

(52) Mušević, I.; Škarabot, M.; Kityk, A. V.; Blinc, R.; Moro, D.; Heppke, G. *Ferroelectrics* **1997**, *203*, 133.

(53) (a) de Vries, H. *Acta Crystallogr.* **1951**, *4*, 219. (b) Chandrasekhar, S.; Prasad, J. S. *Mol. Cryst. Liq. Cryst.* **1971**, *14*, 115. (c) Isaert, N.; Berthault, J.-P.; Billard, J. J. *Opt.* **1980**, *11*, 17. (d) Cano, R.; Chatelain, P. *Compt. Rend.* **1964**, *259*, 352. (e) Baessler, H.; Laronge, T. M.; Labes, M. M. *J. Chem. Phys.* **1969**, *51*, 3213.





**Figure 6.** (a, top) CD spectra (ordinate on the left, displaying molar circular dichroism) and (b, bottom) UV-vis absorption spectra (ordinate on the right, displaying molar extinction coefficient) of **3** in dodecane: (—) when the concentration is  $2.0 \times 10^{-2}$  M and the path length is  $10 \mu\text{m}$  and (---) when the concentration is  $2.0 \times 10^{-5}$  M and the path length is  $10 \text{mm}$ . The inset (c) displays emission spectra (excitation at  $325 \text{nm}$ ) of dodecane solutions of **3** in a  $10 \mu\text{m}$  cell: (—) when the concentration is  $2.1 \times 10^{-2}$  M and (---) when the concentration is  $2.1 \times 10^{-5}$  M solutions.

is  $2 \times 10^{-2}$  M as when it is  $2 \times 10^{-5}$  M, and as reported previously,<sup>1</sup> so are the specific rotations ( $[\alpha]_{\text{D}} 410$  and  $413$  ( $\text{deg cm}^2/10 \text{g}$ ). Furthermore, the pure material in a  $10 \mu\text{m}$  cell rotates plane-polarized light at  $589 \text{nm}$  by  $0.11^\circ$ , corresponding to  $[\alpha]_{\text{D}} 1300$  ( $\text{deg cm}^2/10 \text{g}$ ).<sup>1,48,50</sup> When viewed under a microscope between crossed polarizers, it is isotropic. These properties contrast with those of nonracemic **1**, whose CD and UV-vis absorption spectra (Figure 1), fluorescence emission spectra,<sup>1</sup> and specific rotations (Table 1) change greatly when its solutions in dodecane are concentrated and which under a polarizing microscope is seen to be highly anisotropic.<sup>1,2</sup> We suppose the reason that **1** aggregates, whereas **3** does not, is that donor-acceptor interactions between electron-rich rings of one molecule and electron-poor rings of the adjacent molecules stabilize columnar stacks,<sup>54</sup> and **3**, unlike **1**, has only electron-rich rings. An alternative explanation might be that stacking is inhibited in **3** by the bulk of the additional acetate groups, but a helicene that has ester groups at *one* end does organize into columns.<sup>7</sup> In any case, an essential point is that, for helicenes to stack, it seems that many side chains alone do not suffice.

**Differential Scanning Calorimetry and Kinetics of Racemization.** Table 2 summarizes the differential scanning calorimetric (DSC) analyses of nonracemic and racemic **1**.<sup>55</sup> Only one transition is seen in the first heating cycle, at  $230.7^\circ\text{C}$ , but in subsequent cooling and heating cycles, two transitions are seen initially and then only one, at a temperature  $21^\circ\text{C}$  lower.

(54) The notion that  $\pi$ -donor-acceptor interactions stabilize aggregating columnar systems was also proposed by others: ref 38a,b. Also see: (a) Green, M. M.; Ringsdorf, H.; Wagner, J.; Wüstefeld, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1478 and references therein. (b) Mohr, B.; Wegner, G.; Ohta, K. *J. Chem. Soc., Chem. Commun.* **1995**, 995.

(55) In the initial publication,<sup>1</sup> the DSC was scanned to only  $210^\circ\text{C}$  and therefore just missed the phase transitions recorded here.

**Table 2.** DSC Transition Temperatures and Enthalpies for Nonracemic and Racemic **1**<sup>a</sup>

cycle	first transition $T$ , $^\circ\text{C}$ ( $\Delta H$ , kJ/mol)	second transition $T$ , $^\circ\text{C}$ ( $\Delta H$ , kJ/mol)
Nonracemic <b>1</b>		
heating		230.7 (45.0)
cooling	195.6 (−7.9)	212.7 (−18.2)
heating	206.4 (23.6)	222.8 (15.7)
cooling	197.4 (−21.0)	
heating	209.4 (23.6)	
cooling	192.8 (−9.2)	
Racemic <b>1</b>		
heating	206.7 (36.2)	
cooling	191.5 (−30.2)	

<sup>a</sup> The temperature was scanned between  $30$  and  $250^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ .

