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Preparation and Structural Properties of 7,8-Dioxa[6]helicenes and 7a,14c-Dihydro-7,8-dioxa[6]helicenes

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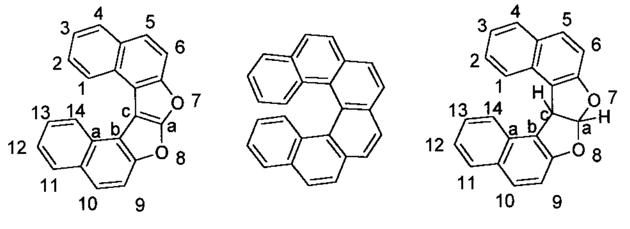
The potentially chiral 7,8-dioxa[6]helicenes **1**−**1c** have been prepared by oxidation of their precursors the 7a,14c-dihydro-7,8-dioxa[6]helicenes **3**. The crystal structure determination of **3b** *cis*-7a,14c-dihydro-3,12-dibromo-7,8-dioxa[6]helicene unambiguously confirms the *cis* configuration of the 7a,-14c hydrogens in compounds **3** as previously implied from NMR measurements and also shows that **3b** crystallizes in a chiral conformation in the solid state. Selective deuteration of the sterically crowded 1,14 positions of 7,8-dioxa[6]helicene **1** influenced the crystal structure. The deuterium labeled compound **D_2-1** exhibits a disordered structure, whereas **1** had been found to crystallize in a complex structure which can be described as an analogous partly ordered modulated superstructure. When dehydrogenation of compound **3** to obtain compound **1** was attempted, harsh synthetic conditions gave the unexpected halogenated compounds 5-chloro-7,8-dioxa[6]helicene **1c** and *cis*-7a,14c-dibromo-7,8-dioxa[6]helicene **3c**. Compounds **1d** and **3b** were identified by solving their crystal structure.

Introduction

7,8-Dioxa[6]helicene **1**[1] is a so-called six ring heterohelicene. The two oxygen atoms on the outer rim of the helix represent a π isoelectronic substitution of the −CH=CH− fragments characteristic of the parent benzenoid [6]helicene **2** (Figure 1). Aromatic and heteroaromatic helicenes are classes of molecules with a characteristic helical structure and a high specific optical rotation of the separated enantiomers.[2]

Our interest in compounds such as **1** arose from the fact that the apparent contraction of the periphery caused by the atomic substitution could lead to a low inversion barrier of the “opened” horseshoe, i.e., the marginal possibility of a helical geometry of compound **1**. We had prepared compound **1** earlier and solved the very complicated crystal structure[3] which indeed confirmed the expectation of easy structural interconversion as we observed eight different enantiomers (three P and three M helices and two disordered molecules) and a low inner pitch[4] of 1−1.3 Å of the individual helices. In accordance with this finding it was not possible to isolate enantiomers due to rapid interconversion in solution as discussed below. Previously, the sulfur analogue of compound **1**, 7,8-dithia[6]helicene, had been prepared by a completely different route, but no structural information was given.[5]



1 **2** **3**

Figure 1. Structures of **1**, **2**, and **3**.

Compound **1** was first obtained by oxidation of 7a,14c-dihydro-7,8-dioxa[6]helicene **3** with DDQ or in partial sunlight with NBS.[3] Both procedures proved difficult to control in terms of reproducible yields and also gave the unexpected compounds **1c** or **3c,** respectively. We have worked out a reproducible oxidation process (see Scheme 1). To investigate the effect on the helicity of compound **1** of sterical effects of substituents in the 1,14 positions, the 1-mono- and 1,14-dideuterated 7,8-dioxa[6]helicenes (**D-1** and **D_2-1**) were prepared.

The starting materials 7a,14c-dihydro-7,8-dioxa[6]-helicene **3** are readily obtained as was first reported by Dischendorfer[6] by a regioselective double condensation of glyoxal with 2-naphtholes under acidic conditions. This condensation reaction under acidic or basic conditions has been further investigated by Kito and co-workers[7−9] and Coxworth.[10] The dihydro compound, **3**, has been assumed

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(1) In the text we use the simple names 7,8-dioxa[6]helicenes and 7a, 14c-dihydro-7,8-dioxa[6]helicenes for the compounds of type **1** and **3**. In the Experimental Section, correct IUPAC names are used throughout.

(2) Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, 1271.

(3) Krebs, F. C.; Faldt, A.; Thorup, N.; Bechgaard, K. *Cryst. Eng.* **1999**, 6.

(4) The pitch corresponds to the increment of the helix per turn, see: Navaza, J.; Tscoucaris, G.; le Bas, G.; de Rango, C. *Bull. Soc. Chim. Belg.* **1979**, *88*, 863.

