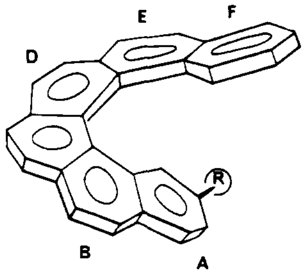
Hexahelicene. The Absolute Configuration[1,2]

David A. Lightner,* Daniel T. Hefelfinger,[3] Thomas W. Powers,[4]
Gerard W. Frank, and Kenneth N. Trueblood

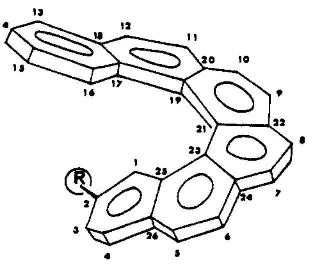
Contribution No. 2869 from the Department of Chemistry of the University of California, Los Angeles, California 90024. Received August 16, 1971

Abstract: The absolute stereochemistry of hexahelicene (**1**) has been determined from an X-ray study of optically active 2-bromohexahelicene (**2**). Levorotatory 2-bromohexahelicene (**2a**) with a left-handed chirality was converted to levorotatory hexahelicene (**1a**). Thus (−)-hexahelicene (**1a**) also has a left-handed helical configuration.

Hexahelicene (**1** = **1a** + **1b**) was first synthesized[5] and resolved[5,6] by Newman and Lednicer. Moscowitz later indicated[7] that hexahelicene constitutes a prime example of a class of chromophores termed inherently dissymmetric.[7,8] The dissymmetry of hexahelicene extends in a helical manner through the entire chromophore (molecule) as shown in structures **1** and **2**.



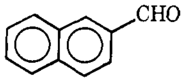
1a, R = H
2a, R = Br



1b, R = H
2b, R = Br

Although hexahelicene was resolved[5,6] over 15 years ago, and calculations[7,9–13] were performed to relate the sign of the optical activity and the stereochemistry of the molecule, until recently[1] the absolute configuration remained undetermined.

Detailed optical rotatory dispersion (ORD) and circular dichroism (CD) analyses of hexahelicene[13–15] and sulfur heterohelicenes[16,17] have appeared recently. Furthermore, the absolute configuration of some heterohelicenes has been reported.[16–18] On the basis of an X-ray determination, the heterohelicene (−)-benzo[*d*]naphtho[1,2-*d′*]benzo[1,2-*b*:4,3-*b′*]dithiophene was assigned a left-handed chirality, and it was more generally observed[16] that other (+)-heterohelicenes have a right-handed chirality. However, the circular dichroism and optical rotatory dispersion spectra of the sulfur heterohelicenes proved to be quite different from those of hexahelicene, and an extension to hexahelicene of the optical activity sign–absolute stereochemistry correlation derived for heterohelicenes seemed tenuous. For numerous reasons, therefore, determination of the absolute configuration of hexahelicene was desirable.



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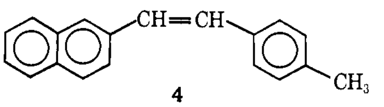

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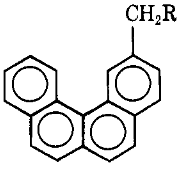
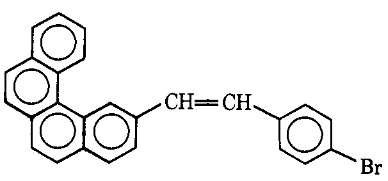


5a, R = H
b, R = Br
c, R = $P(C_6H_5)_3{}^+Br^-$



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Synthesis and Stereochemistry

Martin's photochemical procedure for the preparation of helicenes[19,20] was followed in our synthesis of 2-bromohexahelicene (**2**). Thus, 2-naphthaldehyde (**3**) was converted in 90% yield to the known 1-(2-naphthyl)-2-(*p*-tolyl)ethylene (**4**)[21] by a Wittig reaction with *p*-xylyltriphenylphosphonium bromide. The first photocyclization step (on **4**) led to an 82% yield of the known 2-methylbenzo[*c*]phenanthrene (**5a**).[22] Benzylic bromination of **5a** with *N*-bromosuccinimide gave a 69% yield of pure bromide (**5b**) which was converted to its triphenylphosphonium salt (**5c**) in 94% yield. Reaction of the ylide derived from **5c** with *p*-bromobenzaldehyde gave in 73% yield 1-(*p*-bromophenyl)-2-(2-benzo[*c*]phenanthrenyl)ethylene (**6**) which was converted in

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[1] For a preliminary account of this work, see D. A. Lightner, D. T. Hefelfinger, G. W. Frank, T. W. Powers, and K. N. Trueblood, *Nature (London)*, **233**, 124 (1971).

[2] Financial support by the National Science Foundation (Grant No. GP-9533 to D. A. L. and Grant No. GP-10949 to K. N. T.). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (ACS-PRF-4949 to D. A. L.).

[3] National Institutes of Health Postdoctoral Fellow, 1970–1972.

[4] National Science Foundation Undergraduate Research Participant, 1967–1969.