This unusual behavior would be understandable if the helicene molecules invert configuration during the analyses. In accord with this explanation, racemic **1** exhibits the same DSC characteristics as nonracemic **1** that has been heated and cooled a number of times (Table 2) and nonracemic **1** does racemize sufficiently rapidly at the temperatures in Table 2. Thus, in 1,2,4-trichlorobenzene the half-times for racemization were measured as  $49 \text{min}$  at  $198.0^\circ\text{C}$ ,  $28 \text{min}$  at  $203.0^\circ\text{C}$ , and  $17 \text{min}$  at  $207.5^\circ\text{C}$ . The temperature at which the half-time for racemization is ca.  $1 \text{h}$ ,  $196^\circ\text{C}$ , is thus essentially the same as that for a similar [6]helicenebisquinone that lacks the alkoxy groups in the peri positions,  $190^\circ\text{C}$ ,<sup>9b</sup> and for the parent [6]helicene,  $201^\circ\text{C}$ .<sup>56</sup> However, the enthalpy of activation,  $\Delta H^\ddagger = 48.1 \text{kcal/mol}$ , is much larger than for the racemization of the parent [6]helicene ( $\Delta H^\ddagger = 35.4 \text{kcal/mol}$ ).<sup>56</sup> This might relate to the  $3.9 \text{kcal/mol}$  greater enthalpy of activation for racemization of a [5]helicenebisquinone<sup>11</sup> compared to its parent, [5]helicene.<sup>57</sup> More remarkable, however, is the enormously larger entropy of activation for the racemization of **1** ( $\Delta S^\ddagger = 26 \text{cal mol}^{-1} \text{K}^{-1}$ ) compared to that for the racemization of the parent [6]helicene ( $\Delta S^\ddagger = -1.9 \text{cal mol}^{-1} \text{K}^{-1}$ ).<sup>56</sup> This could be due to the relief of conformational restraints at the peri positions, but we do not have data to address the point. The  $45 \text{kJ/mol}$  enthalpy for the initial DSC transition of nonracemic **1** is 3 times greater than that reported for a helicene liquid crystal<sup>7</sup> and also greater than the  $1\text{--}20 \text{kJ/mol}$  for various discotic liquid crystals,<sup>58</sup> which we associate with the assembly of **1** into fibrous structures that the other materials do not form.

## Conclusions

An improved synthesis of helicene **1** is described. Notable are the 56% yield in the helicene-forming step and the method developed to resolve helicenequinones. Nonracemic helicene **1**, unlike nonracemic **3** and also unlike any previously known helicene, aggregates in solution and in thin films. In dodecane, aggregation occurs even in solutions as dilute as  $5 \times 10^{-4} \text{M}$ . The aggregation is characterized by enhanced circular dichroisms and  $g$  values, red-shifted UV-vis absorptions, increased specific rotations, increased light scattering at an absorption frequency, and, as reported previously, fluorescence emissions that shift to the red and  $^1\text{H}$  NMR resonances that shift upfield. The chiroptical properties of concentrated solutions in dodecane to which  $\text{CHCl}_3$  has been added are similar to those of the most

(56) (a) Martin, R. H.; Marchant, M.-J. *Tetrahedron Lett.* **1972**, 3707. (b) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 347. The values of  $\Delta H^\ddagger$  ( $35.4 \text{kcal/mol}$ ) and  $\Delta S^\ddagger$  ( $-1.9 \text{cal mol}^{-1} \text{K}^{-1}$ ) were recalculated using the kinetic data in the first of these references.

(57) Goedicke, C.; Stegemeyer, H. *Tetrahedron Lett.* **1970**, 937.

(58) See footnote 15 in ref 7.

dilute solutions in dodecane alone, implying that  $\text{CHCl}_3$  causes the aggregates to dissociate. Cast films of the pure material show high specific rotations,  $[\alpha]_D -158\,000$  (deg  $\text{cm}^2$ )/10 g. The CD and UV-vis absorption spectra of spin-coated films are similar to those of the concentrated solutions in dodecane, but the  $g$  values are higher. Unlike the nonracemic material, the racemic material in bulk, after it has been heated and cooled, does not form visible fibers, and it is too insoluble in dodecane to give concentrated solutions.

## Experimental Section

THF and toluene were distilled from Na plus benzophenone,  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_3\text{N}$  from  $\text{CaH}_2$ . Benzoquinone was purified by mixing it with 4 times its weight of basic alumina, a small amount of 4 Å molecular sieves, and  $\text{CH}_2\text{Cl}_2$ . The slurry was filtered through Celite and the solvent removed under reduced pressure.

