

New Functional Hexahelicenes – Synthesis, Chiroptical Properties, X-ray Crystal Structures, and Comparative Data Bank Analysis of Hexahelicenes

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Seven new hexahelicenes (**3–7**, **9**, **10**) containing different functional group substituents have been synthesized and, in three cases (**4**, **8**, **10**), optically resolved. Optical rotations were measured and CD spectra are reported. X-ray crystal structures of the helicenes **1**, **3**, **4**, **8**, and **9** have been determined, of which **4** represents a 1:1 clathrate with acetone. These show a concerted interplay of C–H $\cdots$ O, C–H $\cdots$ π , and $\pi\cdots\pi$ supramolecular interactions in the packings, mostly

yielding stacks of molecules (**1**, **3**, **4**, **8**). Statistical analysis of the molecular dimensions in these and related crystal structures was carried out in order to identify potential parameters relevant to macroscopic phenomena, including optical rotation.

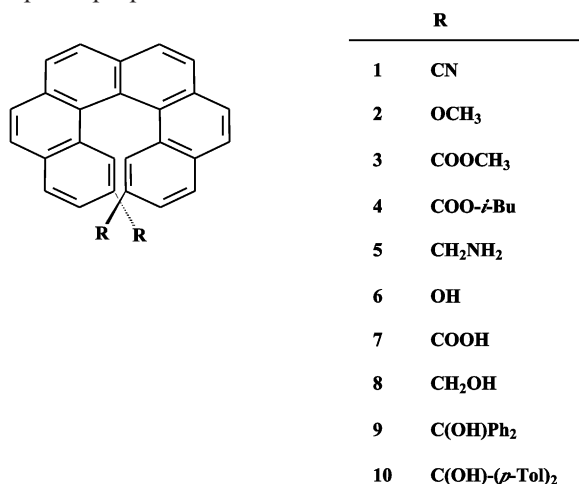
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Introduction

Since the pioneering paper on hexahelicene in 1956,^[1] both the carbo-^[2] and the heterohelicenes,^[3] in which a regular cylindrical helix is formed through an all-*ortho* annelation of aromatic or heteroaromatic rings, have continued to be an attractive class of compounds.^[4] This arises from their specific structural features, involving particular stereochemical and chiroptical properties.^[5] In exploitation of this, helicene backbones have been used to design chiral crown compounds,^[6] molecular recognizing clefts,^[7] and clathrates.^[8] The first chiral phosphane ligands based on the helicene moiety have recently been synthesized,^[9] and have proved successful in enantioselective transition metal catalysis.^[10] The helicene structural element has also attracted some attention in the topical field of crystal engineering,^[11] including helicene alignment in the honeycomb sheets of trimesic acid.^[12] Nevertheless, helicenes (carbohelicenes in particular) bearing functional groups suitable to act as starting points for further structural modification are rare, due to the synthetic efforts required, including separation of the enantiomers.

In a previous work^[13] we demonstrated the use of the time-dependent density functional theory (TDDFT) for investigation of molecular electronic circular dichroism

(CD) of helicenes, using two new functional helicenes (**1**, **2**). Here we report on the synthesis of a further eight functional hexahelicenes **3–10** (Scheme 1), of which seven are new compounds, including successful optical resolution in three (**4**, **8**, **10**) and X-ray crystal structures in five cases (**1**, **3**, **4**, **8**, **9**). The helicene **8** is a known compound,^[6] but was obtained here by a different approach. These new structures encouraged a statistical analysis of the molecular dimensions in these and related crystal structures in order to identify potential parameters that might be relevant to the optical properties.



Scheme 1. Hexahelicenes studied

Synthesis

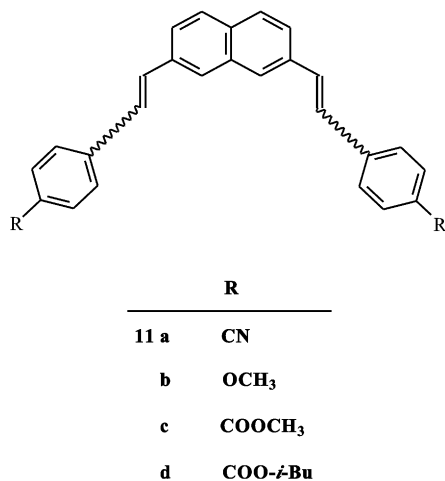
The syntheses of the substituted hexahelicenes **1–4** were accomplished in reasonable yields (14–63%) by use of es-

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established procedures for hexahelicene formation.^[9,10,14] The preparation started from naphthalene-2,7-bis(triphenylphosphonium) dibromide^[9,10,15] and the appropriate benzaldehyde by double Wittig reaction^[16] to give the corresponding distilbenes **11a–d** (Scheme 2), which were subjected a double photocyclodehydrogenation^[17] in diluted solutions (10^{-3} mol·L⁻¹, or suspensions in cases of **11b** and **11c**) in toluene in the presence of iodine as oxidizing agent. The relatively moderate yields of 30 and 14% for **2** and **3**, respectively, are perhaps a consequence of the unfavorable solubility properties of **11b** and **11c** in toluene, necessitating their use as suspensions. The more lipophilic bis(isobutyl ester) **4** was a favorable substitute for **3**, however, and so is used below. As usual,^[9,10] the double Wittig reaction produced distilbenes **11 (a–d)** as mixtures of (*E*) and (*Z*) isomers. This was of no concern, though, since irradiation gives rise to rapid interconversion of the *Z* and *E* isomers.^[18] Nevertheless, we were able to isolate pure (*Z,Z*) isomers on recrystallization of **11b** and **11d** either from methanol or from toluene.



Scheme 2. Distilbene starting compounds

The hexahelicenes **5–10** were synthesized from **1**, **2**, and **4** by modification of their functional groups. More precisely, the diamine **5** was obtained from dinitrile **1** by standard LiAlH₄ reduction,^[19] and the diphenol **6** by ether cleavage of **2** with boron tribromide.^[20] From diester **4**, basic hydrolysis^[21] yielded dicarboxylic acid **7**, LiAlH₄ reduction^[19] the dialcohol **8**, and addition of the respective aryllithium agents^[22] produced the bis-tertiary alcohols **9** and **10**.

Optical Resolution

Although optical resolution of helical compounds, including helicenes, by HPLC on derivatives of cellulose as chiral stationary phases has proved successful,^[10,23] the limitations of solvents for non-destruction elution of the column is a problem.^[24] It also turned out to be a problem here, because of the unfavorable solubility characteristics of these helicenes. The cellulose tris(3,5-dimethylphenylcarba-

Table 1. Specific $[\alpha]$ and molecular $[M]$ rotations of the helicenes in chloroform

Helicene	$[\alpha]_{589}^{20}$	M	c [g/100 mL ⁻¹]
1	3440 ± 400	13027	0.003
2	3271.7 ± 7	12709	0.06
4	3660 ± 100	19348	0.03
8	2672.8 ± 3	10383	0.1
10	1851.1 ± 100	13864	0.03
Hexahelicene ^[1]	$3640 \pm 10^{[a]}$	11950	0.098

[a] $[\alpha]_D^{24}$.

mate) column used for reasons of stability has been reported as being compatible only with solvents such as methanol, 2-propanol, or *n*-hexane.^[24] However, by systematic variation of the solvent composition, we were able to perform optical base-line separation of the helicenes **1**, **2**, **4**, **8**, and **10**, of which **1** and **2** have been reported elsewhere, together with their chiroptical data.^[13]

The optical rotations, including those for **1** and **2**, are summarized in Table 1. The molar rotations (M) vary between 10383, measured for the dialcohol **8**, and 19348, for the bis(isobutyl ester) **4**, indicating influences of the substituents. For comparison, the unsubstituted hexahelicene has a molar rotation of 11950,^[1] which is exceeded by the new helicenes, except in the case of **8**.

The CD spectra of these helicenes were also measured (Figure 1) and indicated that complete optical resolution had occurred, which makes assignment of the absolute configurations possible.^[13,25,26] Figure 1 (top) shows the dichrogram of the bis(hydroxymethyl)-substituted helicene **8**, which is characterized by two intensive bands (around $\lambda = 250$ and 330 nm) of opposite sign, demonstrating no significant change relative to the CD of unsubstituted hexahelicene.^[27] Similar behavior is seen for **10** [Figure 1 (middle)], which is rather unexpected because of the presence of the two bulky bis(4-methylphenyl)hydroxymethyl substituents. Obviously, these substituents do not involve conformational changes effective on dichroism.

On the other hand, the dichrogram of the helicene diester **4** [Figure 1 (bottom)] shows a characteristic change from those of unsubstituted hexahelicene or **8** and **10**. This change involves a splitting of the original single band around $\lambda = 250$ nm into two bands near $\lambda = 240$ and 260 nm, which are also found for the dicyano- and the dimethoxy-substituted helicenes **1** and **2**.^[13] It appears probable that electronic influences of π and lone-pair electrons of the particular functional groups, being conjugated to the helicene framework, are producing an effect here while the non-conjugated substituents in **8** and **10** are ineffective.

X-ray Structural Studies

Crystallographic data for **1**, **3**, **4**:acetone (1:1), **8**, and **9** are given in Table 2. Structural features, including those for hexahelicene, are summarized in Table 3.