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Table I. Crystal Data

Space group: $P2_12_12_1$; Z = 4 molecules/cell	
a = 17.364 ± 0.003 Å; b = 13.344 ± 0.004 Å;	
c = 7.799 ± 0.002 Å	
$\alpha = \beta = \gamma = 90°$; cell volume = 1808 Å^3; mol wt = 407.9	
Calculated density = 1.50 g/cm^3; density measured by flotation = 1.50 ± 0.01 g/cm^3	

Table II. Fractional Atomic Coordinates for Bromine (×10^5) and Carbon Atoms (× 10^4), and Anisotropic Thermal Parameters (×10^4)[a]

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{12}	b_{13}
Br	9471 (5)	19365 (7)	24412 (15)	37 (1)	79 (1)	231 (2)	−25 (1)	−37 (2)	−47 (2)
C(1)	2133 (4)	2864 (5)	4297 (10)	22 (2)	26 (4)	143 (14)	6 (5)	−19 (10)	−6 (13)
C(2)	1421 (4)	2462 (6)	4435 (10)	28 (3)	36 (4)	142 (14)	−5 (6)	5 (11)	4 (16)
C(3)	0986 (5)	2406 (6)	5992 (21)	38 (3)	48 (4)	212 (18)	14 (8)	41 (14)	−1 (17)
C(4)	1318 (5)	2804 (6)	7427 (12)	35 (3)	54 (5)	202 (16)	7 (6)	70 (14)	66 (21)
C(5)	2322 (5)	3824 (7)	8858 (12)	42 (3)	73 (6)	169 (17)	44 (8)	−55 (14)	−58 (20)
C(6)	2977 (5)	4389 (6)	8725 (12)	42 (3)	43 (5)	197 (18)	39 (7)	−55 (14)	−43 (18)
C(7)	4031 (5)	5085 (6)	7040 (12)	37 (3)	47 (4)	269 (21)	19 (7)	−67 (15)	−53 (17)
C(8)	4416 (5)	5200 (6)	5519 (15)	35 (3)	36 (4)	357 (24)	4 (7)	−98 (16)	−22 (21)
C(9)	4668 (4)	4687 (6)	2565 (15)	26 (2)	66 (5)	281 (20)	7 (6)	−13 (19)	84 (26)
C(10)	4560 (5)	4034 (7)	1189 (14)	18 (2)	92 (7)	286 (23)	8 (7)	−3 (15)	117 (23)
C(11)	4064 (5)	2394 (8)	0138 (12)	26 (3)	104 (7)	164 (15)	43 (8)	13 (13)	7 (20)
C(12)	3738 (5)	1499 (7)	0348 (12)	27 (3)	84 (6)	175 (17)	22 (2)	13 (13)	27 (20)
C(13)	3345 (4)	0171 (6)	2412 (14)	28 (2)	53 (4)	270 (19)	9 (6)	−41 (18)	−63 (24)
C(14)	3233 (5)	−0198 (6)	4074 (12)	29 (2)	54 (5)	217 (19)	12 (7)	−12 (14)	−63 (19)
C(15)	3367 (5)	0494 (7)	5440 (12)	30 (3)	63 (5)	219 (18)	22 (7)	5 (15)	−15 (20)
C(16)	3539 (4)	1475 (6)	5153 (11)	27 (2)	40 (4)	184 (16)	4 (6)	27 (12)	39 (16)
C(17)	3620 (4)	1856 (6)	3446 (10)	20 (2)	48 (4)	144 (13)	7 (6)	9 (11)	−38 (16)
C(18)	3550 (4)	1185 (6)	2088 (10)	21 (2)	68 (5)	142 (16)	19 (6)	−10 (11)	−34 (16)
C(19)	3826 (4)	2889 (6)	3108 (10)	19 (2)	45 (4)	154 (14)	12 (5)	−10 (9)	18 (14)
C(20)	4147 (4)	3123 (5)	1476 (11)	24 (2)	63 (5)	161 (14)	28 (7)	14 (11)	68 (17)
C(21)	3768 (4)	3700 (7)	4348 (11)	20 (2)	39 (4)	193 (16)	−7 (6)	−36 (11)	39 (16)
C(22)	4281 (4)	4529 (6)	4110 (13)	21 (2)	61 (5)	262 (21)	3 (6)	−31 (13)	25 (20)
C(23)	3247 (4)	3768 (5)	5804 (10)	26 (2)	28 (4)	176 (16)	3 (6)	−11 (12)	22 (15)
C(24)	3429 (4)	4388 (5)	7174 (11)	31 (3)	35 (4)	187 (18)	15 (6)	−85 (13)	6 (17)
C(25)	2485 (4)	3268 (6)	5833 (10)	20 (2)	50 (5)	126 (14)	12 (6)	0 (10)	17 (15)
C(26)	2048 (4)	3278 (5)	7390 (12)	31 (2)	52 (5)	180 (15)	25 (6)	1 (15)	−64 (20)

[a] Estimated standard deviations given in parentheses refer to least significant digits. Thermal parameters are represented in the form $T = \exp[-(b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl)]$.

82% yield to 2-bromohexahelicene (**2a** and **b**) by the photochemical cyclization procedure.

2-Bromohexahelicene (**2**) was resolved into the levorotatory enantiomer (**2a**), $[\alpha]_{589}$ −3560° (c 0.066, $CHCl_3$), using (−)-α-(2,4,5,7-tetranitro-9-(fluorenylideneaminooxy)propionic acid [(−)-TAPA].[23] Selected crystals from the highest rotating sample of (−)-bromohexahelicene were used for the X-ray determination of its absolute configuration.