Methylolithium (1.6 M in  $\text{Et}_2\text{O}$ , low halide content) was purchased from Acros. The following were purchased from Aldrich and used without further purification: tetrapropylammonium perruthenate (97%), *N*-methylmorpholine *N*-oxide (97%), 4 Å powdered molecular sieves (activated), triisopropylsilyl trifluoromethanesulfonate (97%), heptane (anhydrous, 99%), 1-iodododecane (98%), DMF (anhydrous, 99.8%), (1*S*)-(–)-camphanoyl chloride (98%), and chloranil (99%).

Details of the syntheses of compounds **3**, **4**, **5**, **8**, **9**, and **14** and of the previous synthesis of **1** can be found in the Supporting Information to ref 1.

**4,5-Dihydroxy-2,7-naphthalenedicarboxaldehyde.** EtOH (76 mL, 100%) was injected into a mixture of powdered KOH (2.92 g, 52.0 mmol) and **8** (2 g, 5.2 mmol) that had been evacuated three times and flushed with  $\text{N}_2$  in a flame-dried round-bottomed flask containing a magnetic stir bar. The mixture was stirred for 35 min, by which time a heavy yellow precipitate had formed. Cooling in an ice-water bath and stirring with 1 N HCl and then cold water precipitated the product, which was filtered and washed with much water to remove pivalic acid. Drying, first with air in the funnel for 30 min and then under high vacuum overnight, yielded 1.09 g (a 97% yield) of 4,5-dihydroxy-2,7-naphthalenedicarboxaldehyde, a yellow powder: mp (from EtOH/ $\text{H}_2\text{O}$ ) > 225 °C; IR (NaCl) 1680  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  7.35 (d, 2 H,  $J = 1.3$  Hz), 8.20 (d, 2 H,  $J = 1.3$  Hz), 10.11 (s, 2 H), 10.65 (br s, 2 H);  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  107.9, 120.9, 128.0, 136.7, 137.1, 156.0 192.2; HRMS (FAB) calcd for  $\text{C}_{12}\text{H}_8\text{O}_4$  216.0423, found 216.0418.

**4,5-Didodecyloxy-2,7-naphthalenedicarboxaldehyde (10).** 1-Iodododecane (6.85 mL, 27.8 mmol) and then dry DMF (30 mL) were added to 4,5-dihydroxy-2,7-naphthalenedicarboxaldehyde (1.00 g, 4.63 mmol) and powdered  $\text{K}_2\text{CO}_3$  (3.20 g, 23.1 mmol) that had been evacuated and flushed with  $\text{N}_2$  several times in a flame-dried round-bottomed flask containing a magnetic stir bar. The mixture was stirred at 50 °C overnight, cooled to room temperature, and poured into ice-water. Extraction with  $\text{CH}_2\text{Cl}_2$  (3 $\times$ ), washing with water, drying ( $\text{MgSO}_4$ ), filtration, removal of solvent under reduced pressure, and silica gel chromatography (eluent: first benzene and then 2% EtOAc in benzene) gave 2.50 g of **10** (a 98% yield), a buff-colored, waxy solid: mp (from PhH) 105–107 °C; IR (NaCl) 1699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90 (t, 6 H,  $J = 6.9$  Hz), 1.20–1.70 (m, 36 H), 1.96 (quint, 4 H,  $J = 8.0$  Hz), 4.16 (t, 4 H,  $J = 6.6$  Hz), 7.39 (d, 2 H,  $J = 1.1$  Hz), 7.98 (d, 2 H,  $J = 1.1$  Hz), 10.11 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.3, 29.3–29.7 (m), 31.9, 69.5, 104.4, 123.6, 128.3, 135.5, 136.0, 158.2, 191.7; HRMS (FAB) calcd for  $\text{C}_{36}\text{H}_{56}\text{O}_4$  552.4179, found 552.4185.

**2,7-Diacetyl-4,5-didodecyloxynaphthalene (11).** THF (50 mL) was added to 3.0 g of **10** (5.4 mmol) in a flame-dried 100 mL round-bottomed flask containing a magnetic stir bar. Although cooling to 0 °C gave some precipitate, 10.2 mL of 1.6 M MeLi in  $\text{Et}_2\text{O}$  (16.2 mmol) was syringed in drops into the stirred slurry. After the mixture had stirred at room temperature for 30 min, it was recooled to 0 °C, treated with saturated aqueous  $\text{NH}_4\text{Cl}$  to destroy excess MeLi, and combined with  $\text{H}_2\text{O}$  (20 mL). Extraction (EtOAc, 3 $\times$ ), drying (powdered activated 4 Å molecular sieves), filtration through Celite, and removal of solvent

