Elongation and Contraction of Molecular Springs. Synthesis, Structures, and Properties of Bridged [7]Thiaheterohelicenes

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Received August 20, 2001

A series of bridged [7]thiaheterohelicenes **3a**−**c** and **4** with a variety of helical pitches have been prepared from racemic and optical pure 2,13-bis(hydroxymethyl)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (**1**) in order to investigate the helical structures in solution. Recrystallizations of (*PM*)-**3a**, (*PM*)-**3b**, (*PM*)-**3c**, and (*P*)-**4** from hexane−dichloromethane gave crystals suitable for X-ray crystallography, while recrystallization of (*PM*)-**4** with benzene gave an inclusion complex with a stoichiometry of $(PM\text{-}\mathbf{4})_4\cdot(C_6H_6)$. X-ray analyses of (*PM*)-**3a**−**c**, $(PM\text{-}\mathbf{4})_4\cdot(C_6H_6)$, and (*P*)-**4** indicate that the dihedral angles between terminal thiophene rings of the helical framework significantly vary from 22° for **4** to 59° for **3c**. This represents as increase of 37° or 168%. Although the ^{13}C NMR and UV absorption spectra of bridged helicenes **3a**−**c** and unbridged helicene **5** are essentially the same, the molar rotation of **5** is very large compared with those of **3a**−**c** and **4**. A red shift (15 nm) in the circular dichroism (CD) spectrum is observed for **4**, suggesting that this compound is more planar than **3a**−**c** in solution. In the series of [7]thiaheterohelicenes studied, the minimum helical pitch is 2.70 Å for **4**.

Introduction

Since the first synthesis of hexahelicene ([6]helicene), which was made up of ortho-condensed six benzene rings by Newman in 1955,[1] helicene molecules have received considerable attention because of unique helical nonplanar π-electron system and of their very high rotational values.[2,3] The helicenes containing more than six benzene rings (carbohelicenes) or seven heteroaromatic rings (heterohelicenes) possess a rigid helical framework[2a,4] and are very stable toward acids, bases, and relatively high temperature.[5] In particular, chiral functionalized analogues are promising candidates for chiral ligands and auxiliaries in asymmetric syntheses.[6] The synthesis and properties of functionalized racemic and optically active carbohelicenes such as helical bis(quinones) have been extensively studied by Katz and co-workers, who utilize a Diels−Alder reaction for the construction of the quinones.[7] During the course of our study on the asymmetric synthesis of heterohelicenes, we have recently found that 2,13-bis(hydroxymethyl)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (**1**) interacts with guest molecules such as ethanol, 1,2-dichloroethane, and testosterone to form crystalline inclusion complexes with a variety of host−guest stoichiometric ratios.[8] The X-ray analysis of the inclusion complexes indicates that the dihedral angle between terminal thiophene rings of helicenediol **1** in the clathrates varies from 38.0° for (*PM*-**1**)·(EtOH) to 54.5° for $(PM\text{-}\mathbf{1})\cdot(1,2\text{-dichloroethane})_{0.5}$. These results indicate that the helical conjugated π-electron framework of **1** elongates and contracts as a “spring”.[8] However, due to the flexibility of the molecular spring very little information has been reported on its helical structures in solution. One possible way to attain a better understanding of the structures in solution is to synthe-

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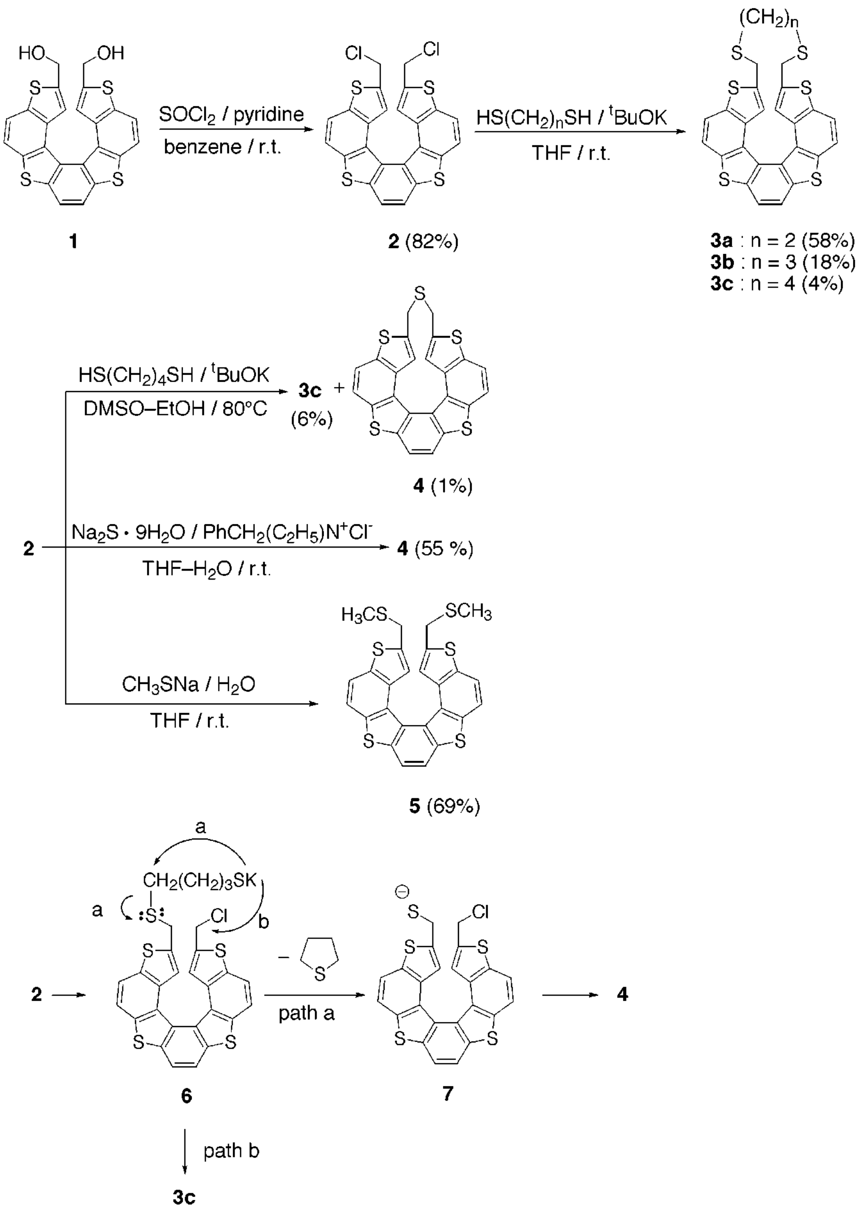
Scheme 1