Structure Determination and Refinement. The space group was determined to be $P2_12_12_1$ from Weissenberg photographs and diffractometric measurements. The unit-cell parameters listed in Table I were refined by least squares from 2θ values measured on 18 reflections. The three-dimensional X-ray data used in solving and refining the structure were collected from a needle-shaped crystal, 0.4 mm long and 0.05 mm in diameter, on a Picker four-circle automated diffractometer. The intensities were measured with graphite crystal-monochromatized Cu Kα radiation out to a maximum $(\sin \theta)/\lambda$ value of 0.58 Å^{-1}. Data were collected by the θ–2θ scan technique, and $\sigma(I)$ was calculated from counting statistics as follows.

$$\sigma(I) = (I_{\text{scan}} + \text{bkgnd}_{\text{left}} + \text{bkgnd}_{\text{right}})^{1/2}$$

A total of 1462 independent reflections in the positive hkl octant met the criterion $I > 2\sigma(I)$ and were used in the crystal structure refinement. Corrections for absorption and secondary extinction were not applied.

The bromine atom was located from peaks in the Harker sections of the three-dimensional Patterson function, and the carbon atoms were located in bromine-phased electron density maps. Refinement of the structural parameters with anisotropic temperature factors was carried out using a modified version of the UCLA full-matrix, least-squares refinement program by Gantzel, *et al.*[24] Scattering factor tables were taken from the "International Tables for X-Ray Crystallography."[25] The R index, defined as

$$R = \sum \lVert F_o| - |F_c \rVert / \sum |F_o|$$

converged to 0.059. Inclusion of 267 unobserved reflections in the structure factor calculation gave an R index of 0.085.

The positions of the hydrogen atoms were calculated assuming planar-trigonal arrangements of atoms and a carbon–hydrogen bond length of 1.09 Å. A difference electron density map phased on the coordinates of the nonhydrogen atoms showed peaks at all expected hydrogen positions. However, these hydrogen positions were not refined. The positional and thermal parameters for the bromine and carbon atoms are presented in Table II. The calculated hydrogen positions are listed in Table III.[26]

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(25) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(26) A list of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society,

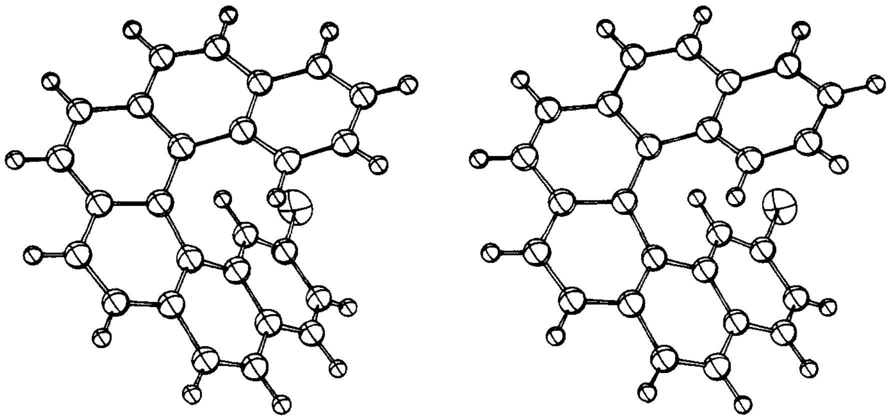

Figure 1. Stereoview of (−)-2-bromohexahelicene (**2a**) as drawn by ORTEP (C. K. Johnson, ORNL).

Determination of Absolute Configuration of (−)-2-Bromohexahelicene. Bijvoet's method[27] was used to determine the absolute configuration of the molecule. Bromine scatters Mo Kα and Cu Kα radiation anomalously. With Mo Kα, $\Delta f' = -0.3$ and $\Delta f'' = +2.5$. With Cu Kα, $\Delta f = -0.9$ and $\Delta f'' = +1.5$.[25] On the basis of the refined structure, structure factor calculations were made for a large number of Friedel pairs and examined according to the criteria: (1) I_{hkl} should be large enough for a statistically significant measurement; and (2) $|I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}|$ should be significantly large relative to I_{hkl}. Fifteen such pairs (Bijvoet pairs) were selected. For each pair the eight related reflections, hkl, $\bar{h}kl$, $h\bar{k}l$, $hk\bar{l}$, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$, $h\bar{k}\bar{l}$, and $\bar{h}\bar{k}\bar{l}$, were measured with Cu Kα radiation and a crystal slightly smaller than that used in the structure determination (0.3 mm long, 0.03 mm in diameter). A structure factor calculation with these data, and the assumption of a left-handed helical molecule, gives an R index of 0.027. The assumption of a right-handed molecule, on the other hand, gives an R index of 0.084. In addition, the intensities for four of the pairs were measured with Mo Kα radiation on a Syntex four-circle automated diffractometer, with completely consistent results. The calculated and observed structure factors (suitably averaged) are given in Table IV. A stereoview of the absolute configuration of (−)-2-bromohexahelicene (**2a**) is provided in Figure 1.