gave 3.0 g of pure diol (a 96% yield), an off-white oil that slowly crystallized: IR ( $\text{CCl}_4$ , KBr) 3616, 3500  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t, 6 H,  $J = 7.0$  Hz), 1.30–1.65 (m, 36 H), 1.47 (d, 6 H,  $J = 6.4$  Hz), 1.93 (quint, 4 H, 8.1 Hz) 3.92 (t, 4 H, 6.5 Hz), 4.75 (q, 2 H, 6.4 Hz), 6.87 (s, 2 H), 7.27 (s, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 24.9, 26.3, 29.4–29.7 (m), 31.9, 69.3, 70.5, 104.2, 116.3, 116.5, 137.1, 144.1, 157.1; HRMS (FAB) calcd for  $\text{C}_{38}\text{H}_{64}\text{O}_4$  584.4805, found 584.4818.

To 3.0 g of this diol (5.13 mmol) were added 2.5 g of 4 Å molecular sieves, 25 mL of dry  $\text{CH}_2\text{Cl}_2$ , 95 mg of tetrapropylammonium perruthenate (0.27 mmol), and 1.58 g of *N*-methylmorpholine *N*-oxide (13.5 mmol). The deep green-black mixture was stirred at room temperature for ca. 1 h and then poured onto a silica gel column (2 in.  $\times$  6 in.).  $\text{CH}_2\text{Cl}_2$  eluted 2.5 g (an 85% yield) of **11**, a slightly yellow, waxy solid: mp (from  $\text{CH}_2\text{Cl}_2$ ) 98–101 °C; IR (NaCl) 1683  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t, 6 H,  $J = 6.9$  Hz), 1.20–1.70 (m, 36 H), 1.93 (quint, 4 H,  $J = 8.0$  Hz), 2.72 (s, 6 H), 4.14 (t, 4 H,  $J = 6.6$  Hz), 7.46 (d, 2 H,  $J = 1.2$  Hz), 8.06 (d, 2 H,  $J = 1.3$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.5, 23.1, 26.7, 26.8, 29.8–30.1 (m), 69.8, 106.2, 122.5, 124.5, 136.1, 136.3, 157.9, 198.0. Anal. Calcd for  $\text{C}_{38}\text{H}_{60}\text{O}_4$ : C, 78.57; H, 10.41. Found: C, 78.48; H, 10.42.

**Bis(enol ether) 6.**  $\text{CH}_2\text{Cl}_2$  (14 mL) and  $\text{Et}_3\text{N}$  (3.6 mL) were syringed into **11** (1.5 g, 2.6 mmol) under  $\text{N}_2$  in a flame-dried round-bottomed flask containing a magnetic stir bar. The flask was cooled to 0 °C, and triisopropylsilyl triflate (1.43 mL, 5.3 mmol) was added in drops from a syringe. The reaction mixture was allowed to warm to room temperature (ca. 10 min) and then recooled to 0 °C. Saturated aqueous  $\text{NaHCO}_3$  was added, and the mixture was extracted with benzene (2 $\times$ ). The combined benzene extracts were washed with saturated aqueous  $\text{NaHCO}_3$ , 1 N NaOH, and water, dried over 4 Å molecular sieves, and filtered through Celite. Removal of solvent and chromatography on a 1 in.  $\times$  3 in. column of neutral alumina in 1:1 benzene–hexane plus 3%  $\text{Et}_3\text{N}$  (eluent: the same solvent) gave, after the product had been heated at 100 °C in a vacuum, 2.2 g of **6** (a 95% yield), a clear, brightly fluorescent oil that slowly crystallized at room temperature:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t, 6 H,  $J = 7.0$  Hz), 1.16 (d, 36 H,  $J = 7.3$  Hz), 1.25–1.60 (m, 42 H), 1.92 (quint, 4 H,  $J = 7.2$  Hz), 4.07 (t, 4 H, 6.7 Hz), 4.51 (d, 2 H, 1.7 Hz), 4.97 (d, 2 H, 1.7 Hz), 7.06 (d, 2 H, 1.3 Hz), 7.67 (d, 2 H, 1.4 Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.1, 14.5, 18.4, 23.1, 26.8, 29.6–30.2 (m), 32.2, 69.7, 91.3, 105.1, 117.9, 118.2, 136.0, 139.8, 156.4, 157.0; HRMS (FAB,  $M + 1$ ) calcd for  $\text{C}_{56}\text{H}_{101}\text{O}_4\text{Si}_2$  893.7238, found 893.7237.