size and characterize the bridged helicenes with fixed helical pitches. In this paper, we describe the synthesis, structures, and spectroscopic properties of bridged helicenes with a variety of helical pitches. It has been found that the angle between two terminal thiophene rings of the helicenes can range from 21.9° to 59.2°; therefore, the helical pitch of the molecular spring could be fine-tuned by proper choice of a spacer group.

Results and Discussion

Treatment of racemic helicenediol **1** with thionyl chloride in pyridine–benzene gave 2,13-bis(chloromethyl)thiaheterohelicene (**2**) in 82% yield. Reaction of **2** with disodium 1,2-ethanedithiolate in the presence of a catalytic amount of NaI in ethanol proceeded smoothly at room temperature to give the 2,5-dithiahexano-bridged helicene **3a** ($n = 2$) in 58% yield. Using a similar procedure, bridged helicenes **3b** ($n = 3$) and **3c** ($n = 4$) were prepared in 18% and 4% yields, respectively. However, helicene **3d** ($n = 5$) was not obtained by the reaction of **2** with 1,5-pentanedithiol (Scheme 1).

When the reaction of **2** and 1,4-butanedithiol was carried out at 80 °C, **3c** was obtained in 6% yield together with unexpected sulfide **4** (1.2%) after separation by flash chromatography. The mechanism of the ring contraction is explained by formation of the monosubstituted intermediate (**6**). The internal nucleophilic attack of thiolate ion of the intermediate ($-(CH_2)_4S^-$) at the methylene carbon atom next to the sulfur atom produces the corresponding helicenethiolate **7**, which then cyclizes to give **4**. The structure of **4** was unambiguously determined by X-ray crystallographic analysis. Although **2** did not react with sodium sulfide in organic solvents such as methanol, THF, and DMSO, the cyclization reaction readily accomplished in the presence of a phase-transfer catalyst in water–THF at room temperature,[9] giving **4** in 55% yield. Unbridged bis(methylthio)helicene **5** was prepared in 69% yield from **2** by treatment of excess amount of sodium methanethiolate in H_2O–THF. Left-handed and right-handed helicenes **3a**–**c**, **4**, and **5** were prepared from optically pure helicenediol **1**, which was

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[9] Landini, D.; Rolla, F. *Synthesis* **1974**, 565–566.

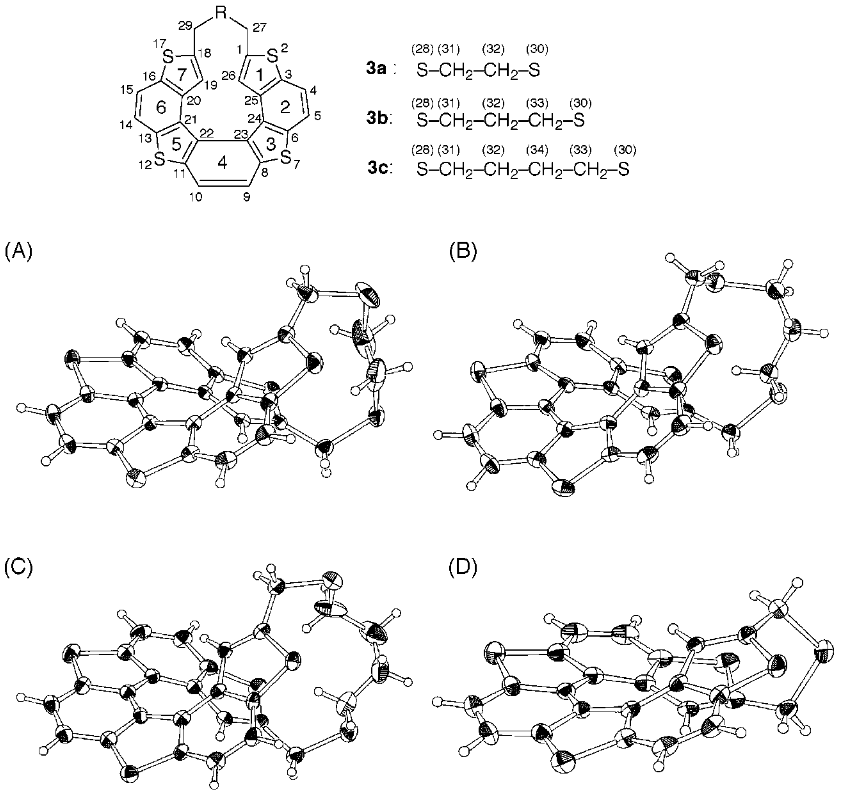

Figure 1. Numbering scheme (top) of bridged helicenes **3a**−**c** and ORTEP drawings of bridged helicenes: (A) **3a**, (B) **3b**, (C) **3c**, and (D) **4**.

