Synthesis of Conjugated Helical Acetylene-Bridged Polymers and Cyclophanes

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Pd(0)-catalyzed reactions of 2,15-diethynyl[6]helicene with derivatives of *p*- and *o*-diiodobenzene give, respectively, polymers **4** and cyclophanes **5**, in which helicenes are linked by diethynylbenzenes. Both are very soluble in many common solvents. The molar rotation of polymer **4** is greater than that of monomeric analogue **12**, and peaks in its UV and CD spectra at wavelengths greater than 350 nm are shifted to the red of those in **12**. Cyclophane **5a**, which contains two helicene rings, could be isolated from the reaction mixture in pure form. Its maxima in the UV and CD spectra are not shifted to the red of those of **12**, most likely because the two helicene rings in **5a** are twisted with respect to one another.

Two types of interesting materials could arise from the Pd(0)-catalyzed reaction[1] of nonracemic 2,15-diethynyl-[6]helicene **1** (Scheme 1) and dihalobenzene derivatives. One is a polymer, which because it contains a long, helical network of delocalized double bonds,[2] might display interesting optical properties.[3] It would be related to optically active poly(arylenevinylenes),[2b] polyarylenes,[2c−e] and poly(aryleneethynylenes)[2f−h] which incorporate the binaphthyl nucleus. A difference would be that it would not possess the large dihedral angle of binaphthyls (~90°),[5] which impedes conjugation between the naphthalenes. Thus, the positions of absorption maxima in the UV spectra of the latter polymers[2a] are similar to those of their nonchiral repeat units. Accordingly, in conjugated polymers of **1**, extended conjugation should shift maxima in the UV−vis and CD spectra to longer wavelengths.[6]

The second interesting material would be comprised of cyclic structures.[8] Although nonracemic cyclophanes derived from helicenes have been prepared,[9,10] none has a conjugating group between the helicenes. Accordingly, the structures considered here would be novel, and their optical properties might be as well.

Reported here are an efficient way to prepare nonracemic **1**, and a study of the Pd(0)-catalyzed reactions of **1** with diiodides **2** and **3** (Scheme 1). Evidence is presented that the product of **1** and **2** is the elongated polymer of structure **4**, and that of **1** and **3** is a mixture of oligomeric cyclophanes of structure **5**.

The chiroptical properties of polymer **4** and cyclophane **5a**, which was isolated from the mixture of oligomers, are compared with those of simpler helicenes.

Results

The initial approach studied to prepare **1** was to photocyclize bis-stilbenes **6a−c** (eq 1).[11]

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[1] Sonagashira, K. In *Comprehensive Organic Synthesis*, 2nd ed.; Trost, B. M.; Fleming, I., Ed.; Pergamon: Oxford, 1993; Vol. 3, pp 521−549.

[2] For a review of optically active, conjugated polymers, see (a) Pu, L, *Acta Polymerica* **1997**, *48*, 118. Also, see (b) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V.; Wagaman, M. W.; Zhang, L.; Lee, T. R.; Pu, L. *Macromolecules* **1996**, *29*, 1082. (c) Hu, Q.-S.; Vitharana, D.; Liu, G.; Jain, V., Pu, L. *Macromolecules* **1996**, *29*, 5075. (d) Hu, Q.-S.; Vitharana, D.; Zheng, X.-F.; Wu, C.; Kwan, C. M. S.; Pu, L. *J. Org. Chem* **1996**, *61*, 8370. (e) Bedworth, P. V.; Tour, J. M. *Macromolecules* **1994**, *27*, 622. (f) Ma, L.; Hu, Q.-S.; Musick, K.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1996**, *29*, 5083. (g) Ma, L.; Hu, Q.-S.; Pu, L. *Tetrahedron: Asymmetry* **1996**, *7*, 3103. (h) Ma, L.; Hu, Q.-S.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1997**, *30*, 204.

[3] Polymeric helical metallocenes,[4a] helical salophen polymers,[4b] and aggregates of helicenes[4c] are related materials.

[4] (a) 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. (b) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274. (c) Nuckolls, C.; Katz, T. J.; Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118*, 3767.

[5] (a) Kranz, M.; Clark, T.; Schleyer, P. v. R. *J. Org. Chem.* **1993**, *58*, 3317. (b) Mori, K.; Masuda, Y.; Kashino, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *49*, 1224.

[6] Bathochromic shifts in UV maxima are observed upon increasing oligomer size in oligo(*p*-phenyleneethynylenes)[7a] and oligo(*o*-phenyleneethynylenes)[7b] up to 8 phenylacetylene repeat units.

[7] (a) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (b) Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149.

[8] For examples of macrocycles which incorporate phenylacetylene subunits, see (a) Young, J. K.; Moore, J. S. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Ed.; VCH: Weinheim, 1995; pp 415−442. (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (c) Höger, S.; Meckenstock, A.-D.; Pellen, H. *J. Org. Chem.* **1997**, *62*, 4556, and references therein.

[9] Known cyclophanes of helicenes (a) Joly, M.; Defay, N.; Martin, R. H.; Declerq, J. P.; Germain, G.; Soubrier-Payen, B.; Van Meerssche, M., *Helv. Chim. Acta* **1977**, *60*, 537. (b) Tribout, J.; Martin, R. H.; Doyle, M.; Wynberg, H. *Tetrahedron Lett.* **1972**, 2839. (c) Numan, H.; Wynberg, H. *Tetrahedron Lett.* **1975**, 1097. (d) Thulin, B.; Wennerström, O. *Acta Chem. Scand.*, **1976**, *B30*, 688. (e) Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 271.

[10] Related materials are binaphthol-derived cyclophanes. See Anderson, S.; Neidlein, U.; Gramlich, V.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1596.

[11] For reviews of the photocyclization of stilbenes and the syntheses of 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.

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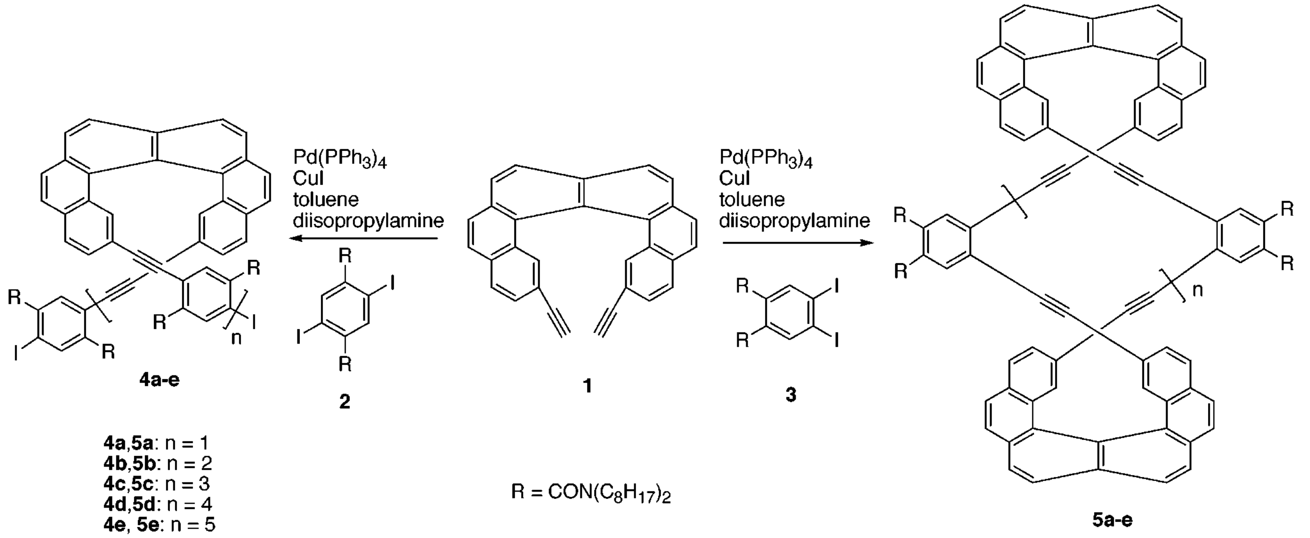
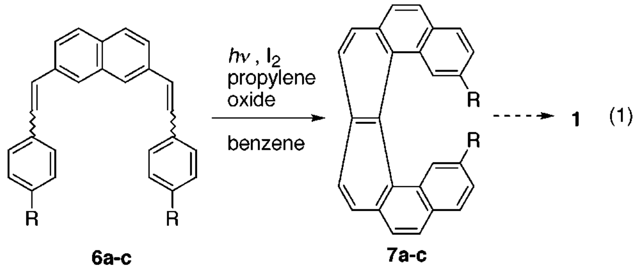
Scheme 1