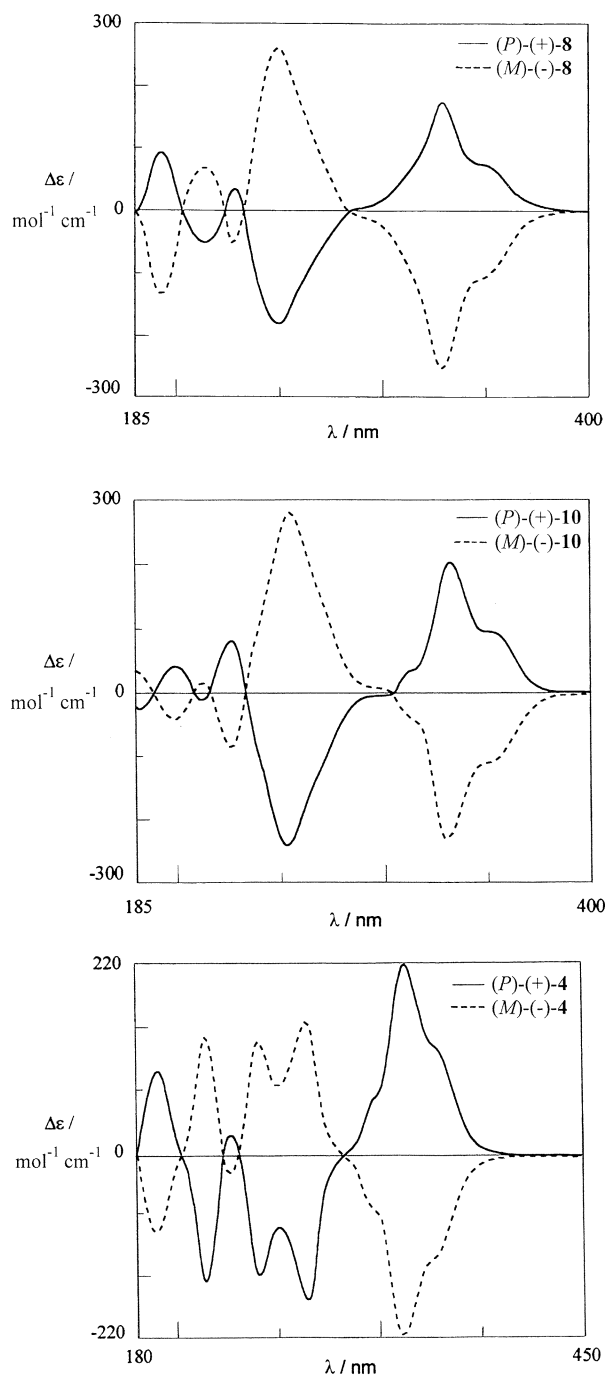


Figure 1. Experimental CD spectra of helicene **8** (top), **10** (middle), and **4** (bottom) in *n*-hexane

Crystallization of the dinitrile helicene derivative **1** (Figure 2) from benzene gave orange-red crystals. The hexagonal space group $P6_122$ indicates that spontaneous resolution had occurred.^[28] The inner pitch elevation (d_1 , C1...C16 distance) is 3.08 Å. The torsion angles at the inner helical rim are also a convenient measure of the helicity. Those over the penultimate bonds 1 and 2 [C(1)–C(16e)–C(16d)–C(16c) and C(16c)–C(16b)–C(16a)–C(16)] are 15.7 and 15.1°. The helicene molecules **1** pack in the crystal in stacks of columns, trivially with

the same helicity, running along the crystallographic *c* axis [Figure 3 (a)]. Adjacent molecules within the stacks are interlocked through their aromatic units, which assume face to face orientations with an average distance of 3.75 Å between ring centers. This distance indicates the presence of well-defined intermolecular π - π -interactions.^[29] The functional groups of the helicene form weak C–H...N hydrogen bonds^[30] [Figure 3 (b)], which are slightly different in their bond lengths [H(5')...N(151) = 2.6 Å, C(5')–H(5')...N(152) = 152°; H(13'')...N(22) = 2.8 Å, C(13'')–H(13'')...N(22) = 151°].

The structural similarity to the dinitrile helicene **1** persists in the crystal packing of the diester helicene **3**. This compound did not undergo spontaneous resolution, though its space group is the noncentrosymmetric $Pna2_1$. The inner pitch elevations (d_1 , C1...C16 distance) of the two independent molecules of the asymmetric unit are 3.10 and 3.06 Å, while the torsion angles 1 and 2 are again moderately elevated, at values of 18.8 and 16.0°, and of 13.1 and 11.7°, respectively, for the two independent molecules. The packing illustrates that the helicene molecules also aggregate in stacks, but that the neighboring stacks have opposite chiralities (Figure 4). Consecutive molecules within a stack are rotated around their helical axis, so that strong π ... π -interactions^[29] develop between the terminal aryl groups (d = 3.66–3.67 Å) of the two independent molecules of the asymmetric unit. This molecular arrangement within a stack produces different binding behavior. Only a proportion of the carbonyl oxygen atoms can form weak intermolecular C–H...O^[30] interactions to methyl and aryl hydrogen atoms.

Recrystallization of the diisobutyl ester **4** from acetone yielded a clathrate with acetone of host-guest stoichiometry 1:1. These crystals are racemic (space group $P\bar{1}$). The crystal structure of helicene **4** (Figure 5) shows that the racemic pair of molecules form a centrosymmetric dimer in the cell. A weak C–H...O hydrogen bond^[30] [C(9)–H(9)...O(22), H(9)...O(22) = 2.59 Å], together with a C–H... π ^[31] interaction between the inner aryl groups, of which the shortest distance is 3.38 Å, link the two host molecules into this dimeric-like arrangement. The crystal packing shows a channel structure along the *a* axis, which is partially occupied by guest molecules (Figure 6). Parts of this lattice voids are occupied by the protruding ester groups of the helicene host molecules, so that an alternating arrangement of guests and substituents occurs. This could be the reason why only pairwise stacking develops here, in contrast to the diester **3**. Another reason could be the steric congestion caused by the substituents on the helicene. The inner pitch elevation (d_1 , C1...C16 distance) is 3.11 Å. The torsion angles 1 and 2 over the penultimate bonds are small, at 13.7° in both cases.

Diol **8** has the functional groups with the smallest steric requirements. Figure 7 reveals that each hydroxy group of the helicene is part of an eight-membered cyclic hydrogen bond system^[32] with almost ideal hydrogen bond geometry [O(18)–H(18)...O(20)_[−0.5+*x*, 0.5−*y*, 0.5+*z*], H(18)...O(20) = 1.74 Å, O(18)–H(18)...O(20) = 168°; O(20)–H(20)...

Table 2. Crystal data and details of the structure determination for the compounds studied

Compound	1	3	4	8	9
Formula	C ₂₈ H ₁₄ N ₂	C ₃₀ H ₂₀ O ₄	C ₃₆ H ₃₂ O ₄ ·C ₃ H ₆ O	C ₂₈ H ₂₀ O ₂	C ₅₂ H ₃₆ O ₂
Molecular mass	378.41	444.46	586.69	388.44	692.8
Crystal system	hexagonal	orthorhombic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 6 ₁ 22 (No. 178)	<i>Pna</i> 2 ₁ (No. 33)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)
<i>a</i> (Å)	9.736(1)	20.040(1)	11.119(4)	13.437(3)	12.540(3)
<i>b</i> (Å)	9.736(1)	16.835(1)	11.426(3)	11.197(3)	22.271(3)
<i>c</i> (Å)	70.731(3)	13.140(1)	13.779(4)	14.643(3)	12.901(3)
α [°]	90	90	94.44(2)	90	90
β [°]	90	90	100.90(2)	115.51(2)	94.51(3)
γ [°]	120	90	104.73(2)	90	90
<i>V</i> (Å ³)	5806.3(9)	4433.1(5)	1647.9(9)	1988.3(9)	3591.8(13)
<i>Z</i>	12	8	2	4	4
<i>D</i> _(calcd.) [g·cm ⁻³]	1.299	1.332	1.182	1.298	1.281
μ [mm ⁻¹]	0.59 (Cu- <i>K</i> α)	0.71 (Cu- <i>K</i> α)	0.08 (Mo- <i>K</i> α)	0.63 (Cu- <i>K</i> α)	0.59 (Cu- <i>K</i> α)
Crystal size [mm]	0.20 × 0.20 × 0.40	0.20 × 0.45 × 0.50	0.20 × 0.3 × 0.5	0.30 × 0.35 × 0.35	0.20 × 0.20 × 0.25
<i>T</i> [K]	298	296	298	298	298
Radiation [Å]	1.5418 (Cu- <i>K</i> α)	1.5418 (Cu- <i>K</i> α)	0.71073 (Mo- <i>K</i> α)	1.5418 (Cu- <i>K</i> α)	1.5418 (Cu- <i>K</i> α)
Total/uniq. data, <i>R</i> _(int)	15515/3989, 0.077	6423/5990, 0.035	5294/4612, 0.080	4260/4086, 0.015	8191/6888, 0.029
Observed data	3053	5143	2338	3417	4436
[<i>I</i> > 2.0 σ (<i>I</i>)]					
<i>N</i> _{ref} , <i>N</i> _{par}	3682, 274	5985, 614	4612, 379	4086, 274	6887, 495
<i>R</i> , <i>wR</i> ² , <i>S</i>	0.0411, 0.1186, 1.06	0.0384, 0.1053, 1.05	0.0842, 0.2686, 0.93	0.0436, 0.1333, 1.05	0.0528, 0.1416, 1.12
Min./max. resd. dens.	−0.12/0.14	−0.13/0.15	−0.22/0.70	−0.17/0.16	−0.18/0.18
[e·Å ⁻³]					

Table 3. Structural features (selected conformations and non-bonding distances of terminal ring atoms) of the helicenes studied, including hexahelicene

Compound	Torsion angle, [°] ^[a,b]				Distance [Å] ^[c]		
	φ 1	φ 2	φ 3	φ 4	<i>d</i> 1	<i>d</i> 2	<i>d</i> 3
1	15.7	15.1	28.1	24.9	3.08	4.21	5.25
3	18.8	16.0	28.8	25.0	3.10	4.20	5.00
	13.1	11.7	27.8	27.8	3.06	4.31	5.00
4	13.7	13.7	26.4	26.4	3.11	4.36	5.44
8	13.4	15.1	22.9	27.6	2.94	3.85	4.89
9	13.0	17.6	25.8	29.7	3.13	4.32	5.44
Hexahelicene	11.3	30.0	30.0	15.2	3.22	4.58	5.63

^[a] Standard deviations are typically 0.3–0.5 ° for the torsion angles (φ) and less than 0.01 Å for the interatomic distances (*d*).

^[b] φ 1 = C(1)–C(16e)–C(16d)–C(16c); φ 2 = C(16)–C(16a)–C(16b)–C(16c); φ 3 = C(16e)–C(16d)–C(16b); φ 4 = C(16a)–C(16b)–C(16c)–C(16d). ^[c] *d*1 = C(1)···C(16); *d*2 = C(2)···C(15); *d*3 = C(3)···C(14).

O(18)_[0.5–x, –0.5+y, 0.5–z], H(20)···O(18) = 1.87 Å, O(20)–H(20)···O(18) = 176°. Accordingly, nets of hydrogen bonds link molecules intimately together. The rigid helicene skeleton and the H-bridge requirements cause both –CH₂OH groups to adopt anticlinical conformations (C–C–O–H torsion angles are –78.0 and –88.2°). The infinite two-dimensional network is characterized by base vectors {1 0 1}, 2: {0 1 0} and in plane: {1 0 –1} so that directed four-membered (O–H···O–H···) rings are formed. The inner pitch elevation (*d*1, C1···C16 distance) is the shortest here, with the value of 2.94 Å. The values of the torsion angles 1 and 2 of the inner helix bonds are again relatively small, at 13.4 and 15.1°. In contrast to the pre-

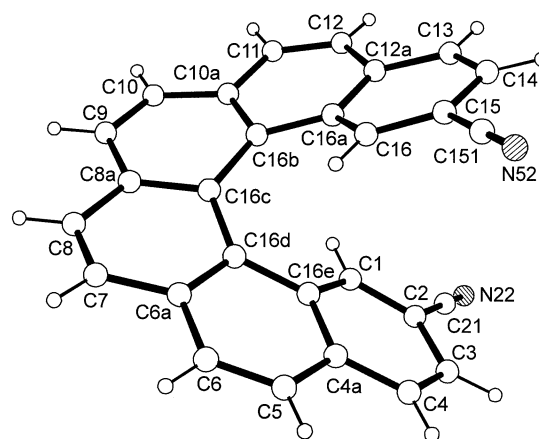


Figure 2. Molecular structure and numbering scheme of helicene 1

vious structures, molecules of opposite configuration are arranged in stacks in which their aryl units assume an edge to face relationship^[33] with C–H pointing into the center of an aromatic ring at an intermolecular distance of 3.0 Å.