**Helicenebisquinone 7.** *p*-Benzoquinone (5.3 g, 49.3 mmol) was added to a solution of **6** (2.2 g, 2.45 mmol) in anhydrous heptane (35 mL) under  $\text{N}_2$ , contained in a flame-dried 100 mL round-bottomed flask, outfitted with a magnetic stir bar and reflux condenser, that had been evacuated and flushed with  $\text{N}_2$  (5 $\times$ ). The reaction mixture was evacuated, flushed with  $\text{N}_2$ , and gently refluxed for 4 d. During the course of the reaction, *p*-benzoquinone that had sublimed into the reflux condenser was scraped back into the reaction flask. The solvent was distilled, and the residue under vacuum was heated at 135 °C to sublime away *p*-benzoquinone and hydroquinone. THF (30 mL),  $\text{Ac}_2\text{O}$  (9.35 mL, 99 mmol),  $\text{Et}_3\text{N}$  (13 mL), and  $\text{Et}_3\text{N}\cdot\text{HF}$  (1.19 g, 9.9 mmol) were added to the residual glassy solid, and the mixture was stirred for 2 h at room temperature.  $\text{CH}_2\text{Cl}_2$  was added, washed with  $\text{H}_2\text{O}$  (3 $\times$ ), dried ( $\text{MgSO}_4$ ), filtered, and removed under reduced pressure. Chromatography on a 2 in.  $\times$  6 in. column of silica gel (eluent: benzene containing amounts of EtOAc that increased from 5 to 10%) yielded 1.2 g of **7** (a 56% yield), a brick-red powder: mp (from PhH) 164–166 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t, 6 H,  $J = 6.9$  Hz), 1.20–1.70 (m, 36), 1.97 (m, 4 H), 2.54 (s, 6 H), 4.22 (m, 2 H) 4.24 (m, 2 H), 6.60 (d, 2 H,  $J = 9.8$  Hz), 6.79 (d, 2 H,  $J = 9.8$  Hz), 7.23 (s, 2 H), 7.95 (s, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.5, 21.6, 23.1, 26.8, 29.8–30.1 (m), 32.3, 70.0, 99.5, 116.7, 121.2, 127.3, 131.0, 132.4, 132.7, 136.9, 139.8, 148.5, 159.0, 168.7, 184.1, 185.9; HRMS (FAB,  $M + 1$ ) calcd for  $\text{C}_{54}\text{H}_{65}\text{O}_{10}$  873.4573, found 873.4578. Anal. Calcd for  $\text{C}_{54}\text{H}_{64}\text{O}_{10}$ : C, 74.29; H, 7.39. Found: C, 74.30; H, 7.45.

(±)-**1.** Anhydrous DMF (10 mL) was syringed into **7** (0.4 g, 0.41 mmol),  $\text{K}_2\text{CO}_3$  (1.26 g, 9.2 mmol), and 1-iodododecane (5.7 mL, 23 mmol) contained in a flame-dried round-bottomed flask with a magnetic stir bar that had been evacuated and flushed with  $\text{N}_2$ . After the reaction



mixture had again been repeatedly evacuated and flushed with N<sub>2</sub>, it was heated to 65 °C and stirred vigorously for 2.5 h. The reaction mixture was cooled to room temperature, and EtOH (10 mL) was added to precipitate the product, which was collected in a fritted funnel on top of a pad of Celite and washed with large amounts of EtOH. CH<sub>2</sub>-Cl<sub>2</sub> was used to wash the product from the Celite, and after the solvent had been removed under reduced pressure, the residue was chromatographed on a 1 in. × 4 in. column of silica gel, which yielded 0.48 g of (±)-**1** (a 93% yield), a red wax whose <sup>1</sup>H and <sup>13</sup>C NMR, IR, and UV spectra were identical to those of samples of **1** prepared according to the published procedure.<sup>59</sup>

**Preparation and Resolution of the Enantiomers of 13.** THF (30 mL) and then water (15 mL) that had been boiled to remove O<sub>2</sub> and cooled under N<sub>2</sub> were added to (±)-**1** (1.0 g, 0.89 mmol) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (2 g, 11.5 mmol) in a flame-dried 100 mL round-bottomed flask with a magnetic stir bar. After the mixture had stirred for 30 min, the color had changed from deep red to lemon yellow, indicating that the bisquinone had been reduced. Distilled CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and H<sub>2</sub>O (10 mL) were added, solvent was removed from the organic layer under reduced pressure, and the residual yellow solid was heated overnight at 100 °C and then cooled to room temperature. (1S)-(-)-Camphanoyl chloride (2.3 g, 10.7 mmol) was added, and the flask containing the two solids was evacuated and flushed with N<sub>2</sub>. After THF (25 mL) had been added and the mixture cooled to 0 °C, Et<sub>3</sub>N (4 mL) was added in drops from a syringe, and the reaction mixture was refluxed and stirred for 24 h. Benzene (20 mL) was added to the cooled mixture and then washed with saturated aqueous NaHCO<sub>3</sub>, dilute aqueous NH<sub>3</sub>, 1 N HCl, H<sub>2</sub>O, and finally saturated aqueous NaHCO<sub>3</sub>, dried (MgSO<sub>4</sub>), filtered, and removed under reduced pressure. Chromatography on a 2 in. × 8 in. silica gel column (eluent: 25% EtOAc–75% hexanes) yielded (-)-**13** (0.70 g, an 85% yield) and then (eluent: 33% EtOAc–67% hexanes) (+)-**13** (0.68 g, an 83% yield), both yellow glassy substances.