4a,**5a**: n = 1
4b,**5b**: n = 2
4c,**5c**: n = 3
4d,**5d**: n = 4
4e, **5e**: n = 5

R = $CON(C_8H_{17})_2$

Although there are some helicenes that have been prepared in high yield from stilbenes that bear electron-withdrawing substituents,[12] yields in other cases are modest,[13] or low.[9a,14] We hoped that the use of propylene oxide and stoichiometric amounts of iodine, a combination that significantly improves yields in photocyclizations of stilbenes bearing bromines, methoxyls, alkyls, or no functional groups,[15] would give good yields of **7a**–**c**. Unfortunately, the yields were low: 45% for **7a**, 30% for **7b**, 30% for **7c**. An alternate route was therefore followed.

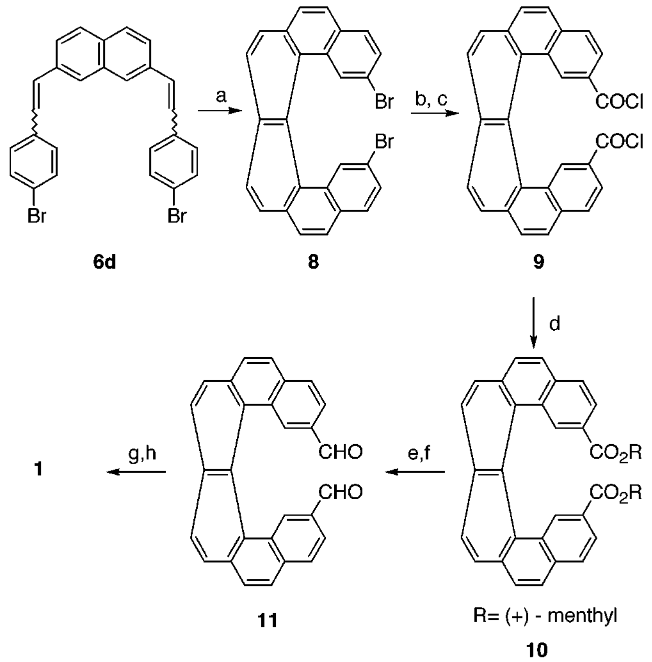


6a, R = CO_2Me
6b, R = CN
6c, R = CO_2-(+)-Menthyl

7a, 45%
7b, 30%
7c, 30%

Because bis-stilbenes that bear bromines photocyclize in higher yields than those that do not,[16] compound **6d** (Scheme 2) was prepared and photoirradiated under the same conditions. The yield of **8** after simple workup, solvent removal, and trituration with hexane was 86%.[17] Because the yield is high, the reaction time short, and the isolation procedure easy, practical quantities (1.5 g) of **8** could be prepared quickly. Thus, the route to (+)-**1** in Scheme 2 was adopted.

Scheme 2.[a] Route to Optically Active Diethynylhelicene (+)-1 from 6d



[a] (a) hν, I_2, propylene oxide, benzene, 2 h (86%); (b) n-BuLi, THF, −78 °C, 1.5 h, then dry ice, −78 °C to room temperature (92%); (c) $SOCl_2$, reflux, 12 h (90%); (d) (+)-potassium mentholate, THF, rt, 10 min, then chromatography (83−89%); (e) DIBALH, toluene, reflux, 2 h (89%); (f) Dess−Martin periodinane, CH_2Cl_2, rt, 45 min (98%); (g) (chloromethyl)triphenylphosphonium chloride, $LiN(Si(CH_3)_3)_2$, THF, −78 °C to room temperature, 30 min, then addition of **11**, reflux, 1 h (94%); (h) MeLi, THF, −78 °C for 1 h, then rt for 1.25 h (100%).

Attempts to form diastereomers **10** directly by treating **8** with n-butyllithium followed by (+)-menthyl chloroformate were unsuccessful. However, a three-step procedure effected the transformation efficiently, and the mixture of diastereomeric helicenes **10** could be separated easily and in high optical purity (>99% de) by column chromatography. The structure of the dextrorotatory diastereomer (+)-**10** was determined by X-ray diffraction analysis.[20] Since the absolute configuration of (+)-

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(12) Jutz, C.; Löbering, H.-G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 418.

(13) (a) Hassine, B. B.; Gorsane, M.; Geerts-Evrard, F.; Pecher, J.; Martin, R. H.; Castelet, D. *Bull. Soc. Chim. Belg.* **1986**, *95*, 547. (b) Vanest, J.-M.; Gorsane, M.; Libert, V.; Pecher, J.; Martin, R. H. *Chimia* **1975**, *29*, 343.

(14) Cochez, Y.; Martin, R. H.; Jespers, J. *Isr. J. Chem.* **1977**, *15*, 29.

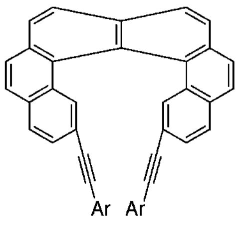
(15) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

(16) (a) Liu, L.; Katz, T. J.; *Tetrahedron Lett.* **1991**, *32*, 6831. (b) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.* **1986**, *27*, 2231.

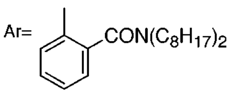
(17) Low yields are reported[9e,18] in preparations of **8** in which propylene oxide was not added. Also, we obtained a high yield without using the modifications in ref 19.

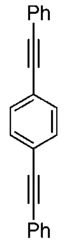
menthol is known, it was possible to determine the absolute configuration of (+)-**10** as well. This analysis shows that (+)-**10** has the (*P*)-configuration. Thus, (−)-**10** has the (*M*)-configuration, and all of the compounds derived from (+)-**10**, including polymer **4** and cyclophanes **5**, have the (*P*)-configuration. DIBALH reduction of (+)-**10**, followed by Dess−Martin oxidation,[21] and chloro-olefination followed by dehydrohalogenation,[22] as also shown in Scheme 2, then provided (+)-**1** in high yield.

Diethynyl[6]helicene **1** was then combined according to Scheme 1 with diiodide **2**, prepared according to the procedure of Zhou and Swager,[23] and **3**, prepared by combining 4,5-diiodophthalic anhydride,[24] dioctylamine, and DCC. The resulting polymer **4** and cyclophanes **5** are both very soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, benzene, toluene, acetone, and THF. Cyclophanes **5** are also soluble in hexane. Compounds **12**, **13**,[25] and **14**[26] were also prepared, so the properties of **4** and **5** could be compared to those of simpler molecules.