Table III. Calculated Hydrogen Positions ($\times 10^3$) for (−)-2-Bromohexahelicene[a]

Name[b]	x	y	z
H(1)	243	287	307
H(3)	042	207	603
H(4)	202	274	865
H(5)	201	378	1007
H(6)	316	485	980
H(7)	419	553	815
H(8)	484	500	538
H(9)	506	533	242
H(10)	478	421	−8
H(11)	427	260	−114
H(12)	362	102	−748
H(13)	329	−34	132
H(14)	304	−97	430
H(15)	334	−22	676
H(16)	361	197	624

[a] Assumed C–H bond length = 1.09 Å. [b] Hydrogen atoms bear the same number as the carbon atoms to which they are bound.

Table IV. Bijovet Pair Data for (−)-2-Bromohexahelicene[a]

h	k	l	$F_o(hkl)$	$F_c(hkl)$	$F_o(\bar{h}\bar{k}\bar{l})$	$F_c(\bar{h}\bar{k}\bar{l})$
2	1	1	504	487	529	523
*2	1	1	513	468	589	529
4	1	3	125	126	140	146
14	1	2	254	259	246	239
1	2	1	364	367	389	394
5	2	1	216	219	273	279
*5	2	1	217	242	325	326
3	3	1	430	431	390	384
1	5	2	270	279	295	306
*1	5	2	256	266	316	316
7	5	2	403	412	440	448
*7	5	2	402	435	469	489
6	2	1	210	214	193	193
10	2	1	335	356	313	328
1	3	3	268	254	245	240
3	3	5	205	192	212	207
4	3	5	146	143	150	157
4	4	1	542	565	566	599
2	6	1	413	396	439	423
2	8	4	105	115	124	132

[a] Asterisks indicate Mo Kα data; data are with Cu Kα otherwise. Values given ($\times 10$).

Aspects of Molecular Geometry. The average estimated standard deviation for the carbon positions, derived from the diagonal terms in the least-squares matrix, is 0.010 Å; that for the bromine position is 0.001 Å. The expected esd for C–C bond lengths is thus 0.014 Å, and that for bond angles is 0.8°. The observed average C–C bond length is 1.41 Å, with an root-mean-square deviation of 0.04 Å. The average bond angle is 119.8° with an rms average deviation of 0.7°. The distortion from planarity in the molecule leads to the expectation of a decrease in double bond character and thus longer bonds. An examination of individual bond lengths (Table V) reveals that the six bonds bordering the "inner core" of the helix (Figure 2) are all longer than the average. This is the region most subject to distortion.

The best least-squares planes were calculated for each ring. The results (Table VI) indicate that while the

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[27] J. M. Bijvoet, A. F. Peerdeman, and A. J. Van Bommel, *Nature (London)*, **168**, 271 (1951).

Table V. Bond Lengths (Å) and Angles (Deg)[a]

Br–C(2)	1.89	C(18)–C(13)	1.42	C(19)–C(21)–C(22)	116
C(1)–C(2)	1.35	C(13)–C(14)	1.40	C(21)–C(22)–C(9)	122
C(2)–C(3)	1.43	C(14)–C(15)	1.43	C(22)–C(9)–C(10)	120
C(3)–C(4)	1.36	C(15)–C(16)	1.36	C(9)–C(10)–C(20)	119
C(4)–C(26)	1.42	C(16)–C(17)	1.43	C(20)–C(19)–C(21)	117
C(26)–C(25)	1.43	Br–C(2)–C(1)	119	C(10)–C(20)–C(19)	122
C(25)–C(1)	1.45	Br–C(3)–C(3)	117	C(10)–C(20)–C(11)	121
C(26)–C(5)	1.44	C(1)–C(2)–C(3)	125	C(18)–C(17)–C(19)	120
C(5)–C(6)	1.37	C(2)–C(3)–C(4)	117	C(17)–C(19)–C(20)	118
C(6)–C(24)	1.44	C(3)–C(4)–C(26)	122	C(19)–C(20)–C(11)	118
C(24)–C(23)	1.39	C(26)–C(25)–C(1)	119	C(20)–C(11)–C(12)	124
C(23)–C(25)	1.48	C(25)–C(1)–C(2)	118	C(11)–C(12)–C(18)	118
C(24)–C(7)	1.40	C(4)–C(26)–C(5)	120	C(12)–C(18)–C(17)	120
C(7)–C(8)	1.37	C(26)–C(5)–C(6)	120	C(12)–C(18)–C(13)	120
C(8)–C(22)	1.44	C(5)–C(6)–C(24)	121	C(14)–C(15)–C(16)	112
C(22)–C(21)	1.43	C(6)–C(24)–C(23)	121	C(15)–C(16)–C(17)	121
C(21)–C(23)	1.45	C(24)–C(23)–C(25)	118	C(16)–C(17)–C(18)	118
C(22)–C(9)	1.39	C(23)–C(25)–C(26)	119	C(17)–C(18)–C(13)	120
C(9)–C(10)	1.39	C(25)–C(26)–C(5)	120	C(18)–C(13)–C(14)	122
C(18)–C(17)	1.39	C(6)–C(24)–C(7)	118		
C(10)–C(20)	1.43	C(23)–C(24)–C(7)	120	C(13)–C(14)–C(15)	116
C(20)–C(19)	1.42	C(24)–C(7)–C(8)	120	C(16)–C(17)–C(19)	122
C(19)–C(21)	1.45	C(7)–C(8)–C(22)	121	C(17)–C(19)–C(21)	125
C(20)–C(11)	1.43	C(8)–C(22)–C(21)	119	C(19)–C(21)–C(23)	128
C(11)–C(12)	1.33	C(22)–C(21)–C(23)	116	C(21)–C(23)–C(25)	122
C(12)–C(18)	1.46	C(21)–C(23)–C(24)	120	C(23)–C(25)–C(1)	122
C(17)–C(19)	1.45	C(8)–C(22)–C(9)	119		

[a] Average esd for C–C bonds = 0.014 Å. Average esd for angles = 0.8°.