In the crowded diol 9, the hydroxy groups are shielded from their external environment (Figure 8). One of the functional groups is visibly turned inward and has its O–H vector directed towards one of the compound's own benzene rings. Analysis of the X–H ring center of gravity distances reveal several weak X–H··· π interactions,^[30] two of which are appreciably shorter than the sum of the C–H van der Waals radii ($\approx$ 2.9–3.0 Å). The strongest of these is the above O–H··· π interaction,^[34] which directs the O–H bond such that it points into the center of the terminal aryl ring of the helicene framework at a distance of 2.71 Å [O(15)–H(15) Cg(1), *d* = 2.71 Å, 171°]. Another short

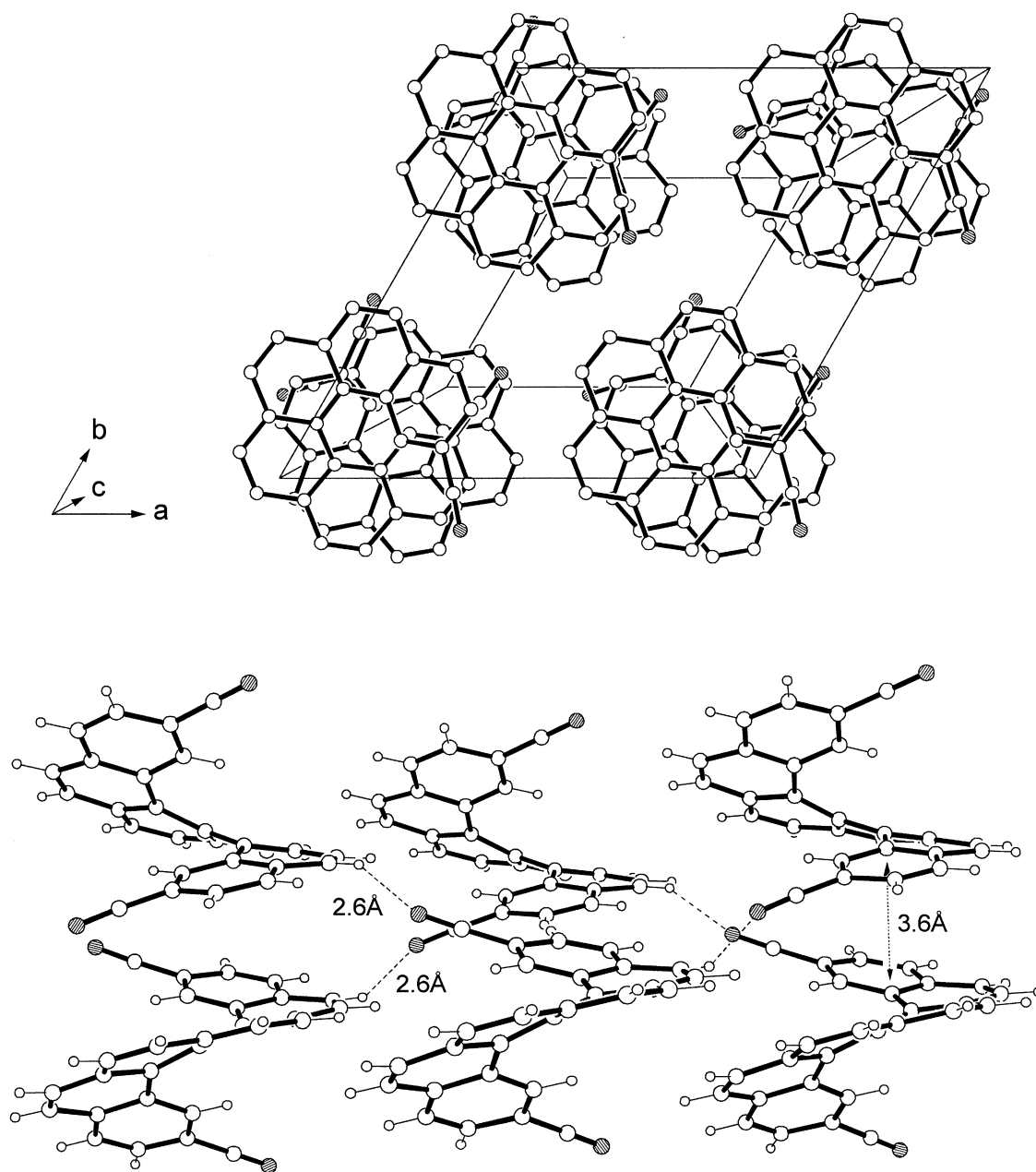


Figure 3. Packing structure of helicene **1**: top: as seen from the crystallographic *c* direction; bottom: a side view indicating C–H $\cdots$ N and $\pi\cdots\pi$ interactions (broken lines)

contact distance of 2.68 Å is from one of the C–H atoms of the ring to a neighboring phenyl ring center of another molecule [C(4)–H(4) Cg(7)_[1-x, -y, 1-z], *d* = 2.68 Å, 172°]. Both contacts maintain near linear angles around these hydrogen atoms. The high steric demand of the diphenylmethanol units results in there being no conventional hydrogen bonds, the shortest intermolecular distance being 2.67 Å [O(22)–H(22) $\cdots$ O(15)_[1-x, y, 1-z], 170.1°]. Helicene **9** has no molecular symmetry within 0.80 Å tolerance. The inner pitch elevation (*d*₁, C1 $\cdots$ C16 distance) is 3.13 Å. The terminal inner helix torsion angles 1 and 2 show somewhat unequal but relatively small opening at 13.0 and 17.6°. Obviously the bulky units of helicene **9** prevent the column-like

packing structure of molecules characteristic of helicenes in general. Instead they are interlocked such that the phenyl groups may form C–H $\cdots\pi$ interactions.^[31]

Data Bank Analysis of Hexahelicene Structures

The question is how one can best compare these rather rigid and mostly symmetric molecules, which, at least in a naive approach, should have *C*₂ symmetry. The answers would perhaps relate solid-state structural variability to their chiroptical properties. Relationships between molecular structures could address chirality-related issues such as the occurrence of spontaneous resolution and so on.

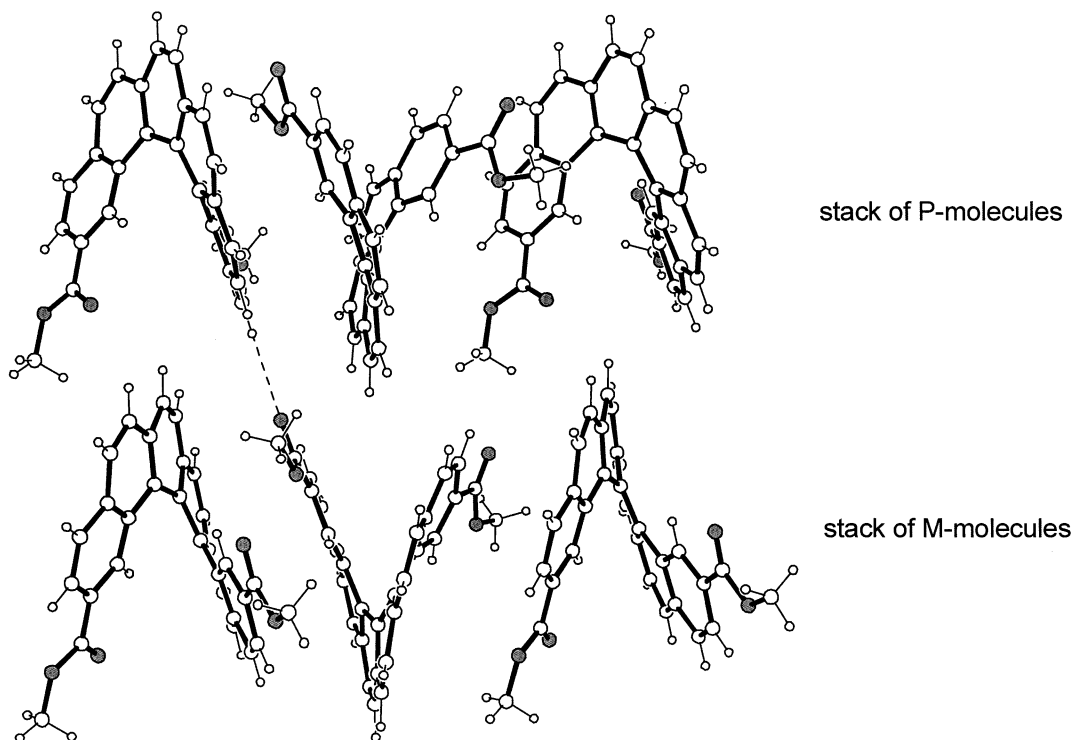


Figure 4. Packing structure of helicene **3** with a C–H...O contact shown in dotted line; chirality of opposite stacks are indicated