**Data for (-)-13:** IR (CCl<sub>4</sub>, KBr) 1798, 1752 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.52 (s, 6 H), 0.61 (s, 6 H), 0.85–1.00 (m, 20 H), 1.05–1.65 (m, 112 H), 1.70–2.10 (m, 12 H), 2.35–2.45 (m, 2 H), 2.72–2.82 (m, 2 H), 4.15–4.32 (m, 6H), 4.52–4.58 (m, 2 H), 6.25 (d, 2 H, *J* = 8.3 Hz), 6.85 (d, 2 H, *J* = 8.3 Hz), 7.17 (s, 2 H), 7.78 (s, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 9.6, 9.8, 14.1, 16.1, 17.0, 22.7, 26.4, 26.6, 28.9, 29.1, 29.4–29.8 (m), 31.1, 31.9, 54.2, 54.4, 54.7, 55.0, 68.2, 69.4, 89.5, 91.4, 97.7, 100.3, 114.8, 117.5, 117.8, 120.2, 121.1, 126.4, 127.1, 128.4, 142.9, 143.5, 153.7, 156.0, 164.9, 166.2, 177.8, 178.1; [α]<sub>D</sub> -431 (*c* 0.17, CH<sub>2</sub>Cl<sub>2</sub>); HRMS (FAB) calcd for C<sub>114</sub>H<sub>160</sub>O<sub>20</sub> 1849.1503, found 1849.1501.

**Data for (+)-13:** IR (CCl<sub>4</sub>, KBr) 1799, 1750 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.47 (s, 6 H), 0.77 (s, 6 H), 0.87–1.05 (m, 20 H), 1.20–1.75 (m, 110 H), 1.87–1.95 (m, 2 H), 2.00–2.18 (m, 10 H), 2.37–2.45 (m, 2 H), 2.72–2.82 (m, 2 H), 4.20–4.38 (m, 6 H), 6.26 (d, 2 H, *J* = 8.3 Hz), 6.86 (d, 2 H, *J* = 8.3 Hz), 7.01 (s, 2 H), 7.73 (s, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 9.6, 9.7, 14.1, 16.3, 16.7, 17.1, 22.7, 26.5, 26.6, 28.6, 28.9, 29.1–29.8, 31.2, 31.9, 54.1, 54.3, 54.4, 54.9, 68.6, 69.6, 90.3, 91.0, 96.6, 100.3, 115.8, 117.6, 118.5, 119.3, 122.4, 125.5, 127.9, 128.9, 142.7, 144.0, 153.9, 156.9, 165.0, 166.2, 177.3, 177.7; [α]<sub>D</sub> +310 (*c* 0.17, CH<sub>2</sub>Cl<sub>2</sub>); HRMS (FAB) calcd for C<sub>114</sub>H<sub>160</sub>O<sub>20</sub> 1849.1503, found 1849.1519.

Among peaks in the <sup>1</sup>H NMR spectra that are isolated and prominent are those at 7.17 ppm in the (-)-diastereomer and at 7.01 ppm in the (+)-diastereomer. The former resonance could not be found in the latter's spectrum and vice versa, and the excellent ratio of signal to noise implied that each diastereomer contained 0.5% or less of the other.

(-)-**1**. THF (15 mL) and then, while stirring, MeLi (3.95 mL 6.32 mmol) in drops were added to (-)-**13** (0.390 g, 0.021 mmol) under N<sub>2</sub> in a flame-dried round-bottomed flask that was cooled to -78 °C. Stirring was continued while the mixture was allowed to warm to room temperature and for an additional 30 min. Saturated aqueous NH<sub>4</sub>Cl was added in drops to the mixture, the mixture was recooled to 0 °C, until excess MeLi had reacted, and then 1 N HCl and benzene were added. The organic layer was washed with water and dried (MgSO<sub>4</sub>). Before the MgSO<sub>4</sub> was filtered, chloranil was added, whereupon the