readily obtained by lipase-catalyzed transesterification of racemic **1** (Figure 1).[10,11]

Single crystals of racemic helicenes **3a**−**c** and optically active helicene (*P*)-**4** suitable for X-ray crystallographic analyses were obtained by recrystallization from hexane−dichloromethane. In contrast, recrystallization of racemic **4** with hexane−benzene gave a crystalline inclusion complex with a stoichiometry of (*PM*-**4**)$_4$·(C_6H_6). The crystal data of all the five helical structures are summarized in Table 1. Although the bridged helicenes (*PM*)-**3a**−**c** possess different lengths of spacer, these all crystallize in the space group of $P2_1/n$ ($Z = 4$). In the crystals of (*PM*)-**3a**, the bridge of one enantiomer of racemic helicenes locates on the central thiophene−benzene−thiophene rings (rings 3−4−5) of the adjacent enantiomer of the same helicity along the crystallographic *b* axis. The C(31)−C(32) bond of the bridge locates perpendicularly to the helical axis as shown in Figure 2. The S(28)−C(31)−C(32)−S(29) dihedral angle of (*PM*)-**3a** is 175.4°, indicating that two sulfur atoms of the bridge are in an anti orientation where the dihedral angle of terminal thiophene rings is 53°. Although the same packing motif is observed in the crystals of (*PM*)-**3b** as in (*PM*)-**3a**, the S(28)−C(33)-C(32)−C(31) and C(31)−C(32)-C(33)−S(30) dihedral angles of **3b** are 44.1° and 66.1°, respectively, indicating that the 2,6-dithiaheptano-bridge is gauche conformation. The crystal lattice of (*PM*)-**3c** has a different packing motif from those of **3a** and **3b** as illustrated in Figure 2C, in which the benzene−thiophene−benzene rings (rings 2−3−4) of one enantiomer of **3c** stack on those of adjacent helicene of the opposite enantiomer alternately along the *a* axis. The S(28)−C(31)−C(32)−C(34), C(31)−C(32)−C(34)−C(33), and C(32)−C(34)−C(33)−S(30) dihedral angles of **3c** are 68°, 60°, and 68°, respectively, showing that the 2,7-dithiaoctano bridge is gauche conformation. Due to the flexible conformations of the bridges of **3a**−**c**, the dihedral angles between terminal thiophene rings do not significantly change. Thus the angle increases slightly from 53° for **3a** to 58° for **3b** and 59° for **3c**.

As shown in Table 2, two crystal structures were observed in (*PM*-**4**)$_4$·(benzene), where helicene molecules of the same helicity are aligned along the crystallographic *c* axis and guest molecules are situated between each enantiomers of helicene molecules. Although the dihedral angle between a benzene ring (ring-6) of helicene of **4** and a benzene molecule is 34.7°, the hydrogen atom on C4 locates on the center of a benzene molecule with 2.67 Å of the H···π distance as shown in Figure 3. These results indicate that a guest benzene molecule is trapped between two helicene molecule by T-type CH/π interaction.[12] In the chiral crystals (*P*)-**4**, however, right-handed helicene molecules stack along the crystallographic *a* axis by p-interaction, which causes the dihedral angle of (*P*)-**4** to increase slightly from 22° for (*PM*-**4**)$_4$·(C_6H_6) to 26.2°. As shown in Table 2, the shortest carbon−carbon distance (C19−C26) between terminal thiophene rings of (*PM*-**4**)$_4$·(C_6H_6) and (*P*)-**4** is 2.70 Å, which is very close to 2.69 Å of [2,2]metacyclophane.[13] This result indicates that

