Novel Redox-Active Cyclophanes Based on 3,3′-Biindolizines: Synthesis and Chirality

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Received August 1, 1995[⊗]

The first compounds of a new series of redox-active cyclophanes were prepared by dehydrocyclization of bridged indolizines of type **1.** The bridged dipyridino-compounds **2a** and **2b** obtained by reaction of 2 mol of lithiated α-picolines with dihalides were used as starting materials. Subsequent treatment of **2a**,**b** with 2 mol of α-bromo ketones gave quaternary pyridinium halides. Ring closure in an alkaline medium (Chichibabin reaction) yielded the starting material for the synthesis of the macrocycles. Oxidative C−C coupling gave the diastereomeric cyclophanes of type **3**. In all cases one pair of the enantiomers was obtained in excess. CV-investigations have shown that the main products are reversible redox systems. To clarify their conformations, compounds **3c** , **3d/1**, and **3d/2** were subjected to X-ray analysis.

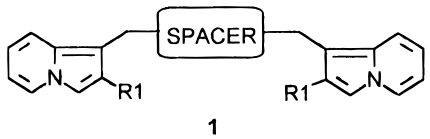
Introduction

Electroactive host or guest compounds are key components for the formation of electrochemically controllable, self-assembled structures. For example, the synthesis of switchable molecular shuttles based on a redox-active guest were reported by A. E. Kaifer.[1] We are interested in the synthesis of switchable macrocyclic host compounds using biindolizines as the electroactive unit. As part of a study directed toward synthesis of such cyclophanes, we recently reported the preparation of a bridged indolizine of type **1**.[2] Upon oxidation, indolizines easily undergo dimerization by C−C-bond formation at their 3-positions.[3] On oxidation of compound **1** (spacer = 1,4-C_6H_4; $R^1 = CH_3$), we observed mixtures of dehydro-dimers and -trimers and higher dehydro-oligomers.[4] The tendency toward formation of higher oligomers is probably due to the rigid spacer group. Use of more flexible spacer groups of sufficient lengths would possibly suppress oligomerization and favor intramolecular formation of a monomer of the ansa-type **3**.

It appeared necessary to work out a new synthesis which would allow preparation of biindolizines with broad variation of the spacer group. We wish to report here on the synthesis and dehydrocyclizations of bridged indolizines linked by dodecamethylene and by 3,6,9-trioxaundecamethylene groups.

Results and Discussion

The bridged indolizines **1** were prepared in the following way: 2 mol of lithiated α-picoline was reacted with 1,12-dibromododecane or bis[2-(2-chloroethoxy)ethyl] ether to give the bis-pyridines **2a** and **2b**, respectively (Figure 2). Subsequent reaction of the crude **2a** or **2b** with either bromoacetone or ω-bromoacetophenone according to Chichibabin[5] yields the bridged indolizines **1a**−**d**. Modeling (Hyperchem) suggested that the spacers have sufficient lengths to favor an intramolecular reaction.



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SPACER: p -C_6H_4-; -$(CH_2)_{10}$-; -$(CH_2$-O-$CH_2)_3$-

Figure 1. Bridged indolizines.

In fact, subsequent treatment of **1a**−**d** with potassium hexacyanoferrate proceeds smoothly with intramolecular oxidative coupling to give the desired products **3a**−**d** (Figure 3).

The new bond between the two indolizines in **3** displays axial chirality due to hindered rotation around this bond. Additionally, both indolizine-subunits in **3** define planes of chirality due to the ansa character of the molecule.

Thus, the question arises, to what degree is the geometry of the two indolizines fixed in **3**? Provided that free rotation around the central bond is sufficiently hindered, compounds **3a**−**d** should contain three independent elements of chirality (one axis, two planes); so we looked first for axial chirality of unbridged 3,3′-biindolizines. It was in fact possible to resolve 3,3′-bi-(1,2-diphenylindolizine) and 3,3′-bi(2-methyl-1-phenyl-indolizine) by means of chiral HPLC. This observation was surprising in the case of the latter compound, which bears only methyl groups near the axis of chirality. Optical activity was retained even after 1 h heating in boiling xylene.