(5) Dopper, J. H.; Oudman, D.; Wynberg, H. *J. Am. Chem. Soc.* **1973**, *95*, 3692.

(6) Dischendorfer, O. *Monatsh. Chem.* **1940**, *73*, 45.

(7) Kito, T.; Yoshinaga, K.; Yamaye, M.; Mizobe, H. *J. Org. Chem.* **1991**, *56*, 3336.

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(9) . Fan, X.; Yanai, T.; Okazaki, H.; Yamaye, M.; Mizobe, H.; Kosugi, Y.; Kito, T. *J. Org. Chem.* **1995**, *60*, 5407.

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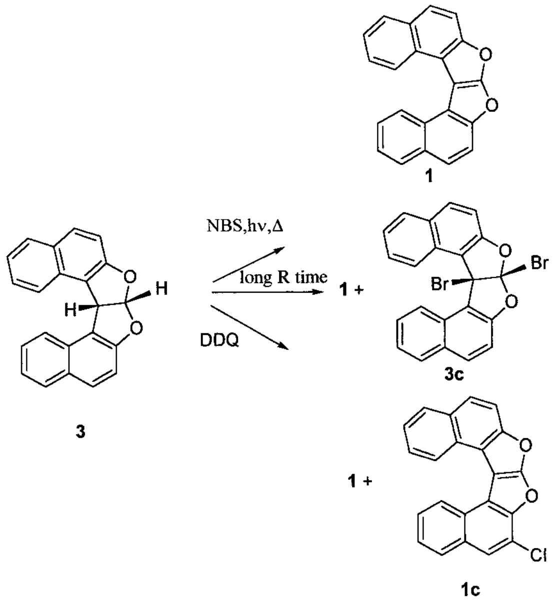
Scheme 1. Preparation of 1, 1c, and 3c



to have the *cis* geometry of the 7a,14c hydrogens following an interpretation of the NMR spectra,[7–9] which is ambiguous. These compounds are generally difficult to crystallize as single crystals, but compound **3b** gave crystals of sufficient quality. The X-ray crystal structure determination did confirm the previously assigned *cis* geometry of the 7a,14c hydrogens. Interestingly compound **3b** is also chiral in the solid state and the geometrical interconversion of the enantiomers was investigated with model calculations.

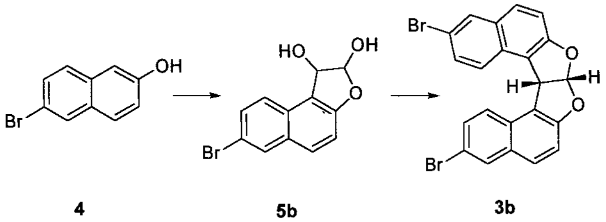
Results and Discussion

Syntheses. The new 7,8-dioxa[6]helicenes **1** are obtained by dehydrogenation of 7a,14c-dihydro-7,8-dioxa[6]helicenes (see Scheme 1). We originally obtained compound **1** in very low yield together with the unexpected compound **1c** by treating compound **3** with DDQ. Reasonable but varying yields of pure **1** were obtained by treating compound **3** with NBS in sunlight. Finally, a reproducible procedure using NBS and controlled UV radiation was used. We suggest that the reaction proceeds by a Wohl–Ziegler radical bromination of the "benzylic" 14c position in compound **3** and derivatives followed by elimination of hydrogen bromide. We anticipate an E_1 type elimination because the X-ray crystallographic investigation of compound **3b** has shown that the hydrogens of the 7a and 14c positions are in a *cis* geometry (see below).

Unexpectedly, after carrying out the UV irradiation of compound **3** for a prolonged amount of time with an excess of NBS, the cis 7a,14c dibrominated compound, **3c**, was isolated in 21% yield. The *cis* dibromo geometry and the identity of **3c** were established by solving the X-ray crystal structure.

As mentioned above, an alteration of the substituents in the 1 and 14 positions of the "inner rim" of the helix of compound **1** may have structural effects. The 1-deuterated compound **D-1** and the 1,14-dideuterated compound **$D_2$1** were thus prepared from deuterated precursors.

Scheme 2. Preparation of 3b



A standard procedure for obtaining the symmetrical precursor dihydrohelicenes such as **3**,**3b** and **D_2-3** has been to treat the appropriate 2-naphthol with acid and glyoxal in a suitable solvent.[6,10] This procedure did not work when attempting to prepare compound **3b**. Compound **3b** was obtained by combining an initial base-catalyzed condensation[9] of glyoxal with 6-bromo-2-naphthol **4** to yield a mixture of 7-bromo-1,2-dihydronaphtho[2,3-*b*]furan-1,2-diol **5b** and compound **4**. This crude mixture on treatment with acid gave the desired compound **3b** (see Scheme 2).