12





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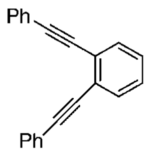

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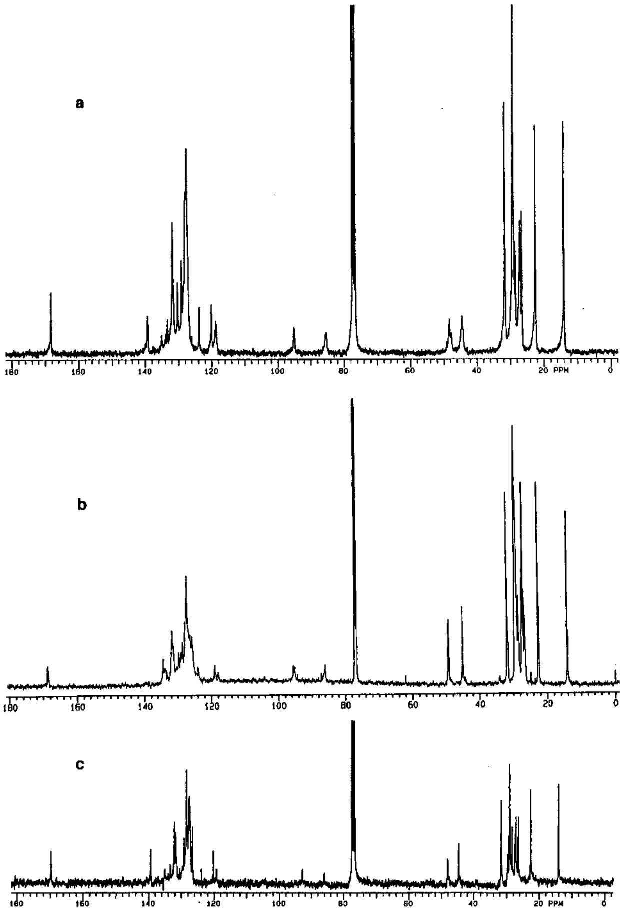

Figure 1. ^{13}C NMR spectra in $CDCl_3$ of (a) **4** (75 MHz), (b) **5** (125 MHz), and (c) **12** (75 MHz).

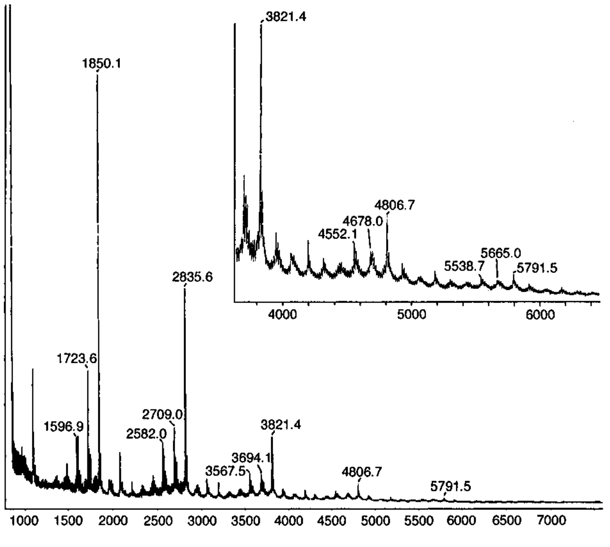

Figure 2. FAB mass spectrum of polymer **4**. The matrix was *m*-nitrobenzyl alcohol.

Evidence for the structures assigned to **4** and **5** is the following. (1) The ^{1}H NMR spectra of **4** and **5** both display resonances for the aromatic and side chain protons in intensity ratios that are appropriate. There are no resonances in the spectra of **4** or **5** related to the acetylenic protons (σ 2.71 ppm) of **1**. (2) The ^{13}C spectra (Figure 1) of **4**, **5**, and **12** all show resonances attributable to the carbonyls of the amides (ca. 168 ppm), the aromatic carbons (140−118 ppm), the two types of acetylenic carbons (ca. 96 and 86 ppm), and the side chains (ca. 49, 45, 32−22, and 14 ppm).

(3) The FAB mass spectra of **4** (Figure 2) shows peaks at *m/z* 1850.1, 2835.6, 3821.4, 4806.7, and 5791.5, which correspond to the masses of **4a**−**e**. Also observed are peaks at *m/z* 1723.6, 2709.0, 3694.1, 4678.0, and 5665.0, which correspond to the loss of one iodine from **4a**−**e**, respectively; and at *m/z* 1596.9, 2582.0, 3567.5, 4552.1, and 5538.7, which correspond to loss of two iodines from **4a**−**e**, respectively.

The FAB mass spectrum of **5** (Figure 3) shows peaks at *m/z* 1970.2, 2955.6, and 3940.9, which correspond to the calculated masses of **5a**−**c**, respectively. The corresponding peaks from **5d**,**e** were too small to be identified. There are also peaks at *m/z* 1730.0, 2715.2, 3700.6,

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[18] Reetz, M. T.; Beuttenmüller, E. W.; Goddard, R. *Tetrahedron Lett.* **1997**, *38*, 3211.

[19] Terfort, A.; Görls, H.; Brunner, H. *Synthesis* **1997**, 79.

[20] $C_{48}H_{52}O_4$ (formula weight 692.90), orthorhombic, $P2_12_12_1$, a = 12.9499(6) Å, b = 14.3973(6) Å, c = 21.3316(10) Å. $\alpha = \beta = \gamma$ = 90°. Z = 4. R (obs data) = 5.92%, wR = 10.85%. R(all data) = 7.73%, wR = 11.55%. GOF = 1.144. See the Supporting Information for full results and details.

[21] (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (b) Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.

[22] Corey, E. J.; Ruden, R. A. *Tetrahedron Lett.* **1973**, 1495.

[23] Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.

[24] 4,5-Diiodophthalic acid was prepared by the method of (a) Higgins, R. W.; Hilton, C. L.; Willard, M. L.; Francis, H. J., Jr. *J. Org. Chem.* **1951**, *16*, 1577. 4,5-Diiodophthalic acid was converted to the anhydride by the method of (b) Pratt, D. S.; Perkins, G. A. *J. Am. Chem. Soc.* **1918**, *40*, 219. Also see (c) Terekhov, D. S.; Nolan, K. J. M.; McArthur, C. R.; Leznoff, C. C. *J. Org. Chem.* **1996**, *61*, 3034.

[25] Deeter, G. A.; Venkataraman, D.; Kampf, J. W.; Moore, J. S. *Macromolecules* **1994**, *27*, 2647.

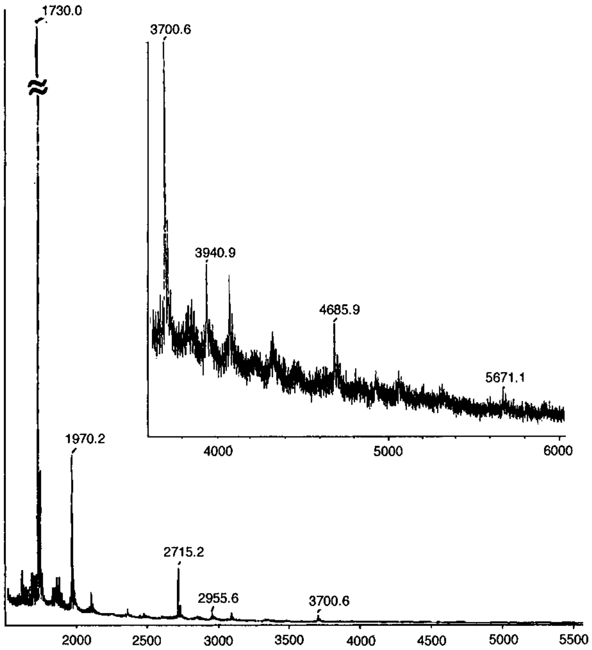

Figure 3. FAB mass spectrum of cyclophanes **5**. The matrix was *m*-nitrobenzyl alcohol.

4685.9, and 5671.1. These peaks are attributed to the loss of $(C_8H_{17})_2N$ from **5a**−**e**. Loss of $(C_8H_{17})_2N$ is also seen in the mass spectrum of **3**, which shows peaks at *m*/*z* 864 (parent), 737 (M − iodine) and 623 ([M − $(C_8H_{17})_2N$]). In contrast, the mass spectrum of **2** shows peaks only at 865 (M + 1) and 612 [(M − 2 iodines) + 1]. The conclusion is that the loss of the fragment $(C_8H_{17})_2N$ from **3** and **5a**−**e** is a characteristic of the ortho placement of the amides.[27] Also, high-resolution mass spectroscopic analysis of the peak at *m*/*z* 1970.2979 in the spectrum of **5** is in close agreement with the theoretical value (1970.3100) calculated for $C_{140}H_{168}N_4O_4$.