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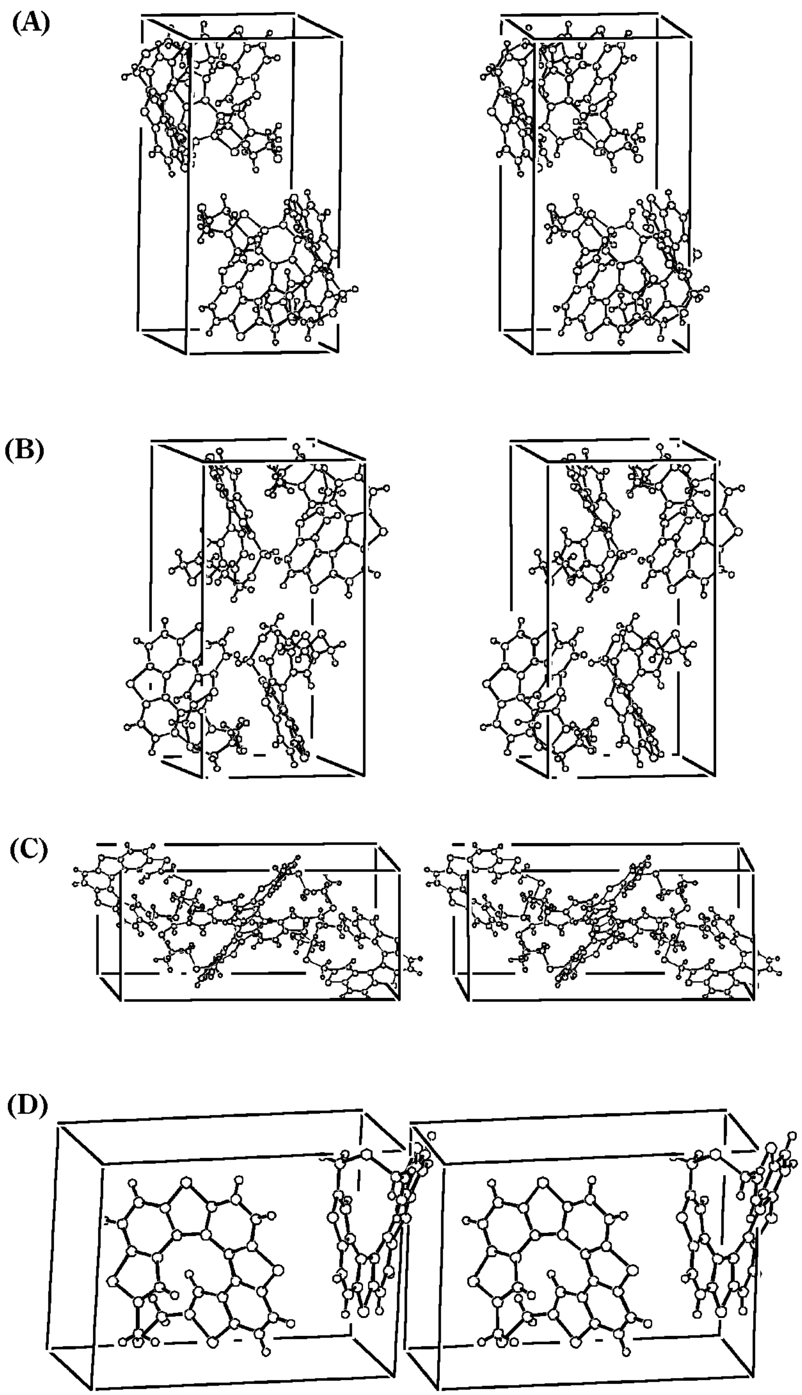

Figure 2. Stereoview of crystal packing of bridged helicenes (*PM*)-**3a** (A), (*PM*)-**3b** (B), (*PM*)-**3c**, and (*P*)-**4** (D).

the dihedral angle of 22° should be the smallest value in the series of [7]thiaheterohelicenes studied.

The ^{1}H and ^{13}C NMR NMR spectra of **3a**−**c**, **4**, and **5** are listed in Table 3. Although the chemical shifts of outer protons H_4, H_5, H_9, H_{10}, H_{14}, and H_{15} of **3a**−**c** and **4** are in the region of 7.9−8.0 ppm, the inner protons H_{19} and H_{26} of **3a**−**c** and **4** resonate at lower fields (6.99, 6.86, 6.69, and 7.16 ppm, respectively). As the nonbonded distance between H_{19} and H_{26} shortens from 3.22 Å for **3c** to 2.70 Å for **4**, the higher field shifts are observed in the inner aromatic protons (H_{19} and H_{26}) and the methylene protons (H_{27} and H_{29}) of **4**. This phenomenon is explained by shielding and deshielding effects of the ring currents by helical aromatic framework. Thus, the proton H_{19} above the terminal benzothiophene ring (ring 1−2) is in the shielding region and also locates in the deshielding region by the rings 3−4−5−6−7. A similar deshielding effect is observed in the case of 2-hydroxymethyl[5]-thiahelicene in which the inner protons occur at 8.15 and 8.24 ppm.[14] In contrast, the ^{13}C NMR spectra of helicenes **3a**−**c** and **5** are essentially the same, indicating that these helicenes **3a**−**c**, **4**, and **5** have the same p-electron densities.

The UV absorption spectra of bridged helicene **3a**−**c** and unbridged helicene **5** have a similar shape to those

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[14] Yamada, K.; Ishii, R.; Nakagawa, H.; Kawazura, H. *Tetrahedron*: *Asymmetry* **1996**, *7*, 737−746.

Table 1. Crystal Data of Bridged and Unbridged Helicenes of (*PM*)-3a−c, (*PM*-4)$_4$·(benzene), and (*P*)-4