Table VI. Least-Squares Planes[a] for Aromatic Rings of (–)-2-Bromohexahelicene

Ring	Average rms dev, Å	Maximum dev, Å	Direction cosines along crystallographic axes of normal to best plane		
A	0.02	0.03	0.410	−0.886	0.217
B	0.06	0.08	0.500	−0.792	0.350
C	0.08	0.12	0.668	−0.635	0.388
D	0.08	0.12	0.816	−0.457	0.352
E	0.06	0.10	0.926	−0.322	0.198
F	0.02	0.03	0.972	−0.232	0.036

Interplanar angles: A–B 11°, B–C 13°, C–D 14°, D–E 14°, E–F 11°

[a] After V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).

average deviation from the plane is only twice the expected esd in the carbon positions for rings A and F (see **1**), it is six times larger in rings B and E, and eight times larger in rings C and D, indicating that distortion from planarity is significant only for rings B, C, D, and E. The "pitch" of the molecule, indicated in Figure 2 by the torsion angles around the inner core, is seen to be steeper in the region of the C and D rings, with torsion angles of −28 and −27°, respectively. Angles between the normals to successive planes (Table VI) also show that the bending of the helix is greater in the region of rings B, C, D, and E.

Figure 2 indicates the shortest C–H intramolecular distances in the molecule's inner core between the observed carbon positions and calculated hydrogen positions. They are of the order of 2.5 Å, considerably shorter than expected for nonbond van der Waals contacts, and thus are presumably the major factor in opening up the helix, although the C(1)–C(17) and C(16)–C(25) distances are also short, about 3 Å. Important nonbonded interatomic distances in the vicinity of the open end of the helix are shown in Table VII.

Discussion

Hexahelicene Absolute Configuration. The X-ray determined absolute configuration of (−)-2-bromohexahelicene is shown in **2a** or Figure 1. The absolute stereochemistry of hexahelicene was determined by converting (−)-2-bromohexahelicene to hexahelicene in the following manner. Partially resolved (−)-2-bromohexahelicene, $[\alpha]_{589}$ −444°, $[\alpha]_{546}$ −582° (*c* 0.076, chloroform), was converted by treatment with *n*-butyllithium in ether followed by water in 97% yield to hexahelicene which was not crystallized (to purify). The rotation of the total crude hexahelicene was $[\alpha]_{589}$ −420°, $[\alpha]_{546}$ −547° (*c* 0.05, chloroform). A mass spectrum indicated that the crude (−)-hexahelicene had a slight impurity of 2-*n*-butylhexahelicene; how-

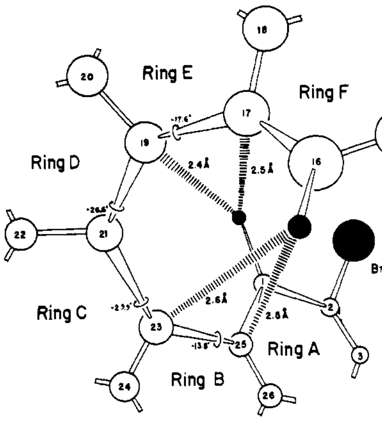

Figure 2. Some interatomic distances and torsion angles in (−)-2-bromohexahelicene (**2a**). Distances between calculated hydrogen positions and carbons in the inner core of the 2-bromohexahelicene molecule. Torsion angles about the inner core carbon–carbon bonds shown in degrees. Bromine atom and hydrogens on carbons 1 and 16 shown as solid black circles.

Table VII. Short Intramolecular Nonbonded Carbon–Carbon Contacts in 2-Bromohexahelicene

Atoms	Distance, Å	Atoms	Distance, Å
1–17	2.98	19–25	3.19
1–21	3.04	17–23	3.21
21–16	3.06	17–25	3.29
16–25	3.06	2–15	4.35
1–19	3.08	2–16	3.94
1–16	3.14	1–15	3.91
16–23	3.14		

ever, rotations of the (−)-hexahelicene so derived may be compared to those of resolved[5] (−)-hexahelicene, $[\alpha]_{589}$ −3640° and $[\alpha]_{546}$ −4820° (chloroform), and our resolved (−)-2-bromohexahelicene, $[\alpha]_{589}$ −3560° and $[\alpha]_{546}$ −4690° (*c* 0.066, chloroform). The conversion of (−)-bromohexahelicene (**2a**) to (−)-hexahelicene thus establishes that *(−)-hexahelicene must also have a left-handed helical configuration* (**1a**) *since the X-ray determined stereochemistry of (−)-2-bromohexahelicene* (**2a**) *requires left-handed helicity.*