(4) One of the cyclophane oligomers was isolated from the mixture **5** by preparative TLC and HPLC. Its aromatic ^{1}H NMR spectrum consists of 3 pairs of doublets and 2 singlets, which is consistent with a symmetrical structure. The FAB mass spectrum of the purified compound shows peaks only at *m*/*z* 1970.1 and 1729.8, consistent with the structure **5a** ($n = 1$). A three-dimensional representation of that structure is displayed in Figure 4.

Solutions of **4** and **5** in THF were analyzed by GPC, monitoring absorption at 254 nm for **4** and 300 nm for **5** and comparing the chromatograms to those of polystyrene standards. A single peak was observed in each of the chromatograms: $M_n = 8400$ and $M_w = 14000$ ($M_w/M_n = 1.68$) for **4**, and $M_n = 7200$ and $M_w = 11100$ ($M_w/M_n = 1.54$) for **5**. However, since the FAB mass spectra of **4** and **5** have no peaks for oligomers with molecular weights greater than 7000, we concluded that GPC overestimates molecular weights of these compounds. Schumm, Pearson, and Tour have shown that, for rigid rod oligomers with phenylacetylene repeat units, M_n was inflated by a factor of 1.4−1.8 relative to the true molecular weights.[7a] Assuming that the molecular weights of **4** and **5** are overestimated by a similar ratio, the average molecular weight of **4** is likely to be ca. 4700−6000, and that of **5** ca. 4000−5100. These figures seem in reasonable accord with the FAB mass spectra.

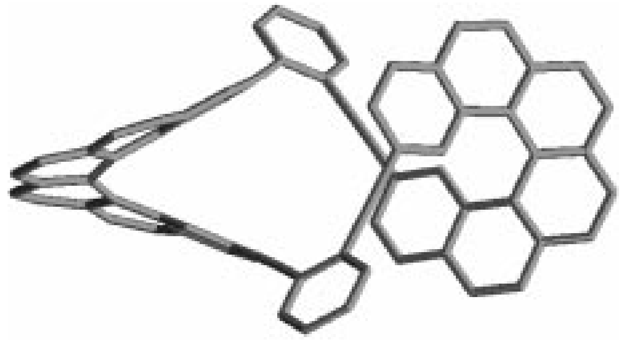

Figure 4. Three-dimensional representation of **5a**, in which the side chains have been omitted for clarity.

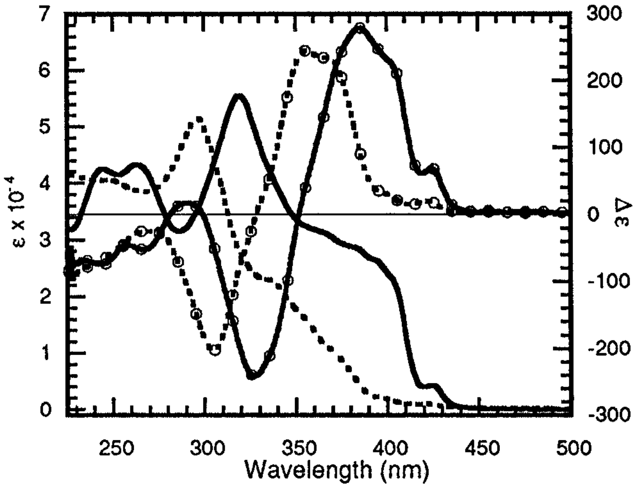

Figure 5. UV (ordinate on the left) and CD (ordinate on the right) spectra of polymer **4** (−, 3.0×10^{-6}, in CH_2Cl_2) and **12** (- - -, 4.4×10^{-6}, in CH_2Cl_2). CD spectra are marked by circles.

The optical properties of polymer **4** are enhanced compared to those of simple molecules, presumably because its conjugation is extended. The molar rotation[28,29] exhibited by the mixture of polymers **4**[30] ($[\Phi]_D = 35230°$, *c* 0.180, CH_2Cl_2) is large. If the monomeric units were unconjugated, the molar rotations would be expected to be more similar to that of **1** ($[\Phi]_D = 19920°$, *c* 0.190, CH_2Cl_2). In contrast, compound **12**, despite its slightly longer path of conjugated double bonds, shows no significant increase in molar rotation ($[\Phi]_D = 20230°$, *c* 0.072, CH_2Cl_2). The UV and CD spectra of polymer **4**[29] and monomer **12** are displayed in Figure 5, and those of isolated cyclophane **5a** are displayed in Figure 6. Three peaks at wavelengths longer than 350 nm are seen in each of the UV and CD spectra of **4**, **12**, and **5a**. The wavelengths, extinction coefficients, and $\Delta\epsilon$'s of these peaks are shown in Table 1.

The UV spectra of **13** and **14** were also recorded and are displayed in the Supporting Information. The maxi-

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[26] Badrieh, Y.; Blum, J.; Amer, I.; Vollhardt, K. P. C. *J. Mol. Catal.* **1991**, *66*, 295.

[27] Similar "ortho effects" are observed in the mass spectra of dialkyl phthalates. see (a) McLafferty, F. W.; Gohlke, R. S. *Anal. Chem.* **1959**, *31*, 2076. (b) McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra*; University Science: Mill Valley, CA, 1993.

[28] $[\Phi]_D = ([\alpha]_D \times \text{MW})/100$.

[29] The molecular weight of the repeat unit of **4** was used to determine $[\Phi]_D$, ϵ, and $\Delta\epsilon$ for the polymer.

[30] The specific rotation was measured using a sample that had first been dissolved in $CHCl_3$ and precipitated with hexane.

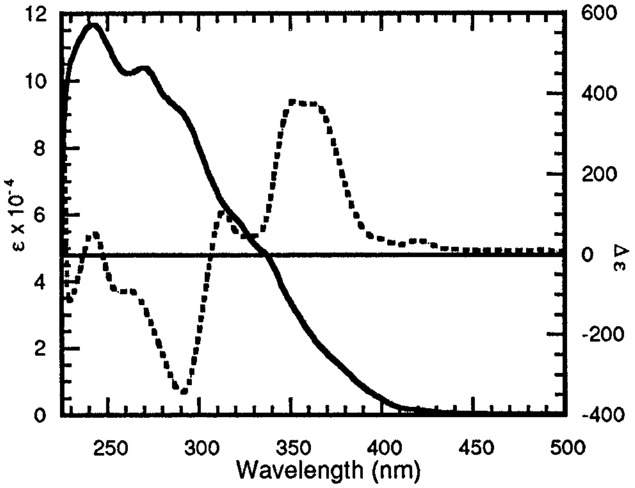

Figure 6. UV (–, ordinate on the left) and CD (- - -, ordinate on the right) spectra of cyclophane **5a** (8.5×10^{-7}, in CH_2Cl_2). The CD spectrum is marked by circles.

Table 1. Assigned Peaks in the UV and CD Spectra of 4, 5a, and 12

	λ (nm)	ϵ	Δϵ
4			
α	425	4283	68
p	403	23100	225
β	385	28300	280
5a			
α	420	1570	35
p	365	21550	375
β	352	32190	382
12			
α	421	1000	21
p	369	10600	235
β	355	16100	245

mum absorbance occurs at 320 nm in the spectrum of *p*-bis(phenylethynyl)benzene **13** (in THF), and at 278 nm in the spectrum of *o*-bis(phenylethynyl)benzene **14** (in THF).