Similarly, when preparing the unsymmetrical compounds **D-3**, we used base-catalyzed condensation of 2-naphthol with glyoxal to prepare compound **5**.[9] Compound **5** was purified by repeated recrystallization to deplete remaining 2-naphthol that could contaminate the desired unsymmetrical compounds. When pure compound **5** was treated with 8-deuterio-2-naphthol**,** the unsymmetrical compounds **D-3** were obtained.

Crystal Structures of the Helicenes 1. The crystal structure of compound **1** has been reported previously.[3] Compound **1** forms stacks of eight different molecular conformations in the asymmetric unit of the solid state. The stacks are organized as homochiral triads of P or M molecules with the triads separated by disordered molecules. The monochlorinated helicene **1c** was obtained as a byproduct from DDQ dehydrogenation of **3** when attempting to prepare **1**. Compound **1c** is the only other helicene of this series for which we have succeeded in solving the crystal structure. The result is quite significant in the discussion of the parent helicene that exhibits very unusual structural properties.[3] The parent helicene **1** exhibits varying pitch of the helices and some disorder, whereas compound **1c** is perfectly ordered (see Table 1). Both compounds crystallize in polar space groups. While enantiomeric excess and a subsequent permanent dielectric polarization in the parent compound **1** are theoretical possibilities, the space group of the crystals of **1c** (*Pna*2_1) gives rise to definite permanent dielectric polarization and, in principle, pyroelectric properties.

The fact that the helicenes are in dynamic equilibrium in solution and that the crystal structure of **1** shows a different degree of helicity in the solid state led us to attempt an investigation of the induction of helicity by substitution in the 1,14 positions. We chose atoms exhibiting only subtle differences in sterical demand when compared to hydrogen and prepared the mono- and dideuterated compounds **D-1** and **D_2-1.** Due to the experimental difficulties described below we concentrated our efforts on a comparison between **1** and **D_2-1**.

The X-ray data collection of **D_2-1** surprisingly gave a much smaller unit cell than found for compound **1**[3] (see Table 2). Also the powder diffraction patterns of **1** and **D_2-1** showed distinct differences as seen in Figure 3. When data were collected in the mentioned smaller unit cell and the structure was solved, it was difficult to obtain

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(10) Coxworth, E. C. M. *Can. J. Chem.* **1967**, *45*, 1777.

Table 1. Crystallographic Data for 5-Chloro-7,8-dioxa[6]helicene

compound	**1c**
formula	$C_{22}H_{11}O_2Cl$
formula wt	342.76
crystal system	orthorhombic
space group	$Pna2_1$
Z	4
a, Å	16.496(3)
b, Å	15.565(3)
c, Å	5.9747(12)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1534.1(5)
ρ, g cm^3	1.484
crystal dimensions, mm	0.38 × 0.15 × 0.075
type of radiation	Mo Kα
μ, cm^{-1}	0.261
T, K	120(2)
number of reflections	15861
unique reflections (with $I > 2\sigma$)	2437
R_{int}	0.0550
$R(F)$, $R_w(F^2)$ all data	0.0393, 0.0942

Table 2. A List of Selected Miller Indices and 2θ-angles for the Two Helicenes Based on Single Crystal Data[a]

label (see Figure 4)	Miller index		2θ-angle	
	1	**D$_2$-1**	**1**	**D$_2$-1**
A	2 0 0	1 0 0	10.492	10.532
B	0 0 2	0 0 2	12.090	11.731
C	0 8 2	0 1 2	19.506	19.438
D	4 0 0	2 0 0	21.066	21.160
E	0 8 3	0 1 3	23.823	23.534
F	−2 8 3	−1 1 3	24.100	24.076
G	−2 8 4	−1 1 4	28.475	28.281

[a] Cell parameters at 295 K, $\lambda = 1.5418$ Å (a, b, c, α). **1**: 17.436 Å, 46.449 Å, 15.145 Å, 104.81°. **D$_2$-1**: 8.630 Å, 5.735 Å, 15.503 Å, 103.32°.