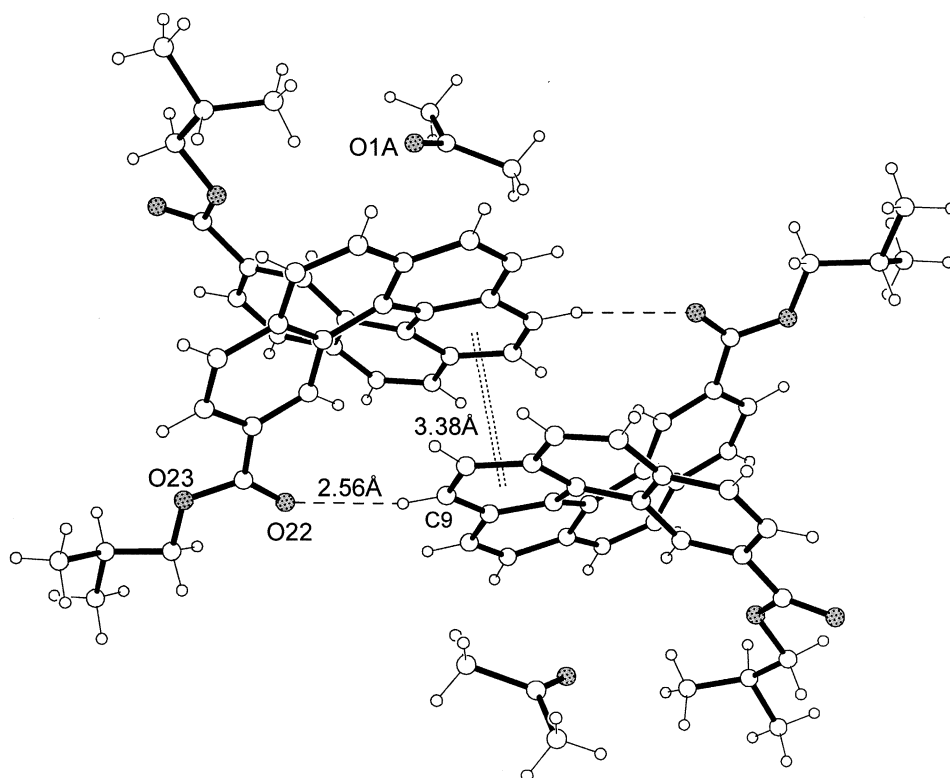


Figure 5. Packing excerpt of helicene **4**·acetone (1:1) with C–H...O contacts (broken lines) and π ... π interactions (dotted lines) in the core of the helicenes

We chose to analyze structural data from our six independent hexahelicene models from five crystals against those from the Cambridge Structural Database^[35] (CSD). Hexa-

helicenes were retrieved from the CSD (Release 5.23, April 2002), merged with our own with the aid of PREQUEST,^[36] and analyzed by use of the statistical package VISTA.^[37]

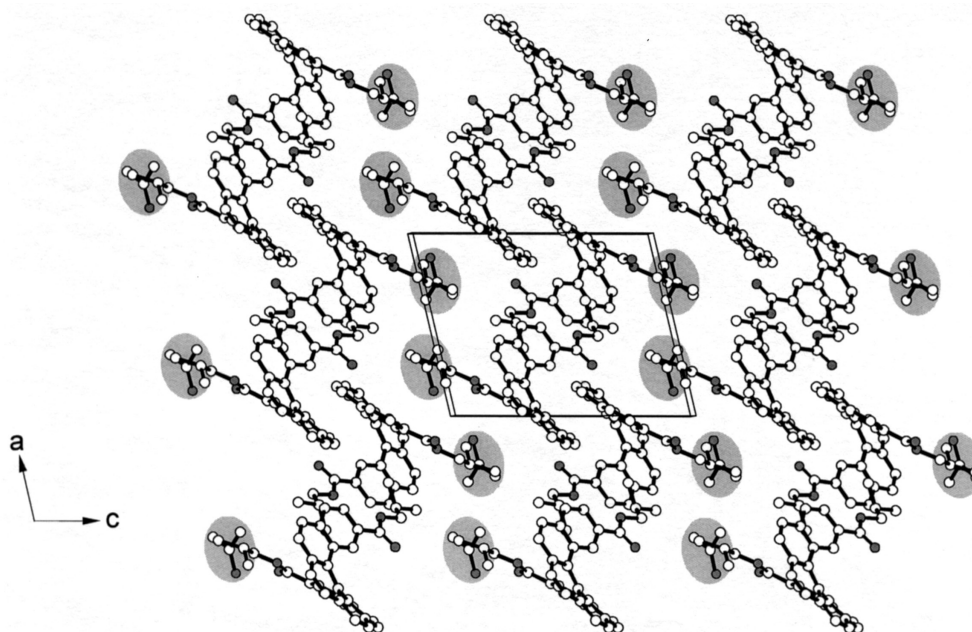


Figure 6. Packing structure of helicene **4**·acetone (1:1); shaded areas are for alternating guest and terminal methyl group sites

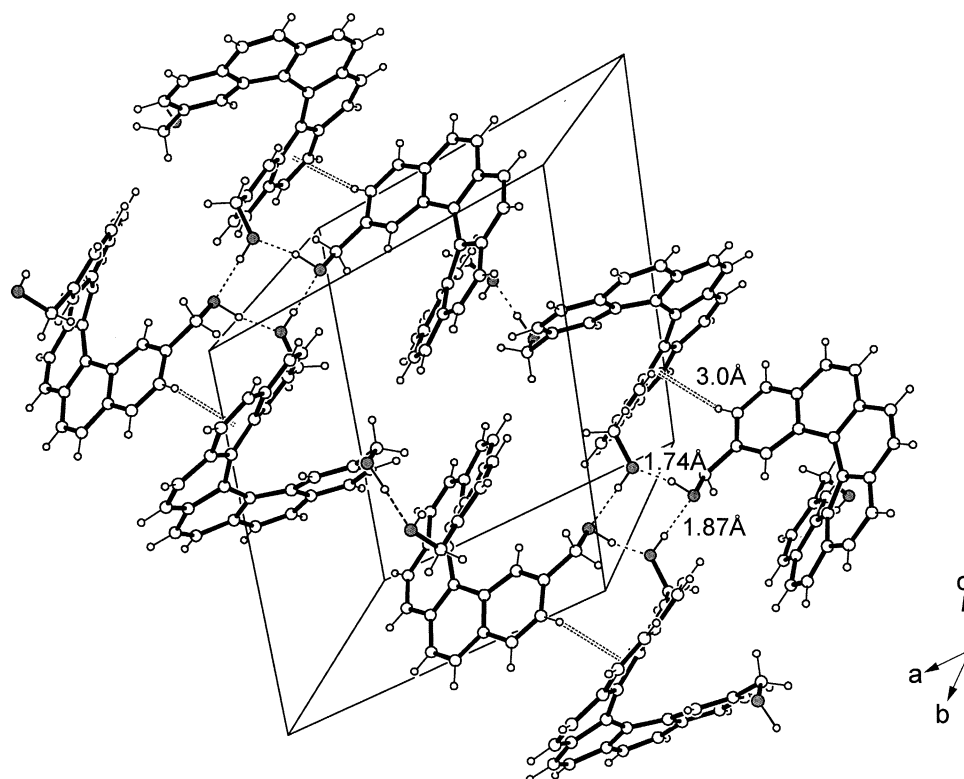


Figure 7. Packing structure of helicene **8** showing some C–H···O intermolecular contact dimensions and C–H··· π approach

An initial three-dimensional connectivity search from the main database gave 24 independent structure hits^[38] containing hexahelicene moieties with no steric constraints such as covalent bonds between either the C1–C16 or the C2–C15 atomic positions (cf. Figure 2). Structures contain-

ing more than one hexahelicene molecule in their asymmetric units (such as compound **3**) or that are polymorphic increase the number of independent observations of hexahelicene moieties up to 36 altogether, including those from this study. No structural fragment was excluded from the

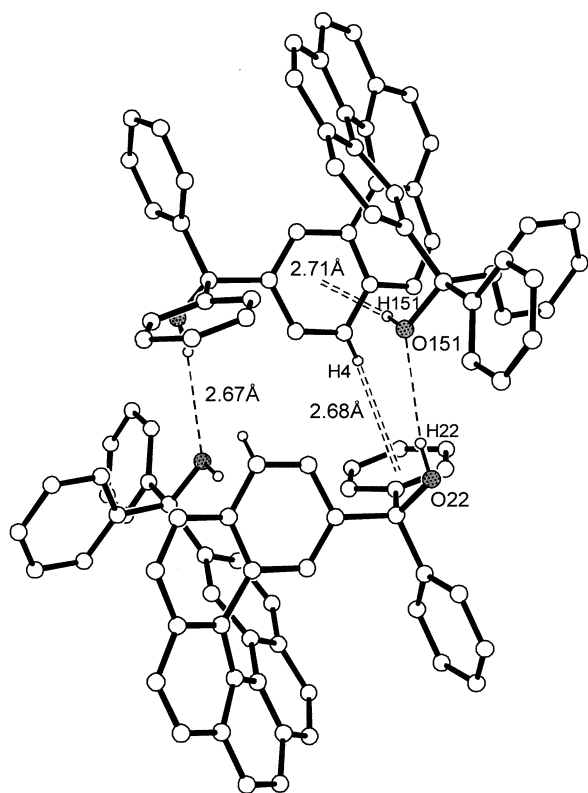
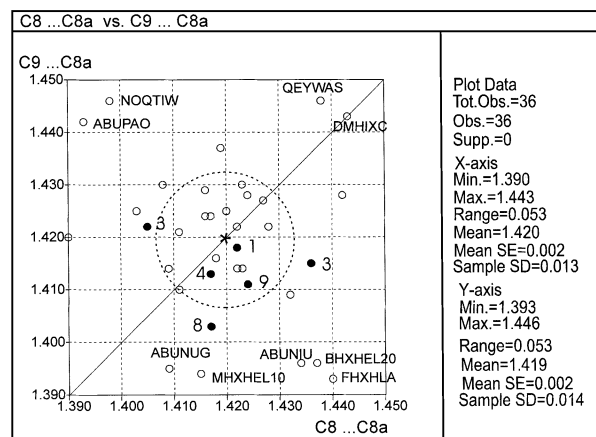


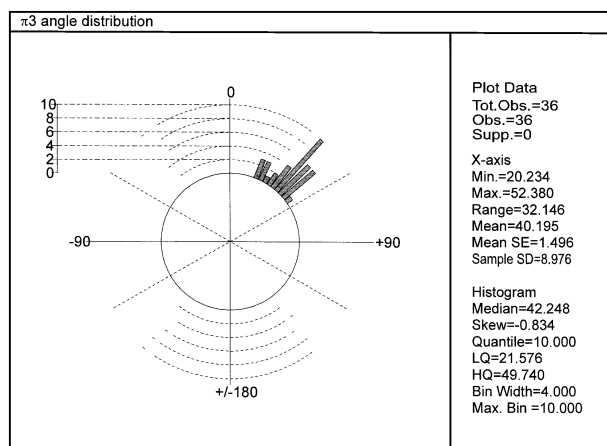
Figure 8. Centrosymmetric pair of helicene molecules **9** indicating significant C–H···O intermolecular contact dimensions and C–H··· π contact distances

further analyses. The following results are listed in an order as one looks at these structures from their innermost bay region out towards the flanks of the molecule.