crystal	(*PM*)-**3a**	(*PM*)-**3b**	(*PM*)-**3c**	(*PM*-**4**)$_4$·(benzene)	(*P*)-**4**
formula	$C_{26}H_{16}S_6$	$C_{27}H_{18}S_6$	$C_{28}H_{20}S_6$	$C_{25.5}H_{13.5}S_5$	$C_{24}H_{12}S_5$
formula wt	520.77	534.80	548.83	480.19	460.66
cryst dimens (mm)	0.16 × 0.26 × 0.10	0.25 × 0.20 × 0.10	0.02 × 0.19 × 0.60	0.40 × 0.20 × 0.12	0.06 × 0.10 × 0.60
a (Å)	10.161	9.875	8.380	11.344	5.490
b (Å)	10.689	11.406	26.138	20.165	15.796
c (Å)	21.107	20.890	11.726	9.762	11.050
α (deg)				93.81	
β (deg)	94.27	95.703	106.45	108.73	98.30
γ (deg)				99.51	
V (Å$^{3)}$	2286	2341.3	2463	2068	948
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1$
Z	4	4	4	4	2
D_{calcd} (g/cm^3)	1.513	1.517	1.480	1.542	1.613
F_{000}	1072	1104	1040	986	472
μ (cm^{-1})	56.25	55.08	5.65	5.72	6.21
radiation	Cu Kα	Cu Kα	Mo Kα	Mo Kα	Mo Kα
T (°C)	20	23	21	23	23
scan type	$\omega-2\theta$	$\omega-2\theta$	ω	$\omega-2\theta$	ω-2θ
no. of reflns measured	7688	3921	6020	10047	2477
no. of observations	2865	2804	1904	6111	1528
	($I > 2.00\sigma(I)$)	($I > 2.00\sigma(I)$)	($I > 2.00\sigma(I)$)	($I > 2.00\sigma(I)$)	($I > 2.00\sigma(I)$)
no. of variables	290	298	307	558	262
R (%)	5.2	5.4	5.9	4.1	4.6
R_w (%)	8.9	8.5	7.9	5.7	6.0
goodness of fit	1.50	1.32	1.20	1.16	1.07

Table 2. Selected Nonbonded Distances between the Terminal Thiophene Rings (Å) and Dihedral Angles (deg)

helicene	(*PM*)-**3a**	(*PM*)-**3b**	(*PM*)-**3c**	(*PM*-**4**)$_4$·(C_6H_6)^a		(*P*)-**4**
C1−C18	4.33	4.48	4.60	3.29	3.27	3.29
C19−C26	3.02	3.11	3.22	2.70	2.70	2.70
C27−C29	5.30	5.54	6.16	2.90	2.87	2.89
ring 1−ring 2	4.42	7.32	10.57	6.26	6.44	5.52
ring 2−ring 3	10.12	9.16	11.11	4.74	4.44	9.47
ring 3−ring 4	12.87	14.33	10.50	10.51	11.49	9.13
ring 4−ring 5	13.32	13.45	12.86	11.69	11.10	12.08
ring 5−ring 6	9.58	11.68	11.45	4.51	5.86	2.13
ring 6−ring 7	7.29	5.77	10.29	6.69	6.63	6.18
ring 1−ring 7	53.5	57.8	59.2	22.5	21.9	26.2

[a] Two independent molecules of bridged helicene **4** exist in crystal lattice; space group is $P\bar{1}$ and $Z = 4$.

of unsubstituted [7]thiaheterohelicene,[15] but there is slight increase in the absorptions with the decrease of the dihedral angle between two terminal thiophene rings. The red shift from 390 to 405 nm in going from **3a** to **4** is due to the increased conjugation of the helical aromatic frameworks. It is noteworthy to mention that the intensity of CD spectra of optically active bridged helicenes **3a**−**c** and **4** increases with the dihedral angles (Figures 5 and 6), due to the enhancement of the electric transition moments by distorted aromatic chromophores.[16] Although we have no information about the crystal structure of bis(methylthio)[7]thiaheterohelicene **5**, we speculate that the dihedral angle of **5** is in the range of 45−48°, because the Cotton effect and molar rotation (+11630°) are very similar to those of dimethyl[7]thiaheterohelicene (+12480°) (Table 4).[17]

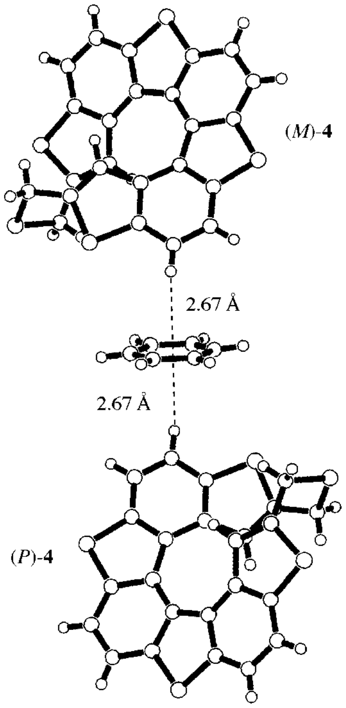

Figure 3. CH−π interaction between π-electrons of benzene and H-atoms of helicenes.

In conclusion, racemic and optically active [7]thiaheterohelicenes with a variety of helical pitches were prepared by reaction of 2,13-bis(chloromethyl)[7]thiaheterohelicene **2** with 1,*n*-alkanedithiolate. It demonstrated that elongation and contraction of the helicene molecule could be achieved by incorporating a spacer between the terminal rings. Thus, the C27−C29 distance of the series of [7]heterohelicenes varies from 2.87 Å for (*PM*-**4**)$_4$·(C_6H_6) to 6.16 Å for (*PM*)-**3c**. This represents an increase of 3.29 Å or 115%.

Experimental Section

Melting points were determined on a Yanagimoto hotstage apparatus and are not corrected. IR spectra were recorded on a SHIMADZU FT IR DR8000/8100 infrared spectrometer. NMR spectra were obtained with a Varian Gemini 200 (200

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(17) Tanaka, K.; Suzuki, H.; Osuga, H. *J. Org. Chem.* **1997**, *62*, 4465−4470.