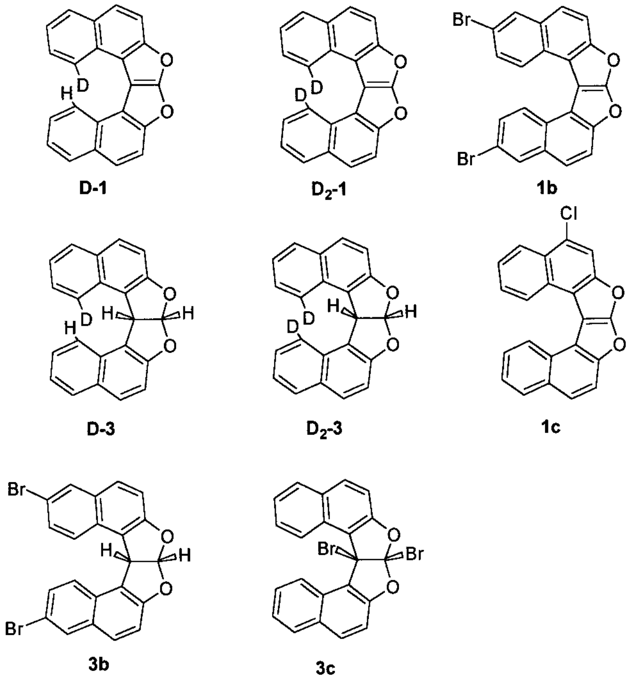

Figure 2. Structures of the 7,8-dioxa[6]helicenes and dihydro precursors.

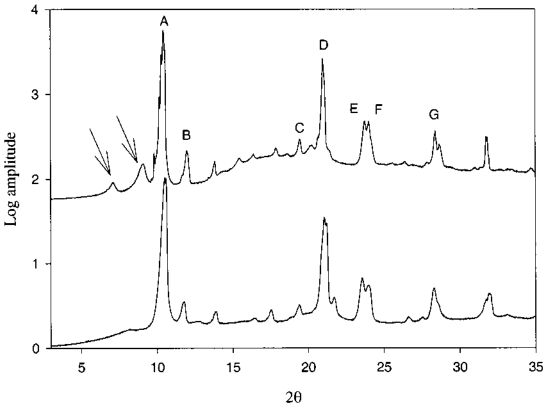

Figure 3. The observed powder diffractograms for **1** (above) and **D$_2$-1** (below). While the diffractograms are quite similar, there is a noticeable distinction at low angles (indicated by arrows) where only the parent helicene **1** shows diffraction peaks originating from the superstructure.

a good model. The best model for **D$_2$-1** was a disordered model with both P and M molecules superimposed on each other and placed on a center of symmetry thus suggesting an average of the structure observed for **1**. Attempts were made both at 120 K and at 295 K with the same structural result being obtained for both temperatures albeit with differences in the crystallographic details (number of observed reflections, cell parameters, etc.).

The calculated powder diffraction patterns based on the full "superstructure" of **1** and on the disordered model for **D$_2$-1** corresponded well with the observed powder diffraction patterns given in Figure 3 (and Table 2). A further comparison of Weissenberg photographs of **1** and **D$_2$-1** showed that while the superstructure reflections are very strong for the parent helicene, they are extremely weak for **D$_2$-1** and only observed after a long exposure time. Their actual presence however indicated that **D$_2$-1** should exhibit the same superstructure properties as **1** but with a smaller degree of correlation. We finally realized that even compound **1** itself could also be made to exhibit the disordered behavior of the deuterated analogue if recrystallized from CCl_4. The appearance of the superstructure of compound **1** is thus ascribed to a thermal annealing effect that is only observed upon slow cooling from toluene or by sublimation in a sealed tube. In contrast, the deuterated compounds always failed to give crystals with a fully developed superstructure even under annealing conditions.

Structural and Computational Results of *cis*-Dihydrohelicenes 3, 3b, and 3c. As mentioned in the introductory part, the 7a,14c-dihydro-7,8-dioxa[6]helicenes such as compound **3** and other dihydrofurofuranes are expected to have a *cis* configuration of the 7a,14c hydrogens and possibly a mirror plane in the molecule. These assumptions were supported by NMR spectra in solution and by MNDO calculations.[9,10] The NMR results are not conclusive because the average dihedral angles 0° and 180° for the *cis* and *trans* conformation, respectively, imply the same proton−proton coupling constants of 5−6 Hz for the two configurations. As seen in Figure 4, which shows the X-ray crystal structure of **3b**, the cis configuration of the hydrogens in the 7a,14c positions of compound **3b** was finally unambiguously experimentally established.