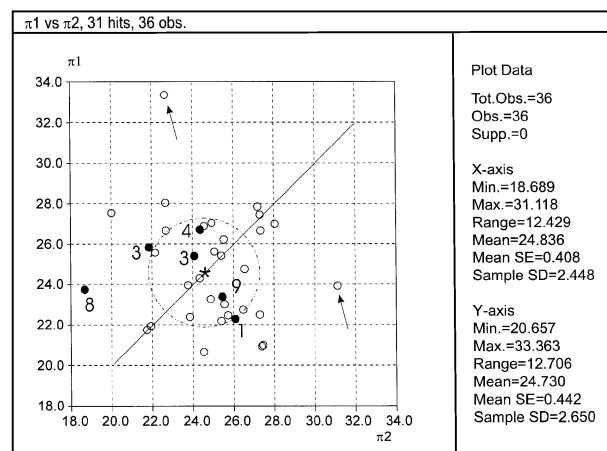
The Outer C–C Bond Lengths Opposite the Bay Region of Hexahelicene: In an attempt to describe the shape of hexahelicenes in general, a good starting point seems to be to look at different aspects of their ability to preserve their C_2 symmetry more or less perfectly. This is first analyzed by selecting two chemical bonds that should reflect C_2 symmetry violations at bond length levels. A C_2 axis would dissect an ideal C_2 symmetry molecule at the outer aromatic C–C bonds (junction of C8–C8a and C9–C8a bonds, cf. Figure 2). As bond lengths usually deviate from ideal aromatic values here, it is equally interesting to see how far this deviation goes. Figure 9 (a) shows this distribution, indicating that only four out of the 36 data points fall on the ideally symmetric diagonal line. However, the majority of values lie within one sample standard deviation (1SD), so these could be considered practically symmetric for many of the cases, also including our five crystal structures. An apparent elongation of these bonds against an aromatic C_{sp^2} – C_{sp^2} standard is also quite obvious, with the mean value of 1.420 Å of the sample. However, there are a few outliers with slightly eccentric behavior that is also obvious in the following charts. Among these, one finds asymmetrically substituted hexahelicenes at positions 1 and 2 (MXHELI0, BXHELI20 and FHXLIA). Environmental effects oper-



(a)



(b)



(c)

Figure 9. (a) Scattergram of the C8–C8a and C9–C8a bonds in the database of thirty hexahelicene crystal structures. Numbered black dots relate to the crystal structures of the respective compounds from this paper in this and in the following diagrams throughout; diagonal represents ideally symmetric bonding; dotted circle indicates approximate standard deviation range from the mean value of the sample, indicated by an asterisk; (b) polar histogram of the π_3 angle (°) distribution for 36 observations, with the mean value of 40.2°; (c) scattergram of the π_1 vs. π_2 angles (°); diagonal line indicates positioning of ideally symmetric $\pi_1 = \pi_2$ cases (not a regression line); the asterisk * denotes placement of the mean value; broken circle indicates one sample standard deviation ranges (1SD) from the mean; arrows indicate two prominent outliers from the mean (POZFIT01 and QEYWAS in CSD)

ate in another branch of these outliers, too. Signs of steric congestion, either intramolecular (QEYWAS, NOQTIW) or intermolecular (due to heteromolecular association) in nature (ABUPAO; ABUNIU, ABUNUG), are probably manifested in these deviations.

The Hexahelicene Opening Angle ($\pi 3$) (for specification see ref.^{[12])}: This is perhaps the most characteristic general molecular shape descriptor (cf. Figure 2), so its distribution merits mention. The polar histogram in Figure 9 (b) shows a slightly bimodal, or strongly distorted Gaussian distribution with a relative large spread of about 32° , unexpected in a rigid molecule. The relative small number of data in the sample does not allow for a lengthy discussion of this histogram though. We do note though, that those samples at the minor peak are all from crystal structures with chiral space groups ($P1$ and $P2_12_12_1$).

Comparison of the Flank Angles ($\pi 1$ and $\pi 2$) (for specification see ref.^{[12])}: The angles of these least-squares planes measure the tilt of the planes of the last ten atoms of each flank against a central ten-atom plane (i.e. how three, partially overlapping naphthalene moieties kink pairwise towards each other). It should therefore again be expected that a perfectly symmetric hexahelicene must have these angles equal: along the diagonal of Figure 9 (c). As this case is again somewhat similar to that in Figure 9 (a), here we consider those that lie within 1SD value of the mean as being practically symmetric within error limits. Here again are two notable outliers: those possessing either non-centrosymmetric or chiral space groups. Compound **8** from this study also lies far from the diagonal, albeit **8** has a trivial centrosymmetric space group $P2_1/n$. The relatively large distortion is thus caused by a strong asymmetric hydrogen bond involvement in a centrosymmetric space group.

The Hexahelicene Opening Angle ($\pi 3$) Against the Non-bonded Distance ($d1$), $\pi 3$ vs. $d2$ and $\pi 3$ vs. $d3$ (for specification of $d1$ – $d3$ see Table 3): The purpose of these three consecutive diagrams [Figure 10 (a–c)] is to illustrate how distortions from the hexahelicene center propagate towards the flanks of these molecules. This is best shown by the $\pi 3$ angle [cf. Figure 9 (b)]. Figure 10 (a) shows that no correlation exists between $\pi 3$ and $d1$, a minor surprise since a rigid helicene model would imply that these two parameters correlate well. A substantial number of structures lie outside the 1SD limiting circle. Thus, opposing atoms C1 and C16 (Figure 2) suffer from substantial strain, forcing them away from the planes made up by neighboring atoms. A mean value of this C1...C16 distance also shows this clearly. It is of only 3.14 Å, about 0.4 Å shorter than the van der Waals radii sum. As we proceed from $d1$ towards the outer elevation distances $d2$ and $d3$, we see this correlation developing nicely [Figure 10 (b–c)]. The elevation distance between the atom positions C2...C15 ($d2$) shows a fair correlation (corr. coefficient: 90.9%). Compound **8 is still deviating, as are some of the noncentrosymmetric crystal structures. There still is a tendency for the scatter of the distances to increase as the $\pi 3$ angle reduces. An obvious interpretation of this is steric congestion. Correlation between the $\pi 3$ angle and the $d3$ distance is almost perfect [Figure 10 (c), corr. co-**

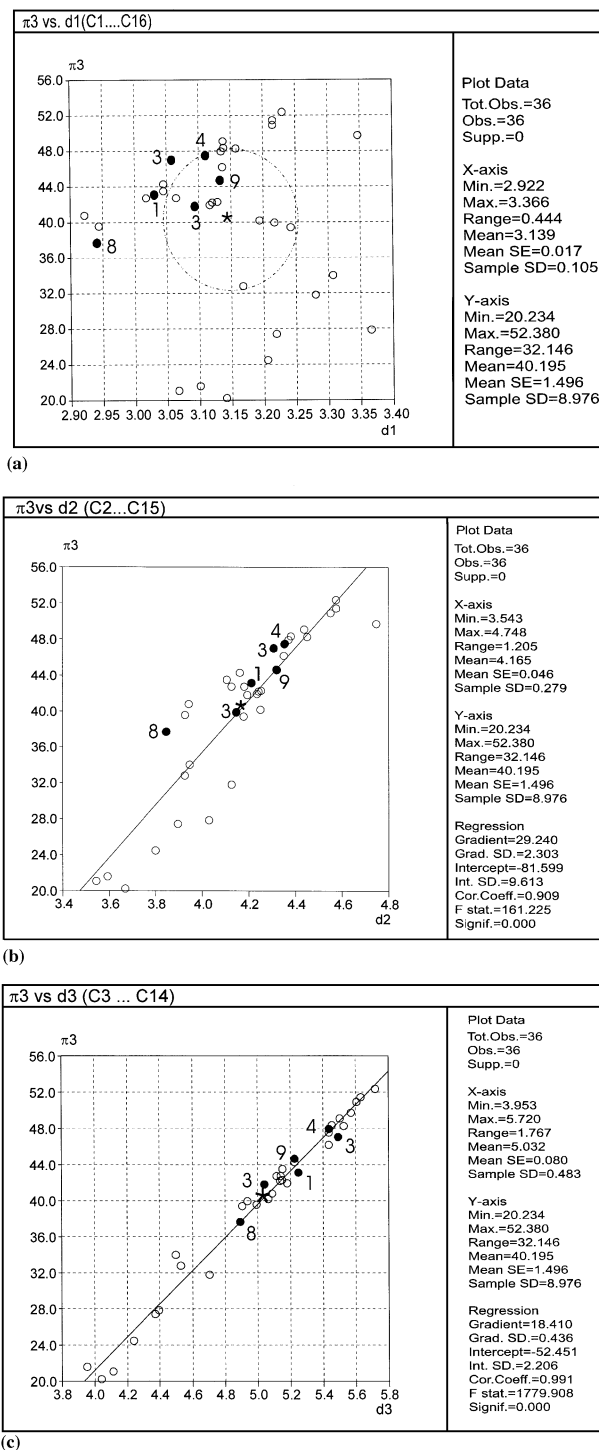


Figure 10. (a) Scattergram of the $\pi 3$ angles ($^\circ$) vs. $d1$ distances (Å); an asterisk * denotes placement of the mean value (40.2° , 3.139 Å); broken circle indicates one sample standard deviation ranges (1SD) from the mean; (b) scattergram of the $\pi 3$ angles ($^\circ$) vs. $d2$ distances (Å); an asterisk * denotes placement of the mean value (40.2° , 4.165 Å); regression line is computed for all 36 data; (c) scattergram of the $\pi 3$ angles ($^\circ$) vs. $d3$ distances (Å); an asterisk * denotes placement of the mean value (40.2° , 5.032 Å); regression line is computed for all 36 data

eff. = 99.1%]. On looking through all these structures, it becomes clear that this pattern is fairly independent of the substituent positions. Substituents, albeit differing slightly

in their relative frequencies and also in whether they are mono- or disubstituted, occur at all three positions.

A further analysis was also made for non-bonding $\pi\cdots\pi$ type interactions. Overlap would be expected to appear pre-eminently on the more aromatic outer flank regions between symmetry-related phenanthrene rings. Analysis of outer ring center distances shows that appreciable overlap of this type occurs only in six cases, three of which, as alluded to earlier, are from the compounds reported in this paper. Compounds **1**, **3**, and **4** have $\pi\cdots\pi$ ring center distances under 4.0 Å of this kind (3.74 and 3.75 Å for **1**, 3.66 and 3.67 Å for **3**, and 3.98 Å for **4**). The other three structures (FHXHLA, FHXHLB, and GOJDAK) have all their respective ring center distances longer than 4 Å.

Distribution of Chiral, Centric, and Acentric Space Groups in the Sample: Crystallographic shorthand is used to designate centrosymmetric space groups (centric) and also non-centrosymmetric ones (acentric). Caution is again advised, since the sample distribution is unequal and especially undersized for acentric crystals. There are 15 centric, 11 chiral, and only three acentric space group occurrences in the sample, including the five structures reported in this work. Apparently the occurrence of more than one molecule in the asymmetric unit (i.e. $Z' > 1$) seems to be frequent in acentric crystals (two out of three) while it is perhaps less frequent both in centric crystals (two out of 15) and in chiral ones (one out of 11). However, this disparity may also be due to the relatively small number of cases, and caution is advised even for hexahelicene itself when classifying it in the chiral class.^[39] There seems to be no clear tendency between substitution site and the frequency of these molecules crystallizing either in chiral or in non-centrosymmetric space groups.