Table 3. ^{1}H and ^{13}C NMR Chemicla Shifts (ppm) of Helicenes 3a−c, 4, and 5

	3a	**3b**	**3c**	**4**	**5**
H_9, H_{10}	7.97	7.96	7.97	7.98	7.97
H_4, H_5, H_{14}, H_{15}	7.95	7.93	7.92	7.91	7.91
H_{19}, H_{26}	6.99	6.86	6.69	7.16	6.65
H_{27}, H_{29}	3.48, 3.65	3.50, 3.55	3.32, 3.49	3.80, 3.99	3.45, 3.47
C_1, C_{18}	145.3	144.2	145.2	*a*	142.3
C_{19}, C_{26}	124.8	123.9	124.2	131.0	124.3
C_9, C_{10}	121.1	121.1	121.3	121.1	121.2
C_4, C_{15} or C_5, C_{14}	120.5	120.3	120.2	120.9	120.3
C_5, C_{14} or C_4, C_{15}	119.2	118.8	118.7	119.6	118.6
C_{27}, C_{29}	34.9	31.8	32.4	31.3	33.2

[a] Only 11 peaks of aromatic carbons were obseved in the case of **4**.

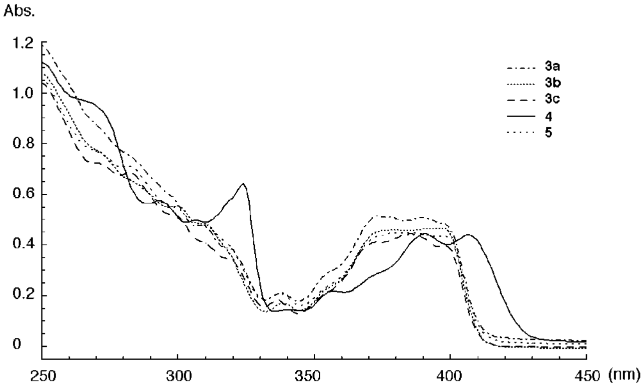

Figure 4. UV spectra of [7]thiahelicenes **3a**−**c**, **4**, and **5**.

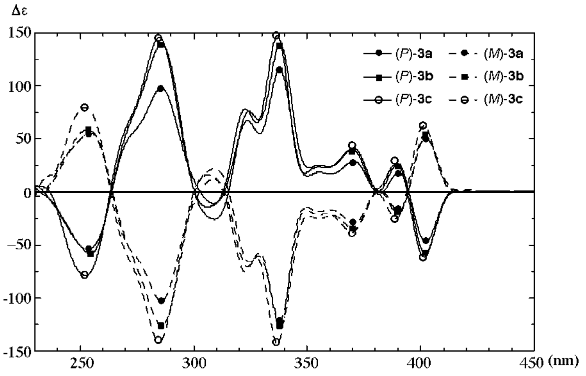

Figure 5. CD spectra of bridged helicenes **3a**−**c** in $CHCl_3$.

MHz) and JEOL JNM-AL300 (300 MHz) spectrometer in $CDCl_3$ solution with tetramethylsilane as a internal standard and *J* values were given in Hz. Optical rotation were measured in 1 dm path length cells of 10 cm^3 on a JASCO model DIP181 polarimeter; $[\alpha]_D$ values are given in 10^{-1} deg·cm^2·g^{-1}. CD spectra were measured in 1 cm path length cells on a JASCO J-720W spectropolarimeter. THF was distilled under argon atmosphere from sodium benzophenone ketyl immediately before use. Benzene was distilled from calcium hydride and stored over molecular sieves 4A. Silica gel (Wakogel C-200) of the size 100−200 mesh was used for column chromatography. Optical purity of helicenediol was determined by HPLC analysis with a Hitachi instrument equipped with UV detector L-4000 using Sumichiral OA-2000I.

2,13-Bis(chloromethyl)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (2). 2,13-Bis(hydroxymethyl)-dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene **1** (232 mg, 0.50 mmol) and dry pyridine (1.0 mL) were dissolved in dry benzene (40 mL) at room temperature under argon. Thionyl chloride (0.20 g, 2.00 mmol) was added, and the solution was allowed to stir for 12 h. The mixture was poured into ice−water (100 mL) and extracted with benzene three times. The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated in vacuo to give 205 mg (82%) of **2** as a yellow solid. Since this compound was unstable for silica gel column chromatography, **2** was used for next step without any further purification: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85 (s, 2H), 7.80 (s, 4H), 6.51 (s, 2H), 4.21 (s, 4H).

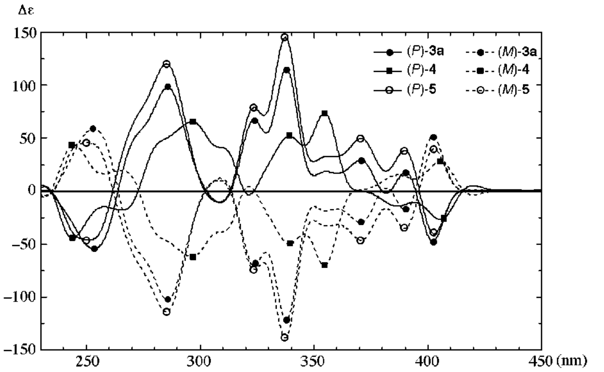

Figure 6. CD spectra of [7]thiahelicenes **3a**, **4**, and **5** in $CHCl_3$.