Theory and Absolute Configuration. The absolute configuration of hexahelicene has been treated theoretically by a number of authors.[9–13] Thus, the Fitts and Kirkwood[9] model of pairwise interactions of benzene rings and, later, Tinoco and Woody's[11] free-electron treatment of a helix model and Brewster's[12] classical treatment led to the prediction that (+)-hexahelicene should have a right-handed chirality. Alternatively, Moscowitz's[10] use of unperturbed one-electron wave functions derived from simple Hückel molecular orbital theory predicted that (+)-hexahelicene would correspond to a left-handed helix. An adequate discussion of these theoretical approaches may be found in the work of Groen and Wynberg.[16] These authors utilize the Moscowitz approach in their treatment of sulfur heterohelicenes for which they conclude that the (+) enantiomer possesses a right-handed chirality. Very recently, Mason, *et al.*,[13] have applied the Moscowitz theoretical treatment of hexahelicene using π-electron self-consistent field (SCF) wave functions and performing a more complete configuration interaction (CI). Their calculations, in contradiction to the results of Moscowitz,[10] dictate a right-handed helix for (+)-hexahelicene. The reason[28] for this discrepancy in what is essentially the same type of calculation is not lodged in the nature of the calculated molecular orbital wave functions but rather in the configuration interaction performed on them. Thus, in his original π-electron calculations, Moscowitz performed a configuration interaction on selected molecular orbitals of the same symmetry. However, in the large π system of hexahelicene, the density of upper π states is so great that the number of states of the same symmetry is much larger than was originally foreseen,[10] and these mix in and lead to a long wavelength Cotton effect with sign opposite to that which was originally predicted.[10] Consequently, Mason's[13] π–π^* SCF–CI calculation, which included 30 lowest singlets and a complete CI, correctly predicts the Cotton effect sign (+ for a right-handed helix) and Moscowitz's[10] calculation did not, as it estimated the CI arising only from the degeneracies occurring in an alternant π system. It is well to note here, however, that the disproportionately large bending in the vicinity of the lower half of the molecule (atom 21 in the C and D rings of Figure 2) points to an impending breakdown of the σ–π separability condition in π-electron calculations and suggests therefore that more complete molecular orbital treatments should take into account an additional mixing in the σ–π^* and π–σ^* configurations.

Experimental Section[29]

2-Naphthoyl Chloride. To 188 g (1.09 mol) of 2-naphthoic acid in a 500-ml, round-bottomed flask, equipped with reflux condenser and magnetic stirrer, was added 166 g (1.40 mol, 100 ml) of thionyl chloride. The flask was heated with a water bath and stirred magnetically for 1.5 hr (or until hydrogen chloride evolution had ceased). The excess thionyl chloride was then removed by distillation, and the product was vacuum distilled. The acid chloride obtained (186.4 g, 0.976 mol) in 89% yield had bp 115–117° (1 mm) and mp 51–52°.

2-Naphthaldehyde (3). (a) **The Preparation of Lithium Tri-*tert*-butoxyaluminohydride.**[30] Lithium aluminum hydride (21.1 g of the commercially obtained gray solid, Alfa Inorganics, Ventron) was placed in a Soxhlet thimble (tare 5.9 g) and extracted with 1000 ml of anhydrous ether (dried by distillation from lithium aluminum hydride) for about 10 hr using a 3-l. three-necked, round-bottomed flask as reservoir. After extraction the thimble was withdrawn, placed in a vacuum dessicator, and pumped on until dry. The thimble contained 3.0 g of insoluble residue, and it was assumed therefore that the clear ether solution contained 18.1 g (0.478 mol) of lithium aluminum hydride. The flask containing the ethereal solution of the purified hydride was fitted with a reflux condenser, mechanical stirrer, and dropping funnel. Anhydrous *tert*-butyl alcohol (105.5 g, 1.42 mol) in 500 ml of anhydrous ether was dropped into the stirred hydride solution at a rate sufficient to maintain a gentle reflux. During the addition of the last one-third of the alcohol a white precipitate formed. When all of the alcohol had been added, the reaction mixture was stirred for an additional 0.5 hr. Then all of the ether was removed by passing a stream of dry nitrogen through the flask while simultaneously stirring and heating gently with a steam bath. After removal of all of the ether, enough anhydrous diglyme (dried by distillation from lithium aluminum hydride) was added to the white product to make 500 ml of solution.

(b) **Reduction of Naphthoyl Chloride.** 2-Naphthoyl chloride (89.0 g, 0.467 mol) was dissolved in 500 ml of anhydrous diglyme and placed in a 2000-ml, three-necked round-bottomed flask, equipped with mechanical stirrer, low-temperature thermometer, dropping funnel, and a Dry ice–2-propanol cooling bath. With the reaction mixture under a nitrogen atmosphere, the solution of lithium tri-*tert*-butoxyaluminohydride in diglyme (produced above) was added dropwise over 3 hr with vigorous stirring. The temperature of the reaction mixture was maintained at about −71° throughout. After the addition of the hydride was complete, the reaction mixture was stirred for an additional 2 hr, after which time it was slowly brought to room temperature. The reaction was worked up by carefully adding 500 ml of cold, aqueous 5% hydrochloric acid and stirring well. Then 400 ml of ether was added and the mixture was shaken in a separatory funnel. The layers were separated and the aqueous layer was further extracted with ether (200 ml). The organic extracts were combined, washed with water (5 × 250 ml), dried over anhydrous magnesium sulfate, and concentrated to about 100 ml. The aldehyde was vacuum distilled through a 6 in. Vigreux column (bp 107–110° at 0.2 mm) to give 40.2 g (0.258 mol) of aldehyde, mp 58–59° (lit.[31] mp 59–60°). The yield was 55%.