Discussion

The absorptions in the spectra of **4**, **5a**, and **12** were assigned by comparing them to the spectra of the parent [5]–[9]helicenes. Three long wavelength $\pi-\pi^*$ absorptions, the α-, p-, and β-bands[31] (in order of increasing energy), are characteristic of the spectra of condensed aromatic hydrocarbons.[32] The p-transition is polarized transverse to the long axis of the molecule, whereas the α- and β- transitions are polarized longitudinally. These absorbances have been assigned in the spectra of the [5]–[9]helicenes,[33] and it is observed that, as the size of the helicene increases, these bands shift to the red. In helicenes,[33] as for other aromatic hydrocarbons,[32] the intensity of the α-band is much smaller than that of either the β- or p-band. Similarly, the circular dichroism of the α-band is much smaller than those of the p- and β-bands.[33] In the absorption spectra of [6]helicene, for example, the position of the α-, p-, and β-bands are 413, 347, and 325 nm, their extinction coefficients are ca. 400, 22000, and 65000, and the magnitude of their circular dichroisms (Δϵ) are −2.8, 73.0, and 196.0, respectively.[33c]

As is the case for the parent [5]–[9]helicenes, the absorption at longest wavelength in each of the spectra of **4**, **5a**, and **12** is considerably less intense than the other two peaks. Thus, the longest wavelength peak was assigned to the α-band, the peak closest to it in wavelength was assigned to the p-band, and the remaining peak was assigned to the β-band. These assignments are listed in Table 1. The p- and β-bands of **4** are shifted by 34 and 30 nm, respectively, to the red of the analogous bands in the spectrum of **12**. The α-band of **4** is also shifted to the red of the corresponding band in the spectrum of **12**, although the shift is less significant (4 nm). These bathochromic shifts are presumably a result of conjugation in **4** that extends from one helicene moiety to the next. This extended delocalization contrasts with its absence in chiral polyaryleneethynylenes derived from binaphthol, in which rotation about the single bond of the binaphthol linkage quenches it.[2a,f,h]

The maximum of greatest intensity in the UV spectrum of **4** (320 nm) also occurs at longer wavelength than the corresponding peak in the spectrum of **12** (298 nm). However, the maximum at 320 nm in **4** is probably related to the para relationship of the acetylenes, since λ_{max} for bis-*p*-(phenylethynyl)benzene **13** also occurs at this wavelength, whereas λ_{max} for bis-*o*-(phenylethynyl)benzene **14** occurs at 278 nm. The peak in the CD spectrum of **4** at ca. 325 nm is probably related to the maximum in the UV spectrum that occurs at 320 nm, which accounts for its shift to the red from the corresponding peak in the CD spectrum of **12**, at ca. 305 nm.

The peaks at wavelengths longer than 350 nm in the CD and UV spectra of isolated cyclophane **5a** (420, 365, and 352 nm) occur at wavelengths similar to those in the spectra of **12**, not that of polymer **4**. This is reasonable, for **5a** is held in a rigid conformation, with its helicene rings twisted with respect to one other (Figure 4), and thus delocalization between the two helicenes is inhibited.

Conclusions

Helical, conjugated polymers with elongated structures **4** can be made by the Pd(0)-mediated reaction of diethynyl-[6]helicene **1** with *p*-diiodobenzene derivative **2**. Alternatively, reaction of **1** with *o*-diiodobenzene derivative **3** gives cyclic structures **5**, from which cyclophane **5a** could be isolated. The CD and UV spectra imply that conjugation extends between the helicene moieties of **4**, but not those of **5a**.

Experimental Section

THF and toluene were distilled from Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. Certified ACS grade benzene was purchased from Fisher and used for photocyclizations without further purification. Diisopropylamine (99.5%) was used as purchased from Aldrich. (Chloromethyl)triphenylphosphonium chloride was purchased from Aldrich and heated at 90 °C under vacuum for 2 h before use. Potassium hydride, purchased as a 35 wt % dispersion from Aldrich, was freed of mineral oil by rinsing it with hexane and filtering it on a fine-fritted funnel. Dry KH should be handled with caution under an atmosphere of inert gas. The apparatus used for photocyclizations was the same as that previously described.[15] All

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[31] The α-, p-, and β-bands are also referred to as the L_b, L_a, and B_b bands, respectively. See Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.

[32] Clar, E. *Polycyclic Hydrocarbons*; Academic: New York, 1964.

[33] For a table which lists the α-, p-, and β-bands of the parent [5]–[9]helicenes, see (a) ref 11b, p 104. Also see (b) Obenland, S.; Schmidt, W. *J. Am. Chem. Soc.* **1975**, *97*, 6633. (c) Newman, M. S.; Darlak, R. S.; Tsai, L. *J. Am. Chem. Soc.* **1967**, *89*, 6191. (d) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 343. (e) Brown, A.; Kemp, C. M.; Mason, S. F. *J. Chem. Soc. (A)* **1971**, 751.

glassware was flame-dried under vacuum and cooled under argon. Additions with syringes were made through rubber septa on a gas inlet adapter. All reactions were run under argon unless otherwise noted. Elemental analyses were performed by Desert Analytics. Mass spectra of **4**, **5**, and **5a** were performed on a JMS-HX110A/HX110A tandem mass spectrometer (JEOL), using an Xe beam with ionizing energy of 6 kV, an emission current of 10 mA, an acceleration voltage of 10 kV. *m*-Nitrobenzyl alcohol was the matrix used for all FAB mass spectra. "Chromatography" refers to "flash chromatography".[34]

2,7-Bis[2-(4-bromophenyl)ethynyl]naphthalene (6d). Lithium hexamethyldisilizane (25.0 mL of a 1.0 M solution in THF) was syringed into a stirred mixture of 2,7 bis[(triphenylphosphonio)methyl]naphthalene dibromide[35] (10.00 g, 11.93 mmol) in THF (100 mL) that was cooled by a dry ice/acetone bath. The dry ice bath was removed, the reaction was stirred for 30 min while it warmed to room temperature, and *p*-bromobenzaldehyde (4.86 g, 26.3 mmol), dissolved in minimal THF, was syringed into the now deep red reaction mixture. The color of the mixture immediately turned light brown. After 10 min, the flask was fitted with a condenser and refluxed for 4 h. The mixture was cooled to room temperature, the solvent removed under reduced pressure, methanol added, and the white solid filtered on a Büchner funnel. Rinsing with methanol and drying in vacuo yielded 4.76 g (81%) of **6d**, a mixture of cis/trans isomers which softened at 180−185 °C, but did not completely melt at temperatures lower than 220 °C. IR(KBr): 3020, 2921, 2851, 1484 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.59−7.78 (m, 18H) ppm; ^{13}C NMR (CDCl$_3$, 75 MHz): δ 136.24, 136.04, 135.02, 134.78, 133.68, 132.29, 131.83, 131.41, 130.81, 130.61, 129.46, 129.36, 127.86−128.15 (m), 127.56, 127.44, 126.97, 126.84, 123.61, 121.42, 121.11 ppm; HRMS calcd for $C_{26}H_{18}Br_2$ 489.9756, found 489.9765.

2,15-Dibromo[6]helicene (8). Bisstilbene **6d** (0.300 g, 0.612 mmol) and iodine (0.311 g, 1.22 mmol) in a 1.4 L photocyclization well were dissolved in benzene and purged with nitrogen for 5 min. The nitrogen flow rate was then reduced to about one bubble every 2 s, and propylene oxide (20 mL) was added with a syringe. The mixture was then stirred and irradiated for 2 h, after which time the color of the iodine had almost completely faded. Washing with 10% $Na_2S_2O_3$ consumed any unreacted iodine. The organic layer was dried (MgSO$_4$), the solvent was removed under reduced pressure, and the remaining yellow solid, after trituration with hexane, was dried in vacuo. Six runs on this scale yielded 1.534 g (86%) of **8**, mp > 220 °C (lit.[9e] 246−248 °C). IR(KBr): 2924, 2851, 1589, 1465 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.04 (d, 2H, J = 8.1 Hz), 8.00 (d, 2H, J = 8.1 Hz), 7.96 (d, 2H, J = 8.5 Hz), 7.92 (d, 2H, J = 8.5 Hz), 7.74 (d, 2H, J = 8.4 Hz), 7.71 (s, 2H), 7.39 (d, 2H, J = 8.2 Hz) ppm; ^{13}C NMR (CDCl$_3$, 75 MHz): δ 133.16, 131.91, 130.76, 130.64, 130.02, 129.24, 128.96, 127.64, 127.54, 127.39, 126.78, 126.36, 123.74, 119.23 ppm; HRMS calcd for $C_{26}H_{14}Br_2$ 485.9444, found 485.9486.