Table 4. Optical Rotations of Heterohelicenes (c = 0.050, $CHCl_3$)

helicene	**3a**	**3b**	**3c**	**4**	**5**	dimethyl-[7]thiahetero-helicene[17]
$[\alpha]_D$	+1510	+1540	+1570	+987	+2220	+2720
	−1420	−1450	−1440	−936	−2260	−2690
$[\Phi]_D$[a]	+7870	+8230	+8640	+4550	+11630	+11750
	−7410	−7750	−7900	−4310	−11790	−11621
dihedral angle (deg)	53	58	59	22	(46−49)[b]	46.9

[a] $[\Phi]_D = M_w[\alpha]_D/100$. [b] Estimated angle.

2,13-(2,5-Dithiahexano)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (3a). The chloride **2** (140 mg, 0.28 mmol) and sodium iodide (1 mg) were dissolved in dry THF (5 mL) under argon. The mixture was added to a solution of 1,2-ethanedithiol (27.6 mg, 0.28 mmol) and sodium ethoxide (41.9 mg, 0.62 mmol) in ethanol (10 mL). After the mixture was stirred over 12 h at room temperature, a diluted HCl (70 mL) was added. The mixture was extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated. Chromatography of the residue (silica gel, hexane/EtOAc = 20:1) gave 84.6 mg (58%) of **3a** as a pale yellow solid: mp 288−290 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (s, 4H), 7.95 (s, 2H), 6.99 (s, 2H), 3.65 (d, 2H, J = 14.4 Hz), 3.48 (d, 2H, J = 15.0 Hz), 2.86−2.74 (m, 2H), 2.45−2.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 145.3, 138.0, 137.2, 136.8, 135.9, 131.0, 130.0, 124.8, 121.2, 120.5, 119.3, 34.9, 34.0; IR (KBr) 2894, 1145, 795 cm^{-1}; CD ($c = 2.5 \times 10^{-5}$M, $CHCl_3$), nm (Δε), (*P*)-**3a**: 253 (−54), 286 (98), 324 (67), 338 (115), 370 (29), 390 (18), 402 (−47), (*M*)-**3a**: 253 (59), 286 (−103), 324 (−70), 338 (−122), 370 (−30), 390 (−18), 402 (51). Anal. Calcd for $C_{26}H_{16}S_6$: C, 59.96; H, 3.10. Found: C, 60.29; H, 3.12.

2,13-(2,6-Dithiaheptano)dithieno[3,2-*e*:3′,2′-*e*′]benzo-[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (3b). The chloride **2** (290 mg, 0.58 mmol) and sodium iodide (1 mg) were dissolved in dry THF (10 mL) under argon. The mixture was added to a solution of 1,3-butanedithiol (65.9 mg, 0.609 mmol) and sodium ethoxide (86.8 mg, 1.28 mmol) in ethanol (20 mL). After the mixture was stirred over 24 h at room temperature, a diluted HCl (100 mL) was added. The mixture was extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated. Chromatography of the residue (silica gel, hexane/EtOAc = 20:1) gave 55.0 mg (18%) of **3b** as a pale yellow solid: mp 263−265 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.96−7.92 (m, 6H), 6.86 (s, 2H), 3.55 (s, 2H), 3.50 (s, 2H), 2.8−2.4 (m, 4H), 1.9−1.7 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 144.2, 137.8, 137.1, 136.7, 136.4, 130.9, 130.1, 123.9, 121.1, 120.3, 118.8, 31.8, 31.1, 30.1; IR (KBr) 2908, 1145, 793 cm^{-1}; CD ($c = 2.5 \times 10^{-5}$M, CHCl$_3$), nm ($\Delta\epsilon$), (*P*)-**3b**: 254 (−58), 286 (139), 324 (76), 338 (139), 370 (42), 390 (27), 402 (−58), (*M*)-**3b**: 254 (56), 286 (−126), 324 (−66), 338 (−126), 370 (−35), 390 (−21), 402 (55).

2,13-(2,7-Dithiaoctano)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (3c). The chloride **2** (220 mg, 0.44 mmol) and sodium iodide (1 mg) were dissolved in a mixture of dry THF (12 mL) and dimethyl sulfoxide (5 mL) under argon. The mixture was added to a mixture of 1,4-butanedithiol (57.3 g, 0.469 mmol), ^{t}BuOK (149 mg, 1.33 mmol), and sodium iodide (1 mg) in ethanol (20 mL) under argon. After the mixture was heated at 80 °C for 5 h and cooled to room temperature, water was added. The reaction mixture was extracted with benzene three times. The combined organic phases were dried over anhydrous MgSO$_4$ and concentrated. Chromatography of the residue (silica gel, hexane/CH$_2$Cl$_2$ = 3:1) gave 14.6 mg (6%) of **3c** as a pale yellow solid along with 2.4 mg (1.2%) of **4** as a yellow solid. **3c**: mp 265−268 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.97 (s, 2H), 7.92 (s, 4H), 6.69 (s, 2H), 3.49 (dd, 2H, $J = 15.3$, 1.5 Hz), 3.32 (d, 2H, $J = 15.3$), 2.70 (d, 2H, $J = 12.3$ Hz), 2.13 (d, 2H, $J = 10.8$ Hz), 1.77 (t, 2H, $J = 13.0$ Hz), 1.45 (t, 2H, $J = 9.0$ Hz); ^{13}C NMR (CDCl$_3$) δ 145.2, 137.6, 136.9, 136.7, 136.0, 130.6, 129.8, 124.2, 120.2, 121.3, 118.7, 32.4, 27.8, 23.0; IR (KBr) 2911, 1152, 780 cm^{-1}; CD ($c = 2.5 \times 10^{-5}$ M, CHCl$_3$), nm ($\Delta\epsilon$), (*P*)-**3c**: 252 (−79), 285 (146), 323 (78), 337 (148), 370 (40), 389 (27), 401 (−61), (*M*)-**3c**: 252 (80), 285 (−141), 323 (−75), 337 (−143), 370 (−38), 389 (−25), 401 (62). **4**: see the following data of compound **4**.