Three elements of chirality could give rise to four diastereomers. In the case of the bridged compound **3**, this number is reduced to three due to the equivalency of two of them. Crude cyclophane **3d** could be separated by flash chromatography to give two crystalline diastereomers. Both pairs of enantiomers were characterized by X-ray analysis (structures **3d/1** and **3d/2**). Compound

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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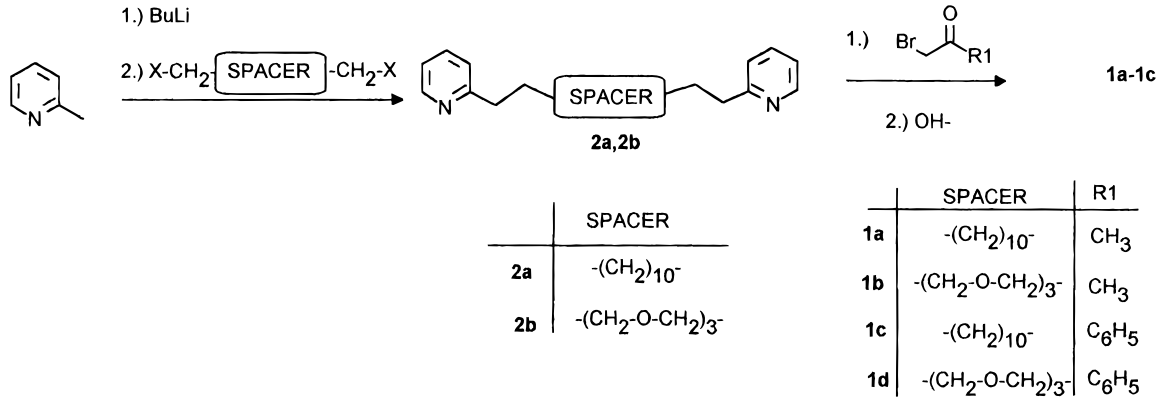
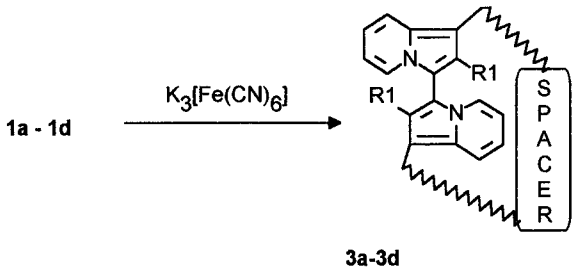


	SPACER
2a	$-(CH_2)_{10}-$
2b	$-(CH_2-O-CH_2)_3-$

	SPACER	R1
1a	$-(CH_2)_{10}-$	CH_3
1b	$-(CH_2-O-CH_2)_3-$	CH_3
1c	$-(CH_2)_{10}-$	C_6H_5
1d	$-(CH_2-O-CH_2)_3-$	C_6H_5

Figure 2. Synthesis of bridged indolizines.



	SPACER	R1
3a	$-(CH_2)_{10}-$	CH_3
3b	$-(CH_2-O-CH_2)_3-$	CH_3
3c	$-(CH_2)_{10}-$	C_6H_5
3d	$-(CH_2-O-CH_2)_3-$	C_6H_5

Figure 3. Synthesis of cyclophanes by intramolecular dehydrocyclization.

3d/1 is favored by a factor of 5:1. The bridge is positioned between the two phenyl groups in **3d/1**, while it is positioned between the phenyl group and the indolizine group of the second part of the molecule in the diastereomer **3d/2**.

Further evidence for the geometry of these compounds has been obtained by NMR-spectroscopy. In contrast to the situation of the main product **3d/1**, the two indolizine systems in **3d/2** differ in their spacial relation to the spacer bridge of the cyclophane system. On the central C-C-bond, also, a half-rotation is impossible. Therefore the indolizine systems in **3d/**2 are not equivalent. Due to this, **3d/2** shows twice as many signals in the ^{13}C-NMR as does **3d/1**. The enantiomers of the cyclophanes **3d/1** and **3d/2** were separated by HPLC using Chiralcel OD columns. The CD spectra of the M and P enantiomers of **3d/1** and **3d/2** are shown in Figure 4. The spectra confirm the existence of enantiomers of the same chiral molecule. The third possible diastereomer **3d/3** was detected only by HPLC and shows a similar UV-spectrum in comparison to **3d/1.**

According to preliminary experiments, an analogous situation can be expected for **3a**−**c**. Each of them could be separated into enantiomers on a chiral column. Compound **3c**, the main product of cyclization of **1c**, was also subjected to X-ray analysis. It was shown that the geometry of **3c** corresponds to that of **3d/1**. Only one diastereomer could be found upon cyclization of **1a**.