solution turned from lemon yellow to deep red. Filtration and rotary evaporation gave a solid, which was chromatographed on a 1 in. × 3 in. silica gel column. Elution with 2.5% EtOAc in benzene, concentration at reduced pressure, dissolution in a small amount of CH<sub>2</sub>Cl<sub>2</sub>, and precipitation by the addition of ethanol yielded 0.22 g (a 95% yield) of (-)-**1**, a red wax: IR (KBr) 1656 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.87 (m, 6H), 1.28 (m, 32H), 1.60 (m, 4H), 1.99 (m, 4H), 4.25 (m, 4H), 6.53 (d, *J* = 11.1 Hz, 1H), 6.70 (d, *J* = 10.8 Hz, 1H), 7.41 (s, 1H), 7.59 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 14.11, 22.70, 26.23, 26.45, 29.06, 29.39, 29.44, 29.63, 29.68, 29.70, 29.73, 29.76, 29.79, 31.94, 69.27, 69.42, 98.81, 102.07, 120.57, 126.46, 128.00, 129.11, 131.78, 132.14, 135.92, 139.73, 156.81, 184.93, 185.26; HRMS calcd for C<sub>74</sub>H<sub>110</sub>O<sub>8</sub> 1126.8200, found 1126.8230.

A similar procedure converted 410 mg of (+)-**13** into 245 mg of (+)-**1** (a 98% yield).

**Preparation and Resolution of (±)-12.** Dry oxygen-free THF (50 mL) and then deoxygenated water (20 mL) were added to **5** (0.5 g, 0.6 mmol) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (1 g, 6 mol) in a dry round-bottomed flask fitted with a reflux condenser. The suspension was refluxed for 30 min and then cooled. Dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and 10 mL of H<sub>2</sub>O were syringed in, and the organic layer was cannulated into another dry oxygen-free flask. Two 10 mL portions of CH<sub>2</sub>Cl<sub>2</sub> washed the remainder over. Stripping yielded a bright yellow solid, which was heated for 3–4 h at 100 °C. Powdered 4 Å molecular sieves, followed by 10 mL of CH<sub>2</sub>-Cl<sub>2</sub>, were added to the air-sensitive bishydroquinone, and after it had cooled to 0 °C, the solution was transferred by cannula to another flask that contained (-)-camphanoyl chloride (1.53 g, 7.1 mmol) at 0 °C. CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was used to transfer residual bishydroquinone. Et<sub>3</sub>N (1 mL, 7.1 mmol) was added in drops from a syringe, and the yellow solution was stirred at 0 °C for 2 h. The cold solution and then repeated CH<sub>2</sub>Cl<sub>2</sub> washings were filtered into 1 M HCl, and the organic solution was separated and washed with 1 M HCl, aqueous NH<sub>3</sub>, 1 M HCl, and saturated aqueous NaHCO<sub>3</sub>. After it had been dried (MgSO<sub>4</sub>) and filtered and the solvent had been stripped, the crude waxy product was chromatographed on a 3.5 in. × 14 in. silica gel column and eluted first with hexanes–EtOAc–CH<sub>2</sub>Cl<sub>2</sub> (4:2:1) and then with hexanes–EtOAc–CH<sub>2</sub>Cl<sub>2</sub> (3:1.75:1). The levorotatory diastereomer, (-)-**12** (351 mg, 76%), eluted first, followed by a small amount (<50 mg) of the mixed diastereomers and then the dextrorotatory diastereomer (445 mg, 96%).

**Data for the (-)-isomer:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 0.33 (s, 6 H), 0.48 (s, 6 H), 0.58 (s, 12 H), 0.92 (s, 6 H), 1.05–1.30 (m, 40 H), 1.37 (m, 2 H), 1.48 (s, 18 H) 1.62 (m, 2H), 1.86 (m, 2H) 2.07 (m, 2H), 2.43 (m, 2H), 2.75 (m, 2H), 6.43 (d, *J* = 8.4 Hz, 2 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 7.39 (s, 2 H), 7.96 (s, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 9.55, 9.79, 16.01, 16.96, 17.01, 18.30, 25.71, 27.38, 28.75, 29.01, 29.48, 31.06, 39.67, 54.06, 54.39, 54.93, 89.54, 91.16, 105.30, 114.59, 115.20, 118.20, 120.64, 121.77, 123.95, 127.38, 128.01, 142.77, 143.87, 146.43, 150.06, 164.74, 165.96, 177.54, 177.98; HRMS calcd for C<sub>88</sub>H<sub>108</sub>O<sub>22</sub>-Si<sub>2</sub> 1572.6870, found 1572.6820.