Principal Component (PC) Analysis of the $d1$, $d2$, and $d3$ Distances (as specified in Table 3) vs. Molar Rotation (M): Since there is some information available on the molar rotation of hexahelicene and the compounds in this study, it is tempting to plot these quantities against some possibly meaningful structural parameter. The principal components (PCs) were derived from the $d1$, $d2$, and $d3$ distance values. Beforehand, we derived mean molecular dimensions (angles and distances) of the two independent molecules of **3** so as to have a single point for this parameter against one M data. PCs were first generated from a set of 35 sample points using all structures. The major component PC1 explains 65.0% of the variation of the three generated components. The minor component PC2 accounts for the rest of the variance (34.8%). PC1 shows high (>97%) correlation with both $d1$ and $d2$, indicating that these two distances explain variance in this small sample equally well (Figure 11, Supporting Information, see also the footnote on the first page of this article).

Next, only sample points with known molar rotation values were kept (i.e., five structures from this study and hexahelicene, Table 1). Since the number of data sets in the sample is reduced here to six, caution is due. A scatter plot of the major PC against the M values (Figure 12, Supporting Information) shows no usable regression. In spite of

this, it does have one interesting feature: the unusually high M value of compound **4**. The association and solvation properties of **4** may be markedly different from those of the other molecules; the inclusion of acetone in its crystal might be an indication of this. It is known that some helicenes exhibit solvent-, concentration-, and temperature-dependent molar rotation and CD spectra.^[40] These dependencies are primarily due to variable self-assembling capabilities of the molecules.

Conclusions

Seven new hexahelicenes (**3–7**, **9**, **10**) containing different functional group substituents in positions 2 and 15 of the helicene framework have been synthesized by a synthetic route involving a double Wittig reaction, a photocyclization, and subsequent modification of functional groups (Scheme 1). A corresponding helicene **8**, a known compound but previously obtained by a different approach,^[6] has also been synthesized by the described reaction sequence, while the known 2,15-disubstituted hexahelicene derivatives **1** and **2** were prepared by literature methods.^[13,14] Optical resolution with a cellulose tris(3,5-dimethylphenylcarbamate) column^[24] was successfully performed in three cases (**4**, **8**, **10**) and the molar rotations of these compounds have been determined. These vary between 10383 and 19348, indicating influences of the substituents relative to the unsubstituted hexahelicene, most distinctly exhibited in **4**, the bulky bis(isobutyl ester). The CD spectra agree with this.

The crystal structures show a beautiful concerted interplay of weaker/stronger C–H $\cdots$ N, C–H $\cdots$ O, and CH $\cdots\pi$ interactions, $\pi\cdots\pi$ overlapping, and dispersion. An outstanding feature of some of the molecules of this study – **1**, **3**, **8**, and **9** – is their capability for association with like molecules, while only **4**, in its inclusion compound with acetone, shows heteromolecular association in the crystal. This is in contrast to a recent comparative and exhaustive study^[12] on the association properties of polyaromatic systems, hexahelicenes among others, which describes heteromolecular association between differing polyaromatic molecules in considerable detail. As pointed out in the databank analysis section, **1** and **3** rely especially upon $\pi\cdots\pi$ interactions to build their crystal lattices. This interaction is only marginally present in the crystal structure of **4**, as well as in three other helicene derivative crystals from the literature.^[38]

Statistical analysis of the molecular dimensions in these and related crystal structures gave hints as to what structural parameters could be relevant to other macroscopic physical phenomena such as optical rotation. Decreased aromaticity in the central molecular portion is obvious, with C_{sp2}–C_{sp2} bonds as long as 1.420 Å mean value. Overall mean values of the experimentally measured C1 $\cdots$ C16 ($d1$), C2 $\cdots$ C15 ($d2$), and C3 $\cdots$ C14 ($d3$) distances are 3.14(2), 4.16(5), and 5.03(8) Å, respectively; the mean $\pi3$ opening angle is 40.2°. Consistently with intuition, the internal bay

regions of these molecules bear considerable strain. Observations relating the distortion of these structures and molar rotation cannot be simply deduced, but apparently molecular association and solvation may play an important role here, also in the solid state. The statistical data also shed light on the difference ranges between some molecules in their solid-state fine structure.

Experimental Section

General: Melting points: Kofler melting point microscope (uncorrected). IR: Perkin–Elmer FT-IR 1600. ^1H NMR (internal standard TMS): Bruker WH 250, WM 300, and WM 400. ^{13}C NMR (internal standard TMS): Bruker WM 250, WM 300, and WM 400. MS: A.E.I MS 50 and Kratos FAB-MS Concept 1H. Elemental analyses: Heraeus CHN rapid analyzer. Column chromatography: Silica gel (63–100 μm , Merck) and Al_2O_3 (150 μm , neutral, Aldrich) – Enantiomeric separation: HPLC (Gilson, $\lambda = 254\text{ nm}$), cellulose-tris(3,5-dimethylphenylcarbamate) (CDMPC), $50 \times 0.46\text{ cm}$ (Mallinkrodt–Baker). Optical rotation: Perkin–Elmer 241 Polarimeter. Circular dichroism: Jasco J-720. Organic solvents were purified by standard procedures. For optical separation, eluents of HPLC quality (Merck) were used, for CD measurement *n*-hexane of Uvasol® quality (Merck).

Naphthalene-2,7-bis(triphenylphosphonium) dibromide was prepared according to the ref.^[9,10,15] procedure. The aromatic aldehydes were purchased from Fluka.

General Procedure. Synthesis of Distilbenes 11a–d: Lithium methoxide (1 M in methanol, 20 mL, 20 mmol) was added over 0.5 h under Ar to a refluxing solution of naphthalene-2,7-bis(triphenylphosphonium) dibromide (6.71 g, 8 mmol) and the corresponding aromatic aldehyde (16 mmol) in dry methanol (25 mL). Heating at reflux was continued for 3 h. The mixture was cooled to room temp. and stirred for 12 h. Compound **11d** was an exception in that dry THF (40 mL) and sodium 2-methylpropoxide were used and room temp. was employed rather than heating at reflux. Details for workup and purification, as well as data for the individual compounds, are given below.

2,7-Bis(4-cyanostyryl)naphthalene (11a): 4-Cyanobenzaldehyde was used. The reaction mixture was hydrolyzed with water and concentrated under vacuum to half its volume. The yellow precipitate was collected and purified by column chromatography (SiO_2 , eluent: dichloromethane, $R_f = 0.60$) to yield 86% of pale yellow solid [(*E,Z*) isomers of **11a**]. M.p. around 155 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 6.63\text{--}6.72$ (m, 4 H, C=C–H), 7.15–7.89 (m, 14 H, Ar–H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 110.73, 123.87, 126.93, 127.57, 127.71, 128.26, 128.93, 129.60, 132.06, 132.23, 132.54, 133.0, 141.76$ ppm. $\text{C}_{28}\text{H}_{18}\text{N}_2$ (EI-MS): calcd. 382.1469; found 382.2.

2,7-Bis(4-methoxystyryl)naphthalene (11b):^[14c] 4-Methoxybenzaldehyde was used. Workup and purification ($R_f = 0.85$) as given for **11a** yielded 86% of a colorless solid [(*E,Z*) isomers of **11b**; recrystallization from methanol yielded the pure (*Z,Z*) isomer]. M.p. 152–154 °C. ^1H NMR (250 MHz, CDCl_3): $\delta = 3.79$ (s, 6 H, OCH_3), 6.59 (d, $^3J_{\text{H,H}} = 12.32\text{ Hz}$, 2 H, C=C–H), 6.68 (d, $^3J_{\text{H,H}} = 12.32\text{ Hz}$, 2 H, C=C–H), 6.75 (d, $^3J_{\text{H,H}} = 8.4\text{ Hz}$, 4 H, Ar–H), 7.25 (d, $^3J_{\text{H,H}} = 8.4\text{ Hz}$, 4 H, Ar–H), 7.35 (d, $^3J_{\text{H,H}} = 8.6\text{ Hz}$, 2 H, Ar–H), 7.57 (d, $^3J_{\text{H,H}} = 8.6\text{ Hz}$, 2 H, Ar–H), 7.65 (s, 2 H, Ar–H) ppm. ^{13}C NMR, (62.9 MHz, CDCl_3): $\delta = 55.15, 113.57,$

126.91, 127.18, 127.77, 128.55, 129.61, 130.07, 130.22, 131.48, 133.58, 135.36, 158.75 ppm. $\text{C}_{28}\text{H}_{24}\text{O}_2$ (EI-MS): calcd. 392.1776; found 392.2.

Ester 11c: Methyl 4-formylbenzoate was used. Workup was as given for **11a**. Column chromatography (Al_2O_3 , eluent: benzene, $R_f = 0.64$) yielded 87% of a colorless solid [(*E,Z*) isomers of **11c**]. M.p. around 195 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 3.90$ (s, 6 H, COOCH_3), 6.69–6.84 (m, 4 H, C=C–H), 7.20–7.95 (m, 14 H, Ar–H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 51.98, 107.41, 121.00, 127.01, 127.48, 128.27, 128.95, 129.57, 129.69, 132.04, 133.46, 134.69, 142.05, 166.86$ ppm. $\text{C}_{30}\text{H}_{24}\text{O}_4$ (FAB-MS): calcd. 448.1675; found 448.1674.

Ester 11d: 2-Methylpropyl 4-formylbenzoate and the diposphonium salt in dry THF (40 mL) were used. Sodium 2-methylpropoxide (1 M in 2-methyl-1-propanol, 20 mL, 20 mmol) was added at room temp. under Ar, and the mixture was stirred for 2 days. After quenching with water, the mixture was extracted with diethyl ether, washed with water, and dried (Na_2SO_4). Evaporation of the solvent under vacuum and column chromatography (SiO_2 , eluent: dichloromethane, $R_f = 0.84$) yielded 91% of a pale yellow solid [(*E,Z*) isomers of **11d**; recrystallization from toluene yielded the pure (*Z,Z*) isomer]. M.p. 189–190 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 1.05$ (d, $^3J_{\text{H,H}} = 8.93\text{ Hz}$, 12 H, CH_3), 2.01 (m, 2 H, CH), 4.01 (d, $^3J_{\text{H,H}} = 9.02$, 4 H, CH_2), 7.25 (d, $^3J_{\text{H,H}} = 11.8\text{ Hz}$, 2 H, C=C–H), 7.4 (d, $^3J_{\text{H,H}} = 11.8\text{ Hz}$, 2 H, C=C–H), 7.60–8.10 (m, 14 H, Ar–H) ppm. ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 19.24, 27.74, 70.59, 125.48, 126.37, 127.41, 127.61, 127.74, 128.40, 128.62, 128.77, 130.19, 131.70, 133.52, 134.71, 166.12$ ppm. $\text{C}_{36}\text{H}_{36}\text{O}_4$ (FAB-MS): calcd. 532.2614; found 532.2613.