[6]Helicene-2,15-dicarboxylic Acid (8a). n-BuLi (3.38 mL of a 2.5 M solution in hexane, 8.46 mmol) was added in drops to a solution of **8** (1.534 g, 3.156 mmol) in THF (10 mL) which was cooled by a dry ice/acetone bath. After this stirred for 1.5 h at −78 °C, excess freshly crushed dry ice was added. The dry ice bath was then removed, and the mixture was allowed to stir while warming to room temperature as the dry ice dissipated. Aqueous NaOH (1.5 M, 80 mL) was added and extracted with ca. 100 mL of ethyl acetate. The aqueous layer was acidified with HCl and then cooled to room temperature. The precipitated yellow solid was filtered on a Büchner funnel, rinsed with HCl (1 M), suction dried, triturated with hexane, and dried in vacuo, yielding 1.20 g (92%) of diacid **8a**, mp > 220 °C. IR(KBr): 3300−2200, 1683, 1616, 1417 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.28−8.23 (m, 6H), 8.17 (s, 2H), 8.11 (d, 2H, J = 8.8 Hz), 7.98 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.3 Hz) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz): δ 166.52, 134.19, 133.02, 131.21, 129.24, 128.46, 127.90, 127.59−127.29 (m), 126.46, 124.94, 122.61 ppm; HRMS calcd for $C_{28}H_{16}O_4$ 416.1049, found 416.1045.

[6]Helicene-2,15-dicarbonyl Dichloride (9). Compound **8a** (1.20 g, 2.88 mmol) and thionyl chloride (100 mL) were refluxed under a drying tube for 12 h, and the SOCl$_2$ was removed by distillation. The green-yellow solid was triturated with hexane and dried at water aspirator pressure to yield 1.18 g (90%) of **9**, mp > 220 °C. IR(KBr): 3043, 2926, 1750, 1603 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.55 (s, 2H), 8.16 (d, 2H, J = 8.7 Hz), 8.14 (d, 2H, J = 8.4 Hz), 8.09 (d, 2H, J = 8.0 Hz), 7.98 (d, 2H, J = 8.7 Hz), 7.91 (d, 2H, J = 8.4 Hz), 7.71 (d, 2H, J = 8.4 Hz) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz): δ 167.71, 136.38, 134.38, 133.93, 132.06, 130.66, 128.89, 128.81, 128.22, 128.13−128.00 (m), 127.43, 125.43, 123.40 ppm; HRMS calcd for $C_{28}H_{14}Cl_2O_2$ 452.0371, found 452.0368.

Preparation and Separation of (±)-[6]Helicene-2,15-dicarboxylic Acid [1*S*-[1α(1*S,2*R**,5*S**),2*β*,5α]] Bis[5-methyl-2-(1-methylethyl)cyclohexyl] Ester (10).** THF (6 mL) was syringed into a flask containing (+)-menthol (0.087 g, 0.740 mmol) and KH (0.021 g, 0.704 mmol). After the mixture had stirred at room temperature for 2.5 h, compound **9** (0.060 g, 0.133 mmol) was added as a solid. This was stirred at room temperature under argon for 10 min and quenched by careful addition of water. After additional water and CH$_2$Cl$_2$ were added, HCl (1 M) was added until the aqueous layer was acidic. The organic layer was separated, and the aqueous layer was again extracted with CH$_2$Cl$_2$. The combined organics were dried (Na$_2$SO$_4$), the solvent was removed under reduced pressure, excess menthol was removed by sublimation at 90 °C under vacuum, and the residue was chromatographed (14 in. × 0.75 in., eluting with CH$_2$Cl$_2$/hexane). The levorotatory diastereomer, (−)-**10** (0.041 g, 89%), mp > 220 °C eluted first, followed by the dextrorotatory diastereomer (+)-**10** (0.038 g, 83%), mp > 220 °C. Both compounds are white solids. A crystal of (+)-**10** suitable for X-ray diffraction analysis[20] was obtained by evaporation of a CH$_2$Cl$_2$ solution.

(+)-10: $[\alpha]_D$ +2620 (c 0.023, CH$_2$Cl$_2$); IR(KBr): 2955, 2863, 1715, 1621 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.28 (s, 2H), 8.07−8.02 (m, 6H), 7.96 (d, 2H, J = 8.4 Hz), 7.81 (d, 2H, J = 8.2 Hz), 7.76 (dd, 2H, J = 8.3, 1.5 Hz), 4.71 (m, 2H), 1.76−1.25 (m, 14H), 1.08−0.76 (m, 18H), 0.70 (d, 2H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl$_3$, 75 MHz): δ 165.87, 134.55, 133.34, 131.54, 129.99, 128.82, 128.37, 128.0−127.3 (m), 127.26, 126.84, 125.50, 123.79, 74.31, 46.84, 40.74, 34.24, 31.34, 25.74, 22.99, 22.01, 21.29, 15.88 ppm; HRMS calcd for $C_{48}H_{52}O_4$ 692.3866, found 692.3864

(−)-10: $[\alpha]_D$ −2120 (c 0.005, CH$_2$Cl$_2$); IR(KBr): 2956, 2867, 1707 cm^{-1}; ^{1}H NMR (CDCl3, 400 MHz): δ 8.37 (s, 2H), 8.08−8.02 (m, 6H), 7.94 (d, 2H, J = 8.3 Hz), 7.80 (m, 4H), 4.59 (m, 2H), 1.90 (d, 2H, J = 11.9 Hz), 1.75(d, 2H, J = 12.2 Hz), 1.65 (d, 2H, J = 12.6 Hz), 1.54−1.17 (m, 6H), 1.03 (d, 6H, J = 6.5 Hz), 1.00−0.80 (m, 6H), 0.71 (d, 6H, J = 7.0 Hz), 0.54 (d, 6H, J = 7.0 Hz) ppm; ^{13}C NMR (CDCl$_3$, 75 MHz): δ 165.48, 134.49, 133.47, 131.56, 130.17, 128.60, 128.53, 128.36, 127.90, 127.62, 127.48, 127.37, 126.61, 125.47, 123.81, 74.14, 46.76, 40.59, 34.48, 31.28, 26.11, 23.49, 22.24, 20.46, 16.34 ppm; HRMS calcd for $C_{48}H_{52}O_4$ 692.3866, found 692.3857.

(+)-[6]Helicene-2,15-dimethanol (10a). DIBALH (2.27 mL of a 1.5 M solution in toluene, 3.41 mmol) was syringed into an ice bath cooled solution of (+)-**10** (0.235 g, 0.341 mmol) in toluene (4 mL). The ice bath was then removed, and the mixture was refluxed for 2 h. The flask was cooled, first to room temperature, and then in an ice bath, and the reaction was quenched by careful addition of water under argon. Toluene (30 mL) and water (30 mL) were then added, followed by the addition of HCl (1 M) to render the aqueous layer acidic. The organic layer was separated, and the aqueous layer twice extracted with CH$_2$Cl$_2$. The combined organics were dried (Na$_2$SO$_4$) and concentrated. The resulting yellow solid was triturated with hexane and dried in vacuo, yielding 0.117 g (89%) of bis-benzylic alcohol (+)-**10a**, mp > 220 °C. $[\alpha]_D$ +3160 (c 0.020, CH$_2$Cl$_2$); IR(KBr): 3535, 3460, 3067, 2864 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.99 (d, 2H, J = 8.1 Hz), 7.94 (d,

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2H, $J = 8.1$ Hz), 7.90 (d, 2H, $J = 8.5$ Hz), 7.86 (d, 2H, $J = 8.5$ Hz), 7.79 (d, 2H, $J = 8.0$ Hz), 7.42 (s, 2H), 7.18 (d, 2H, $J = 8.0$ Hz), 4.04 (d, 2H, $J = 12.4$ Hz), 3.88 (d, 2H, $J = 12.4$ Hz), 0.53 (s, 2H) ppm; ^{13}C NMR (CDCl3, 75 MHz): δ 137.35, 133.15, 131.67, 131.10, 129.53, 127.58, 127.4−127.2 (m), 126.95, 126.88, 124.84, 123.93, 65.23 ppm; HRMS calcd for $C_{28}H_{20}O_2$ 388.1463, found 388.1472.