2,13-(2-Thiapropano)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (4). The chloride **2** (140 mg, 0.28 mmol) and sodium iodide (1 mg) were dissolved in dry THF (5 mL) under argon. The mixture was added to a solution of Na$_2$S·9H$_2$O (28.4 mg, 0.118 mmol) and benzyltriethylammonium chloride (8 mg, 0.035 mmol) in H$_2$O (1 mL) solution. After the mixture was heated at reflux for 6 h and cooled to room temperature, a diluted HCl was added. The mixture was extracted with benzene three times. The combined organic phases were dried over anhydrous MgSO$_4$ and concentrated. Chromatography of the residue (silica gel, hexane/EtOAc = 50:1) gave 28.8 mg (55%) of **4** as a yellow solid: mp 249−252 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.98 (s, 2H), 7.91 (s, 4H), 7.16 (s, 2H), 3.99 (d, 2H, $J = 13.9$ Hz), 3.80 (dd, 2H, $J = 13.9$, 1.8 Hz); ^{13}C NMR (CDCl$_3$) δ 138.6, 138.0, 136.7, 134.1, 131.0, 130.8, 130.4, 121.3, 120.9, 119.6, 31.3; IR (KBr) 2919, 1144, 784 cm^{-1}; CD ($c = 2.5 \times 10^{-5}$ M, CHCl$_3$), nm ($\Delta\epsilon$), (*P*)-**4**: 244 (−45), 266 (−18), 296 (65), 339 (52), 355 (74), 387 (−14), 405 (−27), 420 (5), (*M*)-**4**: 245 (44), 266 (19), 296 (−62), 339 (−50), 355 (−70), 387 (15), 405 (28), 420 (−4). Anal. Calcd for C$_{24}$H$_{12}$S$_5$: C, 62.57; H, 2.63. Found: C, 62.29, H, 2.88.

2,13-Bis(methylthiomethyl)dithieno[3,2-*e*:3′,2′-*e*′]benzo-[1,2-*b*:4,3-*b*′]bis[1]benzothiophene (5). The chloride **2** (0.121 mg, 0.242 mmol) and sodium methanethiolate (15% aqueous solution, 1.13 mL, 2.43 mmol) were dissolved in dry THF (10 mL) under argon. After the mixture was stirred over 12 h at room temperature, brine (10 mL) was added. The mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous MgSO$_4$ and concentrated. Chromatography of the residue (silica gel, hexane/EtOAc = 30:1) gave 88.0 mg (69%) of **5** as a yellow solid: mp 141−145 °C; ^{1}H NMR (CDCl$_3$) δ 7.97 (s, 2H), 7.91 (s, 4H), 6.65 (s, 2H), 3.47 (s, 2H), 3.45 (s, 2H), 1.79(s, 6H);^{13}C NMR (CDCl$_3$) δ 142.3, 137.6, 136.9, 136.8, 136.2, 130.5, 129.9, 124.3, 121.2, 120.3, 118.6, 33.2, 15.2; IR (KBr) 2908, 1145, 789 cm^{-1}; CD ($c = 2.5 \times 10^{-5}$ M, CHCl$_3$), nm ($\Delta\epsilon$), (*P*)-**5**: 252 (−46), 285 (120), 324 (79), 337 (145), 371 (50), 390 (38), 403 (−40), (*M*)-**5**: 251 (46), 285 (−114), 324 (−74), 337 (−139), 371 (−46), 390 (−35), 403 (40). Anal. Calcd for C$_{26}$H$_{18}$S$_6$: C, 59.73; H, 3.47. Found: C, 59.60; H, 3.60.

X-ray Crystallographic Analysis. Data were collected at room temperature using Rigaku AFC5R diffractometer, and the structures were solved and refined using the TEXSAN crystallographic program package of the Molecular Structure Corp. The unit cells were determined by a least-squares analysis of the setting angles of 25 high-angle reflections. The structures were solved by direct methods and computed by standard Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were introduced at calculated position and refined with isotropic displacement parameter. The absolute configulation of (*P*)-**4** was not established by anomalous dispersion effects and has been assigned by reference to an unchanging helical structure in the synthetic procedure.

Acknowledgment. This work was supported by Grants-in-Aid for Exploratory Research (No. 11875212), Scientific Research (B) (No. 12440179), and Encouragement of Young Scientists (No. 13740355) from the Ministry of Education, Science, Sports and Culture. Y.K. acknowledges support from the Japan Society for the Promotion of Science (No. 4561). H.O. acknowledges financial support from the Nissan Science Foundation.

JO016043V