General Procedure. Synthesis of Helicenes 1–4: A solution (or a suspension in the cases of **11b** and **11c**) of the respective distilbene **11** (a–d) (1 mmol) and iodine (38.1 mg, 0.15 mmol) in toluene (1 L) was irradiated for 3.5–4 h in a photoreactor fitted with a water-cooled immersion well and a high-pressure Hg lamp. Evaporation of the solvent and column chromatography (SiO_2) yielded the pure racemic compounds. Enantiomeric separation was effected by HPLC on a cellulose tris(3,5-dimethylphenylcarbamate) column at 25 °C. Experimental details and specific data for the individual compounds are given below.

Hexahelicene-2,15-dicarbonitrile (1):^[13] 2,7-Bis(4-cyanostyryl)naphthalene (**11a**) was used to give 62% of a light yellow solid; $R_f = 0.65$ (eluent: cyclohexane/ethyl acetate, 1.5:1). M.p. > 300 °C (dec.).

2,15-Dimethoxyhexahelicene (2):^[13,14c] 2,7-Bis(4-methoxystyryl)naphthalene (**11b**) was used to give 30% of a lemon solid; $R_f = 0.68$ (eluent: toluene). M.p. 206 °C.

Dimethyl Hexahelicene-2,15-dicarboxylate (3): 2,7-Bis[4-(methoxycarbonyl)styryl]naphthalene (**11c**) was used to give 14% of a colorless solid; $R_f = 0.20$ (eluent: dichloromethane). M.p. 285 °C. IR (KBr): $\tilde{\nu} = 3032.5\text{ cm}^{-1}$ (C–H, Ar), 2939 (C–H, OCH_3), 1712.5 (C=O), 1432 (Ar), 1244 (C–O). ^1H NMR (400 MHz, CDCl_3): $\delta = 3.58$ (s, 6 H, CH_3), 7.74 (d, $^3J_{\text{H,H}} = 8.22\text{ Hz}$, 2 H, Ar–H), 7.75 (d, $^3J_{\text{H,H}} = 8.22\text{ Hz}$, 2 H, Ar–H), 7.82 (d, $^3J_{\text{H,H}} = 8.41\text{ Hz}$, 2 H, Ar–H), 7.96 (d, $^3J_{\text{H,H}} = 8.41\text{ Hz}$, 2 H, Ar–H), 8.02 (d, $^3J_{\text{H,H}} = 8.22\text{ Hz}$, 2 H, Ar–H), 8.05 (s, 2 H, Ar–H), 8.06 (d, $^3J_{\text{H,H}} = 8.22\text{ Hz}$, 2 H, Ar–H) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 51.82, 124.16, 125.49, 125.58, 126.07, 127.55, 127.89, 127.94, 128.58, 128.81, 129.30, 131.00, 132.05, 133.82, 135.18, 166.86$ ppm. $\text{C}_{30}\text{H}_{20}\text{O}_4$ (EI-MS): calcd. 444.1361; found 444.2.

Bis(2-methylpropyl) Hexahelicene-2,15-dicarboxylate (4): 2,7-Bis[4-(2-methylpropyloxycarbonyl)styryl]naphthalene (**11d**) was used to give 63% of a light yellow solid; $R_f = 0.75$ (eluent: dichloromethane). M.p. 162–164 °C (from *n*-hexane). IR (KBr): $\tilde{\nu} = 3051\text{ cm}^{-1}$ (C–H, Ar), 2961 (C–H, aliph.), 1714 (C=O), 1616 (Ar), 1241 (C–O). ^1H NMR (250 MHz, CDCl_3): $\delta = 0.81$ (d, $^3J_{\text{H,H}} = 6.72\text{ Hz}$, 6 H, CH_3), 0.85 (d, $^3J_{\text{H}} = 6.72\text{ Hz}$, CH_3); 1.82 (m, 2 H, CH), 3.78 (dd, $^2J_{\text{H,H}} = 17.68$, $^3J_{\text{H,H}} = 10.76\text{ Hz}$, 2 H, CH_2), 3.80 (dd, $^2J_{\text{H,H}} = 17.68$, $^3J_{\text{H,H}} = 10.68\text{ Hz}$, 2 H, CH_2), 7.72–8.35 (m, 14 H, Ar–H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3): $\delta = 19.25$, 27.68, 70.58, 123.75, 125.46, 126.23, 127.42, 127.60, 127.76, 128.31, 128.65, 128.68, 129.58, 130.16, 131.64, 133.46, 134.66, 166.15 ppm. $\text{C}_{36}\text{H}_{32}\text{O}_4$ (FAB-MS): calcd. 528.2301; found 528. Enantiomeric separation (eluent: *n*-hexane/2-propanol, 9:1, 2 mL·min $^{-1}$, 28 bar): (*M*)-(–)-**4**: $t_r = 15.5\text{ min}$, $k' = 1.0$; (*P*)-(+)-**4**: $t_r = 31.0\text{ min}$, $k' = 3.0$; $\alpha = 3.0$, $R_s = 0.26$. $[\alpha]_D^{20} = 3660 \pm 100$ ($c = 0.03$, CHCl_3).

Hexahelicene-2,15-dimethanamine (5): LiAlH_4 (90 mg, 2.34 mmol) was added to a solution of **1** (100 mg, 0.26 mmol) in dry THF (15 mL). The suspension was stirred at room temp. for 12 h, and then quenched with water and extracted into dichloromethane. The amine hydrochloride was precipitated by addition of diluted hydrochloric acid and separated by centrifugation. The solid was suspended in THF and stirred with aqueous NaOH (20 %). The organic layer was separated, washed with water, and dried (Na_2SO_4). Evaporation of the solvent under vacuum yielded a light yellow solid (45.5 mg, 45%). M.p. 178 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.62$ (s, 4 H, NH_2), 3.16 (d, $^2J_{\text{H,H}} = 14.07\text{ Hz}$, 2 H, CH_2), 3.31 (d, $^2J_{\text{H,H}} = 14.07$, 2 H, CH_2), 7.17 (d, $^3J_{\text{H,H}} = 7.99$, 2 H, Ar–H), 7.48 (s, 2 H, Ar–H), 7.79 (d, $^3J_{\text{H,H}} = 7.99$, 2 H, Ar–H), 7.89 (d, $^3J_{\text{H,H}} = 8.72$, 2 H, Ar–H), 7.92 (d, $^3J_{\text{H,H}} = 8.72\text{ Hz}$, 2 H, Ar–H), 7.98 (d, $^3J_{\text{H,H}} = 8.08$, 2 H, Ar–H), 8.03 (d, $^3J_{\text{H,H}} = 8.08$, 2 H, Ar–H) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 30.67$, 124.43, 125.77, 125.89, 126.35, 126.80, 127.64, 127.71, 127.92, 128.01, 130.23, 131.01, 132.01, 133.57, 136.12 ppm. $\text{C}_{28}\text{H}_{22}\text{N}_2$ (HR MS): calcd. 386.1783; found 386.1777. $\text{C}_{28}\text{H}_{22}\text{N}_2$: calcd. C 87.01, H 5.74, N 7.25; found C 86.80, H 5.90, N 7.22.

Hexahelicene-2,15-diol (6): Boron tribromide (1 M in hexane, 2.1 mL, 2.1 mmol) was added at room temp. over 30 min to a stirred solution of **2** (100 mg, 26 mmol) in dry dichloromethane (10 mL). Stirring was continued at the same temp. for 12 h. The mixture was quenched with ice/water. The precipitate was separated and washed with water. Recrystallization from dichloromethane yielded a light yellow solid (58.1 mg, 62%), sensitive to light. M.p. 295 °C. IR (KBr): $\tilde{\nu} = 3215\text{ cm}^{-1}$ (OH), 2891, 1479.5 (Ar), 1192.5 (C–O). ^1H NMR (400 MHz, $[\text{D}_4]\text{MeOH}$): $\delta = 6.82$ (dd, $^3J_{\text{H,H}} = 8.63$, $^4J_{\text{H,H}} = 2.35\text{ Hz}$, 2 H, Ar–H), 7.00 (d, $^4J_{\text{H,H}} = 2.35\text{ Hz}$, 2 H, Ar–H), 7.71 (d, $^3J_{\text{H,H}} = 8.63\text{ Hz}$, 2 H, Ar–H), 7.75 (d, $^3J_{\text{H,H}} = 8.52\text{ Hz}$, 2 H, Ar–H), 7.86 (d, $^3J_{\text{H,H}} = 8.52\text{ Hz}$, 2 H, Ar–H), 7.95 (d, $^3J_{\text{H,H}} = 8.21\text{ Hz}$, 2 H, Ar–H), 7.98 (d, $^3J_{\text{H,H}} = 8.21\text{ Hz}$, 2 H, Ar–H) ppm. ^{13}C NMR (100.6 MHz, $[\text{D}_4]\text{MeOH}$): $\delta = 111.69$, 117.65, 124.10, 125.67, 127.74, 127.88, 128.07, 128.14, 128.98, 130.15, 133.19, 133.27, 133.99, 156.00 ppm. $\text{C}_{26}\text{H}_{16}\text{O}_2$ (HR MS): calcd. 360.1150; found 360.1152. $\text{C}_{26}\text{H}_{16}\text{O}_2$: calcd. C 86.65, H 4.47; found C 86.64, H 4.36.

Hexahelicene-2,15-dicarboxylic Acid (7): A suspension of **4** (528.7 mg, 1 mmol) in 10 % aqueous NaOH (50 mL) and methanol (10 mL) was heated at reflux for 2 days. After filtration, the filtrate was acidified carefully with diluted hydrochloric acid. The precipitate that had formed was separated and washed with water to yield a light yellow solid (62.5 mg, 15%). M.p. 290 °C. IR (KBr): $\tilde{\nu} = 3440\text{ cm}^{-1}$ (OH), 3049 (C–H, Ar), 1689.5 (C=O), 1619.5 (Ar). ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 7.69$ (d, $^3J_{\text{H,H}} = 8.33\text{ Hz}$, 2 H,

Ar–H), 7.98 (d, $^3J_{\text{H,H}} = 8.33$, 2 H, Ar–H), 8.11 (d, $^3J_{\text{H,H}} = 8.64$, 2 H, Ar–H), 8.15 (s, 2 H, Ar–H), 8.22–8.28 (m, 6 H, Ar–H) ppm. ^{13}C NMR (100.6 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 122.74$, 125.10, 126.54, 127.41, 127.68, 127.75, 127.78, 128.02, 128.12, 128.66, 129.38, 131.37, 133.18, 134.36, 166.68 ppm. $\text{C}_{28}\text{H}_{16}\text{O}_4$ (EI-MS): calcd. 416.1049; found 416. $\text{C}_{28}\text{H}_{16}\text{O}_4$: calcd. C 80.76, H 3.87; found C 80.52, H 3.82.