(+)-[6]Helicene-2,15-dicarboxaldehyde (11). The Dess−Martin periodinane[21b] (0.367 g, 0.866 mmol) was added to a solution of (+)-**10a** (0.112 g, 0.289 mmol) in CH_2Cl_2 (4 mL). After stirring for 45 min, CH_2Cl_2 was added, followed by four washes with 10% $Na_2S_2O_3$, four with saturated sodium bicarbonate, and one with water, each time back extracting with a small amount of CH_2Cl_2. Drying (Na_2SO_4), solvent removal, and drying in vacuo gave 0.109 g (98%) of (+)-**11**, a yellow solid, mp > 220 °C. $[\alpha]_D$ +6060 (*c* 0.005, CH_2Cl_2); IR(KBr): 3046, 2815, 2710, 1687, 1601 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.14 (s, 2H), 8.14 (d, 2H, $J = 8.7$ Hz), 8.12 (d, 2H, $J = 8.1$ Hz), 8.08 (d, 2H, $J = 8.1$ Hz), 7.99 (d, 2H, $J = 8.5$ Hz), 7.94 (s, 2H), 7.90 (d, 2H, $J = 8.1$ Hz), 7.65 (d, 2H, $J = 8.1$ Hz) ppm; ^{13}C NMR (CDCl3, 75 MHz): δ 191.45, 135.35, 134.01, 133.75, 132.65, 131.89, 129.89, 128.86, 128.70, 127.94, 127.79 (2 peaks), 127.57, 123.53, 122.92 ppm; HRMS calcd for $C_{28}H_{16}O_2$ 384.1151, found 384.1150.

(+)-2,15-Bis(2-chloroethenyl)[6]helicene (11a). Lithium hexamethyldisilizane (0.75 mL of a 1.0 M solution in THF) was syringed into a solution of (chloromethyl)triphenylphosphonium chloride (0.279 g, 0.805 mmol) in THF (4 mL), which had been cooled in a dry ice/acetone bath. The dry ice bath was then removed, and the reaction was stirred for 30 min while warming to room temperature. A slurry of (+)-**11** (0.103 g, 0.268 mmol) in dry THF was added to the reaction under a stream of argon. After refluxing for 1 h, the mixture was cooled to room temperature and directly filtered through a short plug of silica gel (2 in. × 1 in., eluting with ca. 150 mL of 30% ethyl acetate/hexane). The solvent was removed under reduced pressure and the yellow solid triturated with hexane and dried in vacuo, yielding 0.113 g (94%) of chloro-olefins (+)-**11a**, a mixture of cis/trans isomers, mp > 220 °C. $[\alpha]_D$ +4870 (*c* 0.011, CH_2Cl_2); IR(KBr): 3046, 3014, 1597; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04−7.12 (m, 14H), 6.24−5.81 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.21, 132.83, 131.73, 131.55, 131.47, 129.49−126.49 (m), 125.45, 123.80, 123.56, 118.18, 118.02, 116.75 ppm; HRMS calcd for $C_{30}H_{18}Cl_2$ 448.0786, found 448.0809.

(+)-2,15-Diethynyl[6]helicene (1). Methyllithium (2.6 mL of a 1.4 M solution in Et_2O) was syringed into a solution of (+)-**11a** (0.104 g, 0.232 mmol) in THF (6 mL) which had been cooled in a dry ice/acetone bath. After the mixture had stirred at −78 °C for 1 h, the dry ice bath was removed, and stirring was continued for 1.25 h while warming to room temperature. Cautious addition of water (30 mL), followed by two extractions with CH_2Cl_2 (50 mL), drying (Na_2SO_4), solvent removal, chromatography (20% EtOAc in hexane), and in vacuo drying yielded 0.087 g (100%) of pure (+)-**1**, a yellow solid, mp > 220 °C. $[\alpha]_D$ +5140 (*c* 0.19, CH_2Cl_2); IR(KBr): 2208, 3038, 2102 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, 2H, $J = 8.2$ Hz), 7.99 (d, 2H, $J = 8.7$ Hz), 7.97 (d, 2H, $J = 8.8$ Hz), 7.92 (d, 2H, $J = 8.4$ Hz), 7.79 (d, 2H, $J = 8.1$ Hz), 7.72 (s, 2H), 7.34 (d, 2H, $J = 8.2$ Hz), 2.71 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.22, 132.04, 131.85, 131.66, 129.02, 128.53, 127.75−127.13, 123.80, 118.24, 83.64, 76.14 ppm; HRMS calcd for $C_{30}H_{16}$ 376.1252, found 376.1264.

Preparation of *o*-Iodo-*N*,*N*-dioctylbenzamide. Dioctylamine (2.16 g, 2.71 mL, 8.97 mmol) was added to a stirring solution of *o*-iodobenzoyl chloride (0.956 g, 3.59 mmol) in CH_2Cl_2 (20 mL) and refluxed overnight. After cooling to room temperature, washing twice with HCl (1 M), once with water, once with sat. $NaHCO_3$, once again with water, and drying ($MgSO_4$), the solvent was removed under reduced pressure. Chromatography (eluting with 5% acetone in CH_2Cl_2) yielded 1.57 g (89%) of a clear oil. IR(neat): 2927, 2855, 1641, 1458, 1424 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, 1H, $J = 8.0$ Hz), 7.36 (dd, 1H, $J = 7.6, 7.6$ Hz), 7.19 (d, 1H, $J = 7.6$ Hz), 7.04 (dd, 1H, $J = 7.7, 7.7$), 3.76 (m, 1H), 3.22 (m, 1H), 3.04 (m, 2H), 1.8−1.2 (m, 24H), 0.86 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.27, 142.92, 139.06, 129.75, 128.04, 127.21, 92.82, 48.50, 44.64, 31.80, 31.65, 29.37, 29.28, 28.94 (2 peaks), 28.31, 27.26, 27.10, 26.54, 22.62, 22.55, 14.09 ppm; HRMS calcd for $C_{23}H_{38}INO$ (M + 1) 472.2076, found 472.2072.

1,2-Bis(*N*,*N*-dioctylcarbamoyl)-4,5-diiodobenzene (3). CH_2Cl_2 (10 mL) and dioctylamine (0.419 g, 0.525 mL, 1.74 mmol) were sequentially added to a flask containing DCC (0.239 g, 1.16 mmol), DMAP (0.212 g, 1.74 mmol), DMAP·HCl[36] (0.239 g, 1.51 mmol), and 4,5-diiodophthalic anhydride[24] (0.232 g, 0.58 mmol). The mixture was refluxed for 3 h and then cooled to room temperature. Additional CH_2Cl_2 was added, followed by washes with HCl (1 M) and sat. $NaHCO_3$, drying (Na_2SO_4), solvent removal and chromatography (12 in. × 1 in., eluting first with 3:1 CH_2Cl_2/hexane, and then CH_2Cl_2, and finally with 3:1 CH_2Cl_2/acetone). Fractions containing compound **3** were pale yellow and eluted with CH_2Cl_2/acetone. Adding hexane to the residue and filtering through Celite removed an impurity and gave 0.420 g (84%) of **3**, a waxy semisolid. IR(neat): 2926, 2855, 1642, 1466, 1426 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (s, 2H), 3.27 (m 4H), 3.03 (m, 4H), 1.50−1.00 (m, 48H), 0.799 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.30, 136.62, 136.03, 107.48, 49.10, 45.13, 31.82, 31.75, 29.42, 29.28, 29.08, 28.44, 27.35, 27.12, 26.59, 22.60, 14.08 ppm; HRMS calcd for $C_{40}H_{71}I_2N_2O_2$ (M + 1) 865.3605, found 865.3602.