***p*-Xylyltriphenylphosphonium Bromide.** Using Geerts and Martin's procedure,[32] a solution of 63.0 g (0.340 mol) of α-bromo-*p*-

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(28) A. Moscowitz, personal communication.

(29) All analytical gas chromatography was done on a Varian Model 1200 instrument with a 5 ft × $^1/_8$ in. column (5% SE 30 on Chromosorb W DMCS). Nmr spectra were determined on a Varian T-60 instrument; mass spectra were run on an AEI MS-9 spectrometer by Miss Elizabeth Irwin. Microanalyses were performed by Miss Heather King. All melting points are uncorrected and were taken on a Mel-Temp heating block.

(30) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **80**, 5377 (1958).

(31) E. B. Hershberg and J. Cason, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 627.

(32) J. P. Geerts and R. H. Martin, *Bull. Soc. Chim. Belg.*, **69**, 563 (1960).

xylene and 90.0 g (0.340 mol) of triphenylphosphine in 800 ml of xylene was refluxed and stirred mechanically for 1 hr. The white precipitate which formed was collected on a Büchner funnel and dried in a vacuum oven. This gave 139.5 g (0.315 mol, 92%) of phosphonium bromide salt, mp 269–273°.

1-(2-Naphthyl)-2-(*p*-tolyl)ethylene (4). According to the procedure of Carruthers,[33] *p*-xylyltriphenylphosphonium bromide (76.0 g, 0.170 mol) was placed in a 1000-ml three-necked, round-bottomed flask, equipped with mechanical stirrer and reflux condenser and kept under a nitrogen atmosphere, along with 500 ml of anhydrous ether. To the stirred suspension was added 0.170 mol of *n*-butyllithium (1.6 *N* solution in hexane, 106 ml added). The reaction mixture turned deep red, then red-orange. The mixture was stirred well for 2 hr, at the end of which time 25.0 g (0.160 mol) of 2-naphthaldehyde in 250 ml of anhydrous ether was added dropwise at a rate sufficient to maintain a gentle reflux. After the addition was complete, the reaction mixture was stirred for an additional 1.5 hr and then filtered. The ethereal filtrate obtained, which contained cis olefin but only a small amount of trans olefin, was evaporated and the resulting oily mixture purified by column chromatography (Merck activity III alumina, chloroform:hexane 2:1). The white, solid residue obtained in the above filtration, which contained trans olefin, triphenylphosphine oxide, and lithium bromide, was washed several times with a 3:1 mixture of methanol–water, air-dried on a Büchner funnel, and purified by column chromatography on activity III alumina (graded mixtures of chloroform–hexane used as eluent). Both pure cis (mp 47–49°) and pure trans (mp 181–183°) were obtained. The isomer distribution from the reaction was judged to be 40% cis and 60% trans. The total amount of olefin (cis and trans) obtained was 35.2 g (0.144 mol, 90%).

2-Methylbenzo[*c*]phenanthrene[22] (5a). A solution of 2.0 g (0.0082 mol) of a mixture of cis and trans olefin (**4**) in 600 ml of benzene was irradiated according to the method of Wood and Mallory[34] for 1.25 hr through Pyrex in the presence of 0.1 g of iodine using a Hanovia 550-W medium-pressure mercury vapor lamp. At the end of the irradiation period no cis olefin could be observed by glc (5% SE-30, column temperature 240°), and the reaction was judged to be complete. The benzene solution was washed with 0.1 *M* aqueous sodium thiosulfate (100 ml) and dried over anhydrous magnesium sulfate. The solvent was removed using a rotatory evaporator leaving a yellow oil. This procedure was repeated 34 times, and the combined crude product was purified by column chromatography on activity II alumina (ligroin used as eluate). (It was subsequently discovered that the chromatography may also be performed on silica gel with pentane as eluate.) The product obtained from the chromatography was recrystallized from benzene–ethanol to yield 55.7 g (0.230 mol, 82%) of pure white crystals, mp 79–80°.

α-Bromo-2-methylbenzo[*c*]phenanthrene (5b). A mixture of 25.0 g (0.103 mol) of **5a**, 16.0 g (0.090 mol) of *N*-bromosuccinimide, and 100 ml of carbon tetrachloride was heated at reflux and stirred for 8 hr. At the end of this time the reaction mixture was cooled and the succinimide produced removed by filtration. The filtrate was washed with 0.1 *M* aqueous sodium thiosulfate (100 ml) and dried over anhydrous magnesium sulfate; the solvent was removed using a rotatory evaporator. The residue was purified by column chromatography on silica gel (benzene eluate) and recrystallized from hexane to give 22.8 g (0.071 mol) of **5b**, mp 96–98°. The yield was 69%, based on starting hydrocarbon.