1,1'-(Hexahelicene-2,15-diyl)dimethanol (8): LiAlH_4 (49.3 mg, 1.3 mmol) was added under Ar to a solution of **4** (528.6 mg, 1 mmol) in dry THF (150 mL). The suspension was stirred at room temp. for 12 h, then quenched with cooling with half-concd. hydrochloric acid and extracted into diethyl ether. The organic layer was washed with water, then with 20 % aqueous solution of sodium carbonate and dried (Na_2SO_4). Evaporation of the solvent under vacuum, recrystallization from ethanol, and column chromatography (SiO_2 , eluent: dichloromethane/acetone, 5:1, $R_f = 0.40$) yielded a pale yellow solid (365.2 mg, 94%). M.p. 234 °C (ref.^[6] M.p. 232–235 °C). IR (KBr): $\tilde{\nu} = 3423\text{ cm}^{-1}$ (OH), 3043.5 (C–H, Ar), 2923 (C–H, aliph.), 1616 (Ar), 102.5 (C–O). ^1H NMR (400 MHz, CDCl_3): $\delta = 3.95$ (d, $^2J_{\text{H,H}} = 12.42$, 2 H, CH_2O), 4.12 (d, $^2J_{\text{H,H}} = 12.42\text{ Hz}$, 2 H, CH_2OH), 7.24 (d, $^3J_{\text{H,H}} = 8.26$, 2 H, Ar–H), 7.50 (s, 2 H, Ar–H), 7.85 (d, $^3J_{\text{H,H}} = 8.26$, 2 H, Ar–H), 7.92 (d, $^3J_{\text{H,H}} = 8.57$, 2 H, Ar–H), 7.96 (d, $^3J_{\text{H,H}} = 8.57$, 2 H, Ar–H), 8.00 (d, $^3J_{\text{H,H}} = 8.23$, 2 H, Ar–H), 8.05 (d, $^3J_{\text{H,H}} = 8.23$, 2 H, Ar–H) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 65.73$, 124.42, 125.31, 127.37, 127.46, 127.47, 127.70, 127.76, 127.86, 128.06, 130.01, 131.58, 132.15, 133.64, 133.83 ppm. $\text{C}_{28}\text{H}_{20}\text{O}_2$ (EI-MS): calcd. 388.1463; found 388.0. Enantiomeric separation (eluent: *n*-hexane/2-propanol, 9:1, 0.4 mL·min $^{-1}$, 49 bar): (*M*)-(–)-**10**: $t_r = 32.5\text{ min}$, $k' = 9.83$; (*P*)-(+)-**10**: $t_r = 51.5\text{ min}$, $k' = 16.17$; $\alpha = 1.64$. $[\alpha]_D^{20} = 2672.8 \pm 3.4$ ($c = 0.1$, CHCl_3).

1,1,1',1'-Tetraphenyl-1,1'-(hexahelicene-2,15-diyl)dimethanol (9): Phenyllithium (1.6 M in cyclohexane/diethyl ether, 1.3 mL, 2.1 mmol) was added at –15 °C under Ar to a suspension of **4** (158.6 mg, 0.3 mmol) in dry THF (8 mL). The mixture was stirred for 1 h at the same temperature, then for 12 h at room temp. and was then heated at reflux for 4 h. After quenching with ice/water, the aqueous phase was extracted with diethyl ether, and the extract was washed with water and dried (NaSO_4). Evaporation of the solvent under vacuum and purification by column chromatography (SiO_2 , eluent: dichloromethane, $R_f = 0.39$) yielded a pale yellow solid (160 mg, 77%). M.p. 223 °C. IR (KBr): $\tilde{\nu} = 3448\text{ cm}^{-1}$ (OH), 3058 (C–H, Ar), 1609.5 (Ar), 1015.5 (C–O). ^1H NMR (400 MHz, CDCl_3): $\delta = 1.72$ (s, 2 H, OH), 6.75–7.20 (m, 20 H, Ar–H), 7.78–7.94 (m, 14 H, Ar–H) ppm. ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 81.88$, 124.13, 126.76, 126.91, 127.12, 127.17, 127.19, 127.26, 127.34, 127.60, 127.61, 127.90, 127.94, 127.99, 128.23, 128.43, 129.84, 131.22, 131.69, 133.40, 143.94, 146.11, 146.89 ppm. $\text{C}_{52}\text{H}_{36}\text{O}$ (EI-MS): calcd. 692.2715; found 692. $\text{C}_{52}\text{H}_{36}\text{O}$: calcd. C 90.14, H 5.24; found C 89.76, H 5.10.

1,1,1',1'-Tetrakis(4-methylphenyl)-1,1'-(hexahelicene-2,15-diyl)dimethanol (10): A solution of 4-methylphenyllithium was prepared by addition, under Ar, of *p*-bromotoluene (359.2 mg, 2.1 mmol) in dry diethyl ether (4 mL) to lithium granules (29 mg, 4.2 mmol) in dry diethyl ether (4 mL), heating at reflux for 1 h, and cooling down. This solution was added over 30 min at –15 °C under Ar to a solution of **4** (158.6 mg, 0.3 mmol) in dry diethyl ether (8 mL). The mixture was stirred at room temp. for 1 h, heated at reflux for 7 h, cooled down, and quenched with ice water. The aqueous phase was extracted with diethyl ether, and the extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent under vacuum and purification by column chromatography (SiO_2 , eluent: di-

chloromethane, $R_f = 0.76$) yielded a light yellow solid (141.6 mg, 63%). M.p. 129 °C. IR (KBr): $\tilde{\nu} = 3472.5 \text{ cm}^{-1}$ (OH), 3065 (C–H, Ar), 2966.5 (C–H, aliph.), 1630.5 (Ar), 1232 (C–O). ^1H NMR (250 MHz, CDCl_3): $\delta = 1.68$ (s, 2 H, OH), 2.18 (s, 6 H, CH_3), 2.31 (s, 6 H, CH_3), 6.64 (d, $^3J_{\text{H,H}} = 8.66 \text{ Hz}$, 4 H, Ar–H), 6.67 (d, $^3J_{\text{H,H}} = 8.66 \text{ Hz}$, 4 H, Ar–H), 6.78 (d, $^3J_{\text{H,H}} = 8.07 \text{ Hz}$, 4 H, Ar–H), 6.90 (d, $^3J_{\text{H,H}} = 8.07 \text{ Hz}$, 4 H, Ar–H), 7.13 (d, $^3J_{\text{H,H}} = 8.42 \text{ Hz}$, 2 H, Ar–H), 7.14 (d, $^3J_{\text{H,H}} = 8.42 \text{ Hz}$, 2 H, Ar–H), 7.79 (d, $^3J_{\text{H,H}} = 8.59 \text{ Hz}$, 2 H, Ar–H), 7.84 (s, 2 H, Ar–H), 7.86 (d, $^3J_{\text{H,H}} = 8.59 \text{ Hz}$, 2 H, Ar–H), 7.88 (d, $^3J_{\text{H,H}} = 8.25 \text{ Hz}$, 2 H, Ar–H), 7.93 (d, $^3J_{\text{H,H}} = 8.25 \text{ Hz}$, 2 H, Ar–H) ppm. ^{13}C NMR (62.9 MHz, CDCl_3): $\delta = 21.59, 21.70, 81.91, 126.88, 127.27, 127.43, 127.50, 127.87, 127.99, 128.11, 128.27, 128.90, 129.21, 130.15, 131.50, 132.01, 133.69, 136.88, 143.56, 144.57, 145.00 \text{ ppm}$. $\text{C}_{56}\text{H}_{44}\text{O}_2$ (FAB-MS): calcd. 748.3341; found 748. $\text{C}_{56}\text{H}_{44}\text{O}_2$: calcd. C 89.81, H 5.92; found C 89.84, H 6.00. Enantiomeric separation (eluent: *n*-hexane/2-propanol, 3:1, 0.5 mL·min $^{-1}$, 6 bar): (*M*)-(–)-**10**: $t_r = 30.4 \text{ min}$, $k' = 1.36$; (*P*)-(+)-**10**: $t_r = 54.3 \text{ min}$, $k' = 3.22$; $\alpha = 2.37$, $R_s = 0.19$. $[\alpha]_D^{20} = 1851 \pm 100$ ($c = 0.03$, CHCl_3).

Crystallography: Information concerning the crystallographic data and structure determination of the five compounds is summarized in Table 2. Crystal structure analyses were performed under almost identical circumstances, so only an outline of these is given with indications of deviating procedures. Experimental data were obtained on automated four-circle diffractometers for all five crystals studied. Crystals were typically mounted on glass fibers, except for **4**, which was mounted in a capillary. All measurements were made at slightly varying room temperatures. Cell parameters were determined by least-squares fits of the setting angles of 25 strong reflections at medium θ angles. Graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used in all but one case (**4**, $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) with ω -2 θ scans. Minimum and maximum θ ranges are given individually in Table 2. The intensities of standard reflections were monitored regularly every hour. The intensities of the standard reflections remained constant within experimental error throughout the data collection. Total numbers of collected reflections, those of unique ones and their merging R values, and number of observed data are all contained in Table 2. No absorption corrections were applied. The initial structure models were given by direct methods^[41] and subsequent difference syntheses where needed. Adjustment of atomic parameters were lastly carried out by anisotropic full-matrix, least-squares refinement on F^2 for all non-hydrogen atoms.^[42] These gave the final R values given in Table 2. The maximum and minimum residual electron density values of the final difference maps indicated no unusual features. Hydrogen atomic positions were always calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the $U(\text{eq})$ values of the atoms to which they were bonded.

CCDC-202186 to -2021189 and CCDC-182891 contain the supplementary crystallographic data (excluding structure factors) for compounds **1**, **3**, **8**, **9**, and **4**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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- [38] Independent hits in this context are crystal structures that resulted from independent measurements or are of independent molecules of the asymmetric units. Supporting information for a list of the REFCODEs of the retrieved compounds together with their literature references are deposited and available upon request from either one of the authors (MC), or from the publisher.
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