Preparation of Polymer 4. Compound **2** (0.060 g, 0.069 mmol, 1.60 mL of a 0.0433M solution in toluene), toluene (2 mL), and diisopropylamine (1.5 mL) were sequentially added to a flask containing (+)-**1** (0.025 g, 0.066 mmol), $Pd(PPh_3)_4$ (0.004 g, 0.0034 mmol), and CuI (0.001 g, 0.0052 mmol). After the mixture was heated at 70 °C for 4 h, it was cooled to room temperature, and water and CH_2Cl_2 were added. Washing twice with HCl (1 M) and once with water, drying ($MgSO_4$), solvent removal, trituration with methanol and then with hexane, and drying in vacuo gave 0.062 g (95%) of polymer **4**, a yellow solid. $[\alpha]_D$ +3580 ($c = 0.180$, CH_2Cl_2); IR(KBr): 2922, 2851, 1633, 1464, 1428 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10−7.10 (m, 16H), 3.80−2.70 (m, 8H), 1.60−0.60(m, 60H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.32, 139.35, 136.0−126.0 (m), 123.74, 120.09, 118.82, 118.65, 95.16, 85.55, 48.0−47.2, 45.2−44.0, 32.21, 31.65, 30.35−28.50 (m), 28.19, 27.42, 27.06, 26.55, 22.52, 14.03 ppm. Anal. Calcd for $C_{320}H_{406}N_{10}O_{10}I_2$:[37] C, 80.0; H, 8.5; N, 2.9. Found: C, 80.2; H, 8.1; N, 2.5.

Preparation of Cyclophanes 5 and Isolation of 5a. Compound **3** (0.023 g, 0.027 mmol, 0.85 mL of a 0.064 M solution in toluene), toluene (1.2 mL) and diisopropylamine (0.8 mL) were sequentially added to a flask containing (+)-**1** (0.010 g, 0.027 mmol), $Pd(PPh_3)_4$ (0.003 g, 0.003 mmol), and CuI (0.0007 g, 0.004 mmol). After the mixture was heated at 90 °C for 5 h 15 min, water and CH_2Cl_2 were added. Washing twice with HCl (1 M), once with sat. $NaHCO_3$, and once with water, drying (Na_2SO_4), and solvent removal gave a solid that was triturated with methanol until the filtrate was clear. This solid was dried, dissolved in CH_2Cl_2, and loaded onto a short column of silica gel (3 in. m~ 0.5 in.). The column was first washed with hexane and CH_2Cl_2. Subsequent elution with 1:1 CH_2Cl_2:acetone gave 0.023 g (88%) of crude cyclophanes **5**, a yellow solid. IR(KBr): 2924, 2854, 1732, 1639, 1465, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.2−6.0 (m, 16H), 3.6−2.8 (m, 8H), 1.8−0.7 (m, 60H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.86, 136.0−123.0 (m), 119.01, 117.90, 95.66, 86.10, 50.32−48.48 (m), 46.11−44.14 (m), 34.0−26.0 (m), 23.48−21.90 (m), 14.76−13.61 (m) ppm. Anal. Calcd for $(C_{70}H_{84}N_2O_2)_n$: C, 85.3; H, 8.5; N, 2.8. Found: C, 82.7; H, 8.3; N, 2.2. Two successive preparative silica gel TLC's (the first was developed with 0.5% EtOAc/CH_2Cl_2, the second with 1.5% EtOAc/benzene) of a 10 mg sample of crude **5**, followed by HPLC

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(36) Boden, E. P.; Keck, G. E. *J. Org. Chem.* **1985**, *50*, 2394.

(37) The CHN analysis was compared to that of **4d** ($C_{320}H_{406}N_{10}O_{10}I_2$, MW = 4806.6 Da), which falls near the lower limit of the estimated MW of the polymer. The calculated value for **4e** ($C_{390}H_{490}N_{12}O_{12}I_2$, MW = 5792.0 Da), the MW of which is near the upper limit of the estimated MW of the polymer, is: C, 80.9; H, 8.5; N, 2.9.

purification (150 × 4.6 mm i.id. column; 3 μm, 120 Å silica gel) using 10% EtOAc/hexane, gave 0.3 mg of **5a** (ca. 3% based on crude **5**). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (d, 4H, $J = 8.2$ Hz); 8.02 (d, 4H, $J = 8.3$ Hz); 7.99 (d, 4H, $J = 8.7$ Hz); 7.95 (d, 4H, $J = 8.3$ Hz); 7.92 (d, 4H, $J = 8.5$ Hz); 7.73 (s, 4H); 7.59 (d, 4H, $J = 8.1$ Hz); 7.3 (s, 4H); 3.29 (m, 8H); 3.10 (m, 8H); 1.32−1.08 (m, 96H); 0.88 (m, 12H); 0.84 (m, 12H). HRMS calcd for $C_{140}H_{168}N_4O_4$ 1970.3100, found 1970.2979.

(+)-2,15-Bis(2-(*N*,*N*-dioctylcarbamoyl)phenylethynyl)-[6]helicene (12). *o*-Iodo-*N*,*N'*-dioctylbenzamide (0.025 g, 0.053 mmol, 0.266 mL of a 0.2 M solution in toluene), toluene (1 mL) and diisopropylamine (0.5 mL) were sequentially added to a flask containing (+)-**1** (0.010 g, 0.027 mmol), $Pd(PPh_3)_4$ (0.005 g, 0.004 mmol), and CuI (0.005 g, 0.026 mmol). After the mixture was heated at 70 °C for 4.75 h, water and CH_2Cl_2 were added. Washing twice with HCl (1 M), once with sat. $NaHCO_3$, once with water, drying ($MgSO_4$), solvent removal, and chromatography (12 in. × 1 in., eluting first with 1:50 acetone/CH_2Cl_2, and then with 4:6 acetone/CH_2Cl_2) gave 0.026 g (93%) of **12**, a brown, waxy solid. $[\alpha]_D$ +1903 (*c* 0.072, CH_2Cl_2); IR(CH_2Cl_2): 2930, 2857, 1723, 1626, 1467, 1429 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10−7.20 (m, 22H), 3.80−2.80 (m, 8H), 2.20−0.70 (m, 60H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.73, 139.34, 135.12, 135.04, 133.34, 132.65−131.49 (m), 130.52, 129.80−126.57 (m), 123.88, 120.19, 119.25, 92.79, 85.99, 48.01, 44.60, 31.67, 29.70−29.02 (m), 28.31, 27.41, 27.10, 26.43, 22.55, 14.06 ppm; HRMS calcd for $C_{76}H_{90}N_2O_2$ (M + 1) 1063.7080, found 1063.7120.

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Supporting Information Available: Graphs showing the ^{1}H and ^{13}C NMR and IR spectra of **3**, **6d**, **8**, **8a**, **9**, (+)-**10**, (−)-**10**, **10a, 11**, **11a**, **1**, and *o*-iodo-*N*,*N'*-dioctylbenzamide, the ^{1}H NMR and IR spectra of **4**, **5** and **12**, the ^{1}H NMR spectrum and FAB mass spectrum of **5a**, the UV spectra of **13** and **14**, the UV and CD specta of **1**, and a listing of the X-ray diffraction analysis of (+)-**10** (63 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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