When the crystal structure of **3b** was solved at temperatures of both 120 and 373 K, it however became apparent that the molecule was chiral in nature in the

Table 3. Crystallographic Data for the 3,12-Dibromo-dihydro-7,8-dioxa[6]helicenes

compound	**3b** (120 K)	**3b** (373 K)	**3c**
formula	$C_{22}H_{12}Br_2O_2$	$C_{22}H_{12}Br_2O_2$	$C_{22}H_{12}Br_2O_2$
formula wt	468.14	468.14	468.14
crystal system	orthorhombic	orthorhombic	monoclinic
space group	$Pna2_1$	$Pna2_1$	$P2_1/c$
Z	4	4	4
a, Å	11.337(2)	11.378(2)	10.167(2)
b, Å	35.031(7)	35.087(7)	26.152(5)
c, Å	4.2090(8)	4.3040(9)	7.0090(14))
α, deg	90	90	90
β, deg	90	90	109.66(3)
γ, deg	90	90	90
V, Å^3	1671.6(6)	1718.2(6)	1755.0(6)
ρ, g cm^3	1.860	1.810	1.772
crystal dimensions, mm	0.33 × 0.03 × 0.03	0.33 × 0.03 × 0.03	0.35 × 0.18 × 0.05
type of radiation	Mo Kα	Mo Kα	Mo Kα
μ, cm^{-1}	4.864	4.732	4.633
T, K	120(2)	373(2)	120(2)
number of reflections	16778	17603	13311
unique reflections (with $I > 2\sigma$)	2843	1822	2631
R_{int}	0.0700	0.1058	0.0412
$R(F)$, $R_w(F^2)$ all data	0.0352, 0.0744	0.0482, 0.1008	0.0405, 0.1120

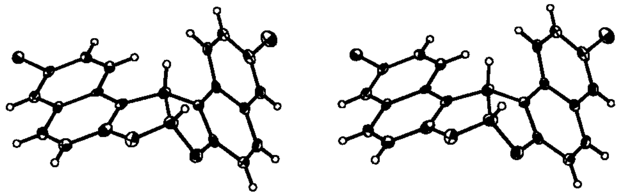

Figure 4. A stereoview of compound **3b** (120 K data) as an ORTEP drawing emphasizing the cis conformation and the absence of a molecular mirror plane.

solid state at both temperatures as shown in Figure 4 (see also Table 3). We then reinvestigated the calculated structure of **3**[10] and the structure of **3b** by computational methods (see Experimental Section for details). Molecular mechanics optimizations show that the isolated (gas phase) molecule **3** is chiral. Ab initio calculations using the local density approximation also find the chiral state to be lowest in energy, but virtually no energy difference exists between the molecule in the chiral conformation and in the C_s-symmetric conformation. The ab initio calculations have been performed on structures forced to be either chiral or of C_s-symmetry. All calculations are performed on isolated molecules. The effects of polarization in the solvent used (CCl_4) are minor because the polarity of the molecule only changes slightly when it crosses the transition barrier. The COSMO polarization model with tetrachloromethane as solvent only stabilizes the enantiomeric forms 0.3 kcal/mol with respect to the transition state.

The potential surface for interconversion between the two enantiomers of the chiral conformation of compound **3** was then calculated with molecular mechanics. The energy minimum occurs for the two enantiomers of the chiral conformation, whereas the transition state adopts the C_s-symmetric conformation. The interconversion barrier is less than 3 kcal·mol^{-1}.

The potential surface for interconversion between enantiomers for **3b** is similar to that of **3** but is more relevant for comparison with the actual crystal structure found for compound **3b**. The potential surface is calculated by varying the two dihedral angles defined in Figure 5. The structure is minimized with the two dihedrals fixed to given values. All other bond lengths, bond angles, and dihedrals are free.

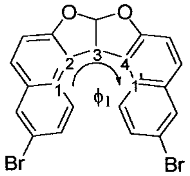

Figure 5. Definition of dihedrals ϕ_1 and ϕ_2 describing the interconversion of the two enantiomers. The dihedral ϕ_1 (atoms 1−2−3−4) is driven between values of 65° to 100°. The dihedral ϕ_2 is obtained through a reflection of ϕ_1 (atoms 1′−4−3−2) and is driven from −100° to −65°.

The minimized energies are plotted against the two dihedrals in Figure 6.

The calculated potential barrier is 2.5 kcal/mol. In the X-ray crystal structure, ϕ_1 and ϕ_2 take the values 66.6° and −88.5°. The fully optimized structure corresponding to the enantiomer minimum shows values of 62.8° and −96.6°. When the molecule is optimized taking into account the full crystal structure ($Pna2_1$), the angles 65.5° and −93.8° are found. The C_s state is a transition state with one negative vibrational frequency. The zero-point vibrational energy for the two states are virtually equal. Our model calculations on a high level do confirm the potentially chiral conformation's for compounds such as **3** and **3b**. The X-ray structural results confirm that the chiral structure can actually freeze out in the solid state.