The different geometry of the diastereomers is important for the redox behavior of the ansa-compounds. We expected that the oxidative formation of a central double bond, which would orient both indolizine systems into a common plane, should be possible only in the *E*-form. The angle between the two indolizines is 62° in **3d/1** according to X-ray analysis and thus corresponds to the calculated angle of simple, unbridged 3,3′-biindolizines. Cyclic voltammetry revealed **3d/1** to be a stable and reversible redox system similar to unbridged biindolizines.[2,4,6] The torsion angle between the two indolizines in **3d/2** is 108° in the crystal. Formation of the *E*-isomer is impossible because of the location of the bridge in **3d/2.** In fact**,** there is a quite different redox system found by cyclic voltammetry (Figure 5). This suggests that simple, unbridged oxidized 3,3′-biindolizines should exist also in the *E*-form only.

In all cases, mass spectroscopy revealed that a intermolecular dehydrocyclization involving two molecules of **1a**−**d** takes place as a side reaction. Repeated flash chromatography of crude cyclized **1a** and **1c** leads to isolation of the dehydro-dimers **4a** and **4b** (Figure 6). Detection of diastereomers of **4a** and **4b** has been unsuccessful so far due to low solubility.

Conclusion

The synthesis of new electroactive cyclophanes by intramolecular C−C coupling of bridged indolizines was successful. The cyclization of **1a**−**d** leads to mixtures of diastereomeric macrocycles. One pair of the enantiomers was obtained in excess. We have demonstrated that the main products of the reactions are reversible redox systems. It was shown by X-ray analysis of **3d/1** that the indolizine−indolizine bond and the oxygen O15 in the middle of the polyether bridge are separated by only 4.8 Å. It seems that for inclusion complexation of organic guests, cyclophanes with longer spacers are necessary. Therefore, we are involved in the synthesis of indolizines bridged by chains with more than 12 atoms. Subsequent cyclization of these compounds should lead to interesting host compounds.

Experimental Section

General. Experimental data were collected as described in references 2 and 4. The working electrode in the CV experiments was a Pt electrode tip, and a glassy carbon electrode was used as auxiliary electrode. The reference electrode was a silver electrode immersed in a 3 M AgCl solution. The experiments were run at room temperature under a dry argon