2-Benzo[*c*]phenanthrylmethyltriphenylphosphonium Bromide (5c). A solution of 20.0 g (0.0623 mol) of **5b** and 16.3 g (0.0623 mol) of triphenylphosphine in 150 ml of xylene was refluxed and stirred for 1 hr. The white precipitate which formed was collected on a Büchner funnel and dried in a vacuum oven. The yield was 34.3 g (0.0586 mol, 94%) of product, mp 308° dec. A small sample was recrystallized several times from ethanol–ether to yield pure crystals, mp 314° dec.

1-(*p*-Bromophenyl)-2-(2-benzo[*c*]phenanthrenyl)ethylene (6). To a stirred solution of 25.0 g (0.0428 mol) of **5c** and 8.1 g (0.0438 mol) of *p*-bromobenzaldehyde in 500 ml of absolute methanol was added 175 ml of 0.25 *M* lithium methoxide in methanol (0.0437 mol of lithium methoxide added). Almost immediately after the addition of the base to the reaction mixture, the contents became cloudy as product began to crystallize from solution. The reaction was stirred for 1 hr, after which time about 167 ml of water was added. The resulting solution was stirred well and filtered. The yellow solid residue was purified by column chromatography on activity III alumina using carbon tetrachloride as eluate. Evaporation of the solvent gave 12.8 g (0.0313 mol) of olefin **6**. The yield was 73%. A small sample of the columned product was recrystallized from benzene–hexane (1:3) to give pale yellow needles, mp 161°.

(±)-2-Bromohexahelicene (2a,b). A solution of 1.0 g (0.00244 mol) of a mixture of cis and trans olefin **5** in 600 ml of benzene was irradiated for 1 hr through Pyrex in the presence of iodine (0.1 g) using a Hanovia 550-W medium-pressure mercury vapor lamp. After the irradiation the benzene solution was washed with 100 ml of 0.1 *M* aqueous sodium thiosulfate and then dried over anhydrous magnesium sulfate. The solvent was removed with a rotatory evaporator to leave a yellow solid. This procedure was repeated ten times, and the combined crude product was purified by column chromatography on activity III alumina (graded mixtures of benzene–hexane used as eluate). Finally, this material was recrystallized from benzene–ethanol to yield 8.1 g (0.0199 mol, 82%) of yellow crystals, mp 245–247°.

Anal. Calcd for $C_{26}H_{15}Br$: C, 76.67; H, 3.71. Found: C, 76.85; H, 3.79.

Resolution of 2-Bromohexahelicene. The resolution of 2-bromohexahelicene was accomplished by employing Newman's reagent in a manner analogous to the procedure used for the resolution of hexahelicene.[5,6] Newman's reagent was prepared and resolved according to the reported procedure[23] to give (−)-TAPA ((−)-α-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid), mp 113–125°, $[\alpha]^{25}_{589}$ −105° (*c* 1.05, chloroform) [lit.[23] $[\alpha]^{25}_{589}$ −97°]. A mixture of 1.0 g (2.45 mmol) of 2-bromohexahelicene and 1.1 g (2.46 mmol) of (−)-TAPA is dissolved by warming in 16 ml of benzene plus 4 ml of ethanol to form a clear, dark red solution. This solution was allowed to crystallize slowly at room temperature until 200 mg of yellow crystals was deposited. The 200 mg of partially resolved 2-bromohexahelicene was separated by pipetting off the mother liquors, and 0.63 g of (−)-TAPA was added along with 8 ml of benzene and 2 ml of ethanol. After dissolving and recrystallizing this mixture, 18 mg of crystals, $[\alpha]^{25}_{589}$ −1317° (*c* 0.052, chloroform), were deposited which were recrystallized twice from benzene to give 7.4 mg of yellow rods, $[\alpha]^{25}_{589}$ −3550°, $[\alpha]_{546}$ −4670°. One further recrystallization from benzene gave 3.31 mg of crystals which were taken to be optically pure and which gave a single crystal, mp 268–268.5°, and the following spectral data: $[\alpha]^{25}_{589}$ −3560°, $[\alpha]^{25}_{578}$ −3790°, $[\alpha]^{25}_{546}$ −4690°, $[\alpha]^{25}_{436}$ −14,000° (*c* 0.066, chloroform).

(−)-Hexahelicene (1a) from (−)-2-Bromohexahelicene (2a). To a solution of 37 mg of (−)-2-bromohexahelicene ($[\alpha]_{589}$ −444°, $[\alpha]_{546}$ −582°) and 30 ml of dry ether under nitrogen there was added 1 ml of *n*-butyllithium in hexane (~1.6 *M*). Immediately a green color developed and the stirring was continued for 25 min at 25°. At this point water was added and the solution became colorless. The ethereal layer was washed with water, dried over $MgSO_4$, and evaporated to dryness to yield 29 mg (97% crude yield), mp 207–208°, $[\alpha]^{25}_{589}$ −420°, $[\alpha]^{25}_{578}$ −444°, $[\alpha]^{25}_{546}$ −547°, $[\alpha]^{25}_{436}$ +1600°. A mass spectrum at 70 eV of the product exhibited an *m*/*e* fragment of 328 as the most predominant fragment plus two minor impurities at *m*/*e* 384 (butylhexahelicene) and 412. The pertinent reported data for resolved (−)-hexahelicene itself are $[\alpha]^{24}_{D}$ −3640°, $[\alpha]^{24}_{546}$ −4820° (*c* 0.098, chloroform), mp 265–267° (racemic mp 231–233°).[5]

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(34) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).