Thus the experimental and theoretical findings for compounds **1** and **3** confirm the anticipated results that the helicenes **1** have low inversion barriers and that chiral conformations can be observed in the solid state. It was found that their precursors the *cis* 7a,14c- dihydro compounds, as exemplified by **3b**, are also prochiral and that similar to the helicenes they can also crystallize in chiral conformations.Finally, the X-ray crystal structure determination of the *cis*-dibromo helicene **3c** implies a chiral solid-state structure even of this compound (see Table 3).

Experimental Section

Calculational Methods. Potential surface calculations and energy minimizations were done using molecular mechanics with the CFF91 force field.[11] Ab initio calculations were done using the local density approximation (LDA). The generalized

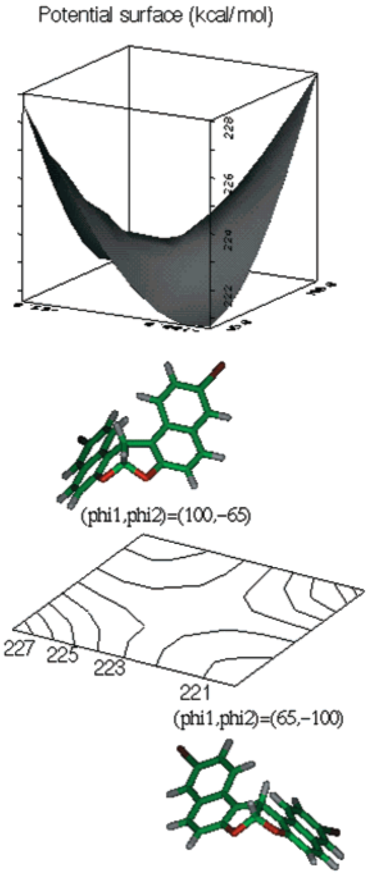

Figure 6. Potential surface for interconversion between enantiomeric forms of **3b**. The potential energy is plotted as a function of two dihedral angles, which defines the conformational path between the two enantiomers. The lower curve is a contour map of the potential surface shown in the upper curve. The energy is given in kcal·mol^{-1} on both curves. The dihedral angles corresponding to the conformations of the two enantiomeric forms are located in the corners of the contour map. The corresponding conformations are depicted in the figure.

gradient approximation by Perdew and Wang[12] and a double numeric polarization (DNP) basis[13] was used. Effects of solvent were evaluated using the COSMO polarization model.[14]

Crystallographic Methods. Single-Crystal Data. General crystallographic details can be found in Tables 1 and 3. Crystals of **1d**, **3b**, **3c,** and **D$_2$-1** were mounted on glass capillaries using epoxy glue. Data were collected on a Siemens SMART platform diffractometer with a CCD area sensitive detector. Absorption corrections were made for compounds **1d**, **3b**, **3c**, and **D$_2$-1** using SADABS.[15] Direct methods for the structure solution and full-matrix least-squares refinements were used for all compounds. For all compounds, hydrogen atoms were included in calculated positions. The programs used were SMART, SAINT, and SHELXTL from Siemens.[16,17] All structures were checked for overlooked symmetry using MISSYM and checked for voids in PLATON.[18]

Powder Data. Powder diffraction patterns were obtained for compounds **1** and **D$_2$-1** on a Phillips PW 1820 powder diffractometer.

Synthesis. 7,8-Dioxa[6]helicene (1), IUPAC Name Naphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan. A 150 mL flask equipped with a Teflon-coated stirring bar, a reflux condenser, and a 9W Pen-Ray UV lamp protected by a quartz tube was charged with 7a,14c-Dihydro-naphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan, **3**[6] (1.88 g, 6.06 mmol), and 100 mL of purified, deoxygenated CCl$_4$. Heating to reflux resulted in almost total dissolution of the substrate. NBS (1.54 g, 8.65 mmol) was added, and the mixture was irradiated while bubbling a slow Ar stream through the mixture and with occasional heating. After 2−4 h, no more HBr was evolved. After the solvent was cooled, it was evaporated in a vacuum. The isolated moist solid was treated with a hot mixture of water (80 mL) and toluene (100 mL) under vigorous stirring. Evaporation of the organic phase yielded tan colored crystals, which, after recrystallization from CHCl$_3$, gave **1** in 35% yield. Mp 244−246 °C.[3]

1-Deutero-naphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (D-1) and 1,14-Dideutero-naphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (D$_2$-1). Compounds **D-3** and **D$_2$-3** were dehydrogenated as described for compound **1** in similar yield. ^{1}H NMR and MS (GC−MS) revealed no H/D exchange during the preparation of the deuterated precursors to **D-1** and **D$_2$-1**.