**Data for the (+)-isomer:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.32 (s, 6 H), 0.45 (s, 6 H), 0.47 (s, 6 H), 0.74 (s, 6 H), 1.13 (s, 18 H), 1.22 (s, 6 H), 1.24 (s, 6 H), 1.26 (s, 6 H), 1.30–1.50 (m, 24 H), 1.64 (m, 2 H), 1.87 (m, 2 H) 2.10 (m, 2H), 2.37 (m, 2H), 2.71 (m, 2H), 6.34 (d, *J* = 8.4 Hz, 2 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 7.12 (s, 2 H), 7.93 (s, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 9.47, 9.59, 16.15, 16.71, 16.91, 18.18, 25.55, 27.27, 28.70, 28.82, 29.90, 30.63, 31.13, 39.60, 53.88, 54.12, 54.57, 54.73, 89.99, 90.62, 90.75, 104.43, 114.8, 116.8, 118.6, 121.62, 122.07, 122.28, 122.49, 122.92, 126.60, 128.17, 128.73, 128.85, 142.53, 144.012, 147.06, 150.47, 165.37, 166.01, 176.75, 177.47.

Among peaks in the <sup>1</sup>H NMR spectra that are isolated and prominent are those at 7.39 ppm in the (-)-diastereomer and at 7.12 ppm in the (+)-diastereomer. The former resonance could not be found in the latter's spectrum and vice versa, and the ratio of signal to noise implied that each diastereomer contained not more than 2% of the other.

**CD, UV–Vis Absorption, Fluorescence Emission, Polarimetry, and Light Scattering Analyses.** UV–vis absorption spectra were recorded using a Perkin-Elmer Lambda 19 UV–vis spectrometer, circular dichroism spectra using a JASCO 720 spectrometer, fluorescence spectra using a Spex Fluorolog 86 fluorimeter, and specific rotations using a JASCO Dip 1000 polarimeter. Dodecane was either

(59) See the Supporting Information to ref 1.

olefin-free material from Fluka or was freed of olefin by shaking with concentrated H<sub>2</sub>SO<sub>4</sub>, washing, drying, and distilling. The cells used to measure the spectra were as follows: a 10 μm quartz cell from Starna Cells, used for ca. 10<sup>-2</sup> M solutions; a 105 μm quartz cell, used for ca. 10<sup>-3</sup> M solutions; a 1 mm and a 2 mm quartz cell, used for ca. 10<sup>-4</sup> M solutions; and a 1 cm quartz cell used for ca. 10<sup>-5</sup> M solutions. The fluorescence and light scattering spectra measured emission from the front faces of 10 μm and 2 mm quartz cells, respectively.

The neat samples of **1** used for the measurements in Figure 5 were prepared by spin coating at 6000 rpm from a 1 × 10<sup>-3</sup> M octane solution onto a quartz plate, which was then mounted in a circular holder that allowed the plate to be rotated through 360° at 30° increments. The film used to measure the specific rotation recorded in Table 1 was prepared by placing a 1 × 10<sup>-3</sup> M octane solution into the well formed by sandwiching a ca. 100 μm Teflon washer (Ace Glass Inc., Vineland, NJ) and a quartz flat (NSG Precision Cells Inc., Farmingdale, NY) in a metal clamp. The well was loosely covered with a glass plate, which allowed the octane solution to evaporate slowly during the course of a day. To remove any remaining solvent, the quartz disk was placed under vacuum overnight. The resulting circular film was centered in the holder described above. A HeNe laser beam that passed through the film had a well-defined center spot, which meant that little light was scattered by the sample. The rotation (α) of a plane-polarized light beam 8 mm in diameter was measured as a function of the angle (φ) through which the sample was rotated in the plane perpendicular to the beam, as follows (φ, α, both in degrees): 0, 0.525; 30, 0.550; 60, 0.530; 90,

0.500; 120, 0.591; 150, 0.510. The average is 0.534 ± 0.03. The absorbance at 550 nm of this film was 4.9 times less than that of a film prepared by crushing the sample between quartz plates separated by a 2 μm aluminum spacer from the Goodfellow Corp., Berwyn, PA.

**Acknowledgment.** We thank the NSF (Grant CHE9802316) and The Kanagawa Academy of Science and Technology for support and numerous colleagues for assistance, especially Professors Timothy Swager and Scott Trzaska of MIT for the DSC analyses, for letting us use their polarizing microscope, and for advice, Professor Louis Brus (Columbia) for the use of his spin-coater, Dr. Steffen Jockusch (Columbia) for help with the light-scattering measurements, Professor Carl Gryte (Columbia) for the use of his microscope, and Evan A. Hendrix for help with the graphics.

**Supporting Information Available:** <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectra of 4,5-dihydroxy-2,7-naphthalenedicarboxaldehyde, (-)-**1**, **6**, **7**, **10**, the diol formed when MeLi is added to **10**, **11**, (+)-**12**, (-)-**12**, (+)-**13**, and (-)-**13**, and DSC traces for (-)-**1** and (±)-**1** (39 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA983248L