D-1. Mp: 245−246 °C.[3] ^{1}H NMR (250 MHz, 300 K, CDCl$_3$): 7.60 (t, 2H, J = 7.5 Hz,), 7.74−7.80 (m, 6H), 8.05 (d, 2H, J = 8.2 Hz,), 9.08 (d, 1H, J = 8.4 Hz,). MS (GC−MS): 309 (80), 281 (29), 251 (61), 125 (100). **D$_2$-1.** Mp: 244−246 °C.[3] ^{1}H NMR (250 MHz, 300 K, CDCl$_3$): 7.58 (t, 2H, J = 7.5 Hz), 7.74−7.79 (m, 6 H), 8.04 (d, 2H, J = 8.2 Hz,). MS (GC−MS): 310 (100), 282 (28), 252 (65), 126 (70).

3,12-Dibromo-naphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (1b). Compound **3b** (2.24 g, 4.78 mmol) and NBS (1.12 g, 6.30 mmol) were suspended in CCl$_4$ (80 mL) and irradiated for 5 h. The mixture was evaporated to dryness and stirred with a hot mixture of water (100 mL) and toluene (100 mL). The phases were separated, and the aqueous phase was extracted with another portion of hot toluene (100 mL). The combined organic phases were washed with hot water (50 mL) and evaporated to dryness. After recrystallization from CHCl$_3$, compound **1b** was obtained as thin, white needles in 21% yield. Mp: 260−264 °C, subl. ^{1}H NMR (250 MHz, 348 K, C$_6$D$_6$): 7.34 (d, 2H, J = 9.1 Hz), 7.49 (d, 2H, J = 9.0 Hz), 7.73 (dd, 2H, J = 8.9 Hz, 2.0 Hz), 8.07 (d, 2H, J = 2.0 Hz), 8.73 (d, 2H, J = 9.0 Hz). MS (GC−MS): 466 (10) (diBr pattern), 385 (6), 278 (17), 250 (60), 125 (100). Anal. Calcd for $C_{22}H_{10}Br_2O_2$: C, 56.69; H, 2.16. Found: C, 56.39; H, 2.22.

5-Chloro-naphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (1c). Compound **1c** was obtained in very low yield by boiling equimolar amounts of compound **3** and DDQ in 1,2-dichlorobenzene for 48 h. The product obtained was a mixture of compounds **1** and **1c**. Preparative HPLC on reverse phase nucleosil (C18, 5μ) gave a few crystals(1−2%) of **1c** , whose identity was determined by solving the crystal structure. No mp recorded. ^{1}H NMR (313 K, CDCl$_3$): 7.1 (s, 1H), 7.61 (t, 1H, J = 8.4 Hz), 7.68−7.86 (m, 5H), 7.94 (s, 1H), 8.05 (d, 1H, J = 8.4 Hz), 8.47 (d, 1H, J = 8.4 Hz), 9.00 (d, 1H, J = 8.5 Hz), 8.05 (d, 1H, J = 8.3 Hz).

1-Deutero-7a,14c-dihydronaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (D-3). Pure compound **5**[9] (recrystallized from CHCl$_3$) (1.80 g, 8.17 mmol) and 8-D-2-naphthol[19] (1.00 g, 6.89 mmol) were dissolved in DME (15 mL). Methanesulfonic acid (4 mL) was added to the solution over 30 min. After the mixture was stirred (1 h), water was added (40 mL) and the mixture was filtered. The crystals obtained where thoroughly washed with water and MeOH yielding white crystals of **D-3** (1.52 g, 71%). Mp: 235−238 °C.[6,10] ^{1}H NMR

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[11] Computational results were obtained using software from Molecular Simulations Inc. Molecular mechanics calculations were done with the Discover program. Ab initio calculations were done with the DMOL(3) program in Cerius2, version 4.0. Graphical displays were printed out from the InsightII molecular modeling interface.

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(300 K, CD_2Cl_2): 5.61 (d, 1H, $J = 6.0$ Hz), 7.12 (d, 1H, $J = 6.0$ Hz), 7.22 (d, 2H, $J = 8.8$ Hz), 7.34 (t, 2H, $J = 7.5$ Hz), 7.50−7.56 (m, 2H), 7.76 (d, 2H, $J = 8.8$ Hz), 7.83 (dd, 2H, $J = 8.3$ Hz $J = 1.1$ Hz), 8.30 (d, 1H, $J = 8.4$ Hz). MS (GC−MS): 311 (100), 282 (53), 253 (32), 126 (34). Anal. Calcd for $C_{22}H_{13}DO_2$: C, 84.87; H/D, 4.86. Found: C, 84.49; H/D, 4.75.

1,14-Dideutero-7a,14c-dihydronaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (D_2-3). D_2-3 was prepared from pure 8-D-2-naphthol[19] according to the literature procedures for the preparation of **3** from 2-naphthol[6] in 56% yield after recrystallization from acetone. Mp: 235−238 °C.[6,10] ^{1}H NMR (300 K, CD_2Cl_2): 5.67 (d, $J = 6.0$ Hz, 1H), 7.17 (d, 1H, $J = 6.0$ Hz), 7.27 (d, 2H, $J = 8.8$ Hz), 7.36−7.42 (m, 2H), 7.58 (d, 2H, $J = 6.4$ Hz,), 7.82 (d, 2H, $J = 8.8$ Hz), 7.88 (dd, 2H, $J = 8.2$ Hz $J = 1.2$ Hz). MS (GC−MS): 312 (100), 283 (48), 254 (29), 127-(48). Anal. Calcd for $C_{22}H_{12}D_2O_2$: C, 84.59; H/D, 5.16. Found: C, 84.50; H/D, 4.69.

***cis*-7a,14c-Dihydro-3,12-dibromonaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (3b) and Intermediate 7-Bromo-1,2-dihydronaphtho[2,3-*b*]furan-1,2-diol (5b).** A 250 mL round-bottom flask was charged with KOH (2.69 g, 0.048 mol) dissolved in water (100 mL). After the mixture was purged with Ar for 15 min, 6-bromo-2-naphthol **4** (10.48 g, 0.047 mol) was dissolved by heating the flask under vigorous stirring, and the solution was transferred to a dropping funnel. Another 250 mL round-bottom flask was charged with 40% aqueous glyoxal solution (31 mL). The naphtholate solution was added dropwise over 45 min under vigorous stirring and the mixture left overnight. The mixture was filtered, and the collected light tan crystals were washed thoroughly with water. Some toluene was added, and evaporation of toluene and water using a rotary evaporator yielded a ca. 1:1 mixture containing only 6-bromo-2-naphthol **4** and 7-bromo-1,2-dihydronaphtho-[2,3-b]furan-1,2-diol **5b** (11.08 g). The ratio was estimated via the GC−MS total ion chromatogram. The mixture was dissolved in DME (200 mL), and under vigorous stirring concentrated H_2SO_4 acid (15 mL) was added dropwise causing white needles to precipitate from the solution. The mixture was left overnight. Filtration gave white needles which were washed with water, methanol, and ether and dried in a vacuum oven yielding *cis*-7a,14c-dihydro-3,12-dibromo -naphtho[2,1-b]naphtho[1′,2′:4,5]furo[3,2-d]furan **3b** in 59% yield. Single crystals for X-ray were grown by sublimation at 180 °C in a sealed evacuated tube. Mp: subl above 200 °C. ^{1}H NMR (250 MHz, 372 K, DMSO-d_6): 5.94 (d, 1H, $J = 5.1$ Hz), 7.32−7.36 (m, 3H), 7.68 (dd, 2H, $J = 9.1$, 1.6 Hz), 7.87 (d, 2H, $J = 8.9$ Hz), 8.16 (d, 2H, 1.6 Hz), 8.30 (d, 2H, $J = 8.7$ Hz). MS (GC−MS): 468 (13, diBr pattern), 439 (3), 359 (6), 279 (18), 250 (53), 139 (92), 125 (100). Anal. Calcd for $C_{22}H_{10}Br_2O_2$: C, 56.44; H, 2.58. Found: C, 56.17; H, 2.30.

7a,14c-Dibromonaphtho[2,1-b]naphtho[1′,2′:4,5]furo[3,2-d]furan (3d). The dehydrogenation of compound **3** was carried out for a prolonged time (approximately 5 h) and with a 50% molar excess of NBS, yielding the dibrominated compound, **3d**, in 21% yield after recrystallization from $CHCl_3$. Compound **3d** has a GC−MS spectrum identical to that of compound **1** but was finally identified as compound **3d** by solving the X-ray structure. Mp: 190−195 °C subl, decomp. ^{1}H NMR (250 MHz, 300 K, $CDCl_3$): 7.24 (d, 2H, $J = 8.9$ Hz), 7.47 (t, s.o., 2H), 7.68 (t, s.o., 2H), 7.88 (d, 4H, $J = 8.6$ Hz), 9.02 (d, 2H, $J = 8.6$ Hz). Anal. Calcd for $C_{22}H_{12}Br_2O_2$: C, 56.44; H, 2.58. Found: C, 56.64; H, 2.72.

Supporting Information Available: Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths, and bond angles for compounds **1c**, **3b**, and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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