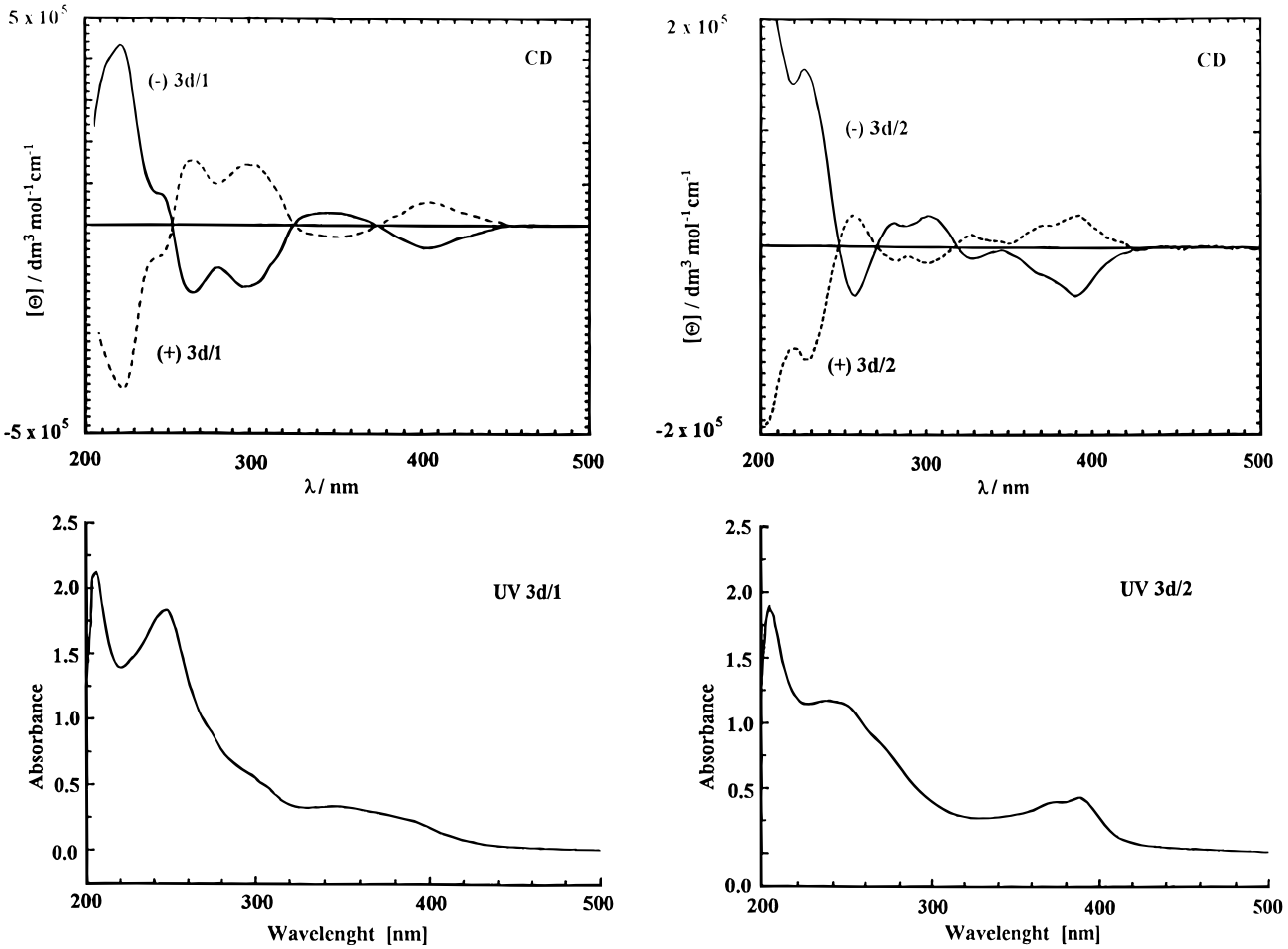


Figure 4. UV and CD spectra of (−)- and (+)-isomers of componds **3d/1** and **3d/2**.

atmosphere. All voltammograms were recorded in CH_2Cl_2 containing 0.01 M $TBAPF_6$. Melting points are uncorrected. Separation of enantiomers was performed on HPLC with Chiralcel OD.

Syntheses of the Bridged Pyridines 2a and 2b. General Procedure. To an ice-cooled solution of α-picoline (5 mL, 50.6 mmol) in 50 mL of THF was added n-BuLi (32 mL, 51.2 mmol, 1.6 M in hexane). Lithiation was completed after 60 min at the same temperature, and 25 mmol of dihalide in 40 mL of THF was quickly added. The reaction mixture was stirred for an additional 4 h and then quenched by addition of water, washed (3 × 10 mL) with water, and dried over $MgSO_4$. After the solvent was evaporated, the crude residue was pure enough for further operations. A part of the product was purified by flash chromatography on silica gel (eluted with hexane:ethylacetate 1:1) or by recrystallization (diethylether: hexane:pentane 1:1:1).

1,14-Bis(pyrid-2-yl)tetradecane (2a): yield ca. 80%, mp 47−50 °C, colorless needles (ether, pentane, hexane 1:1:1); ^{1}H NMR δ 1.29 (m, 20H), 1.72 (quintet, J = 7.8 Hz, 4H), 2.79 (t, J = 7.8 Hz, 4H), 7.10 (m, 4H), 7.57 (td, J = 7.7 Hz, J = 1.8 Hz, 2H), 8.52 (d, J = 4.8 Hz, 2H); ^{13}C NMR δ 29.39 (t), 29.47 (t), 29.53(t), 29.6 (t), 29.6 (t), 29.9 (t), 38.5 (t), 120.8 (d), 122.6 (d), 136.2 (d), 149.2 (d), 162.6 (s); MS (FAB) *m/e* 353 (M + H^+, 100%), 260 (7%). Anal. Calcd for $C_{24}H_{36}N_2$ (352.56): C, 81.76; H, 10.29; N 7.95 . Found: C, 81.51; H, 10.42; N 7.55.

1,13-Bis(pyrid-2-yl)-4,7,10-trioxatridecane (2b): yield ca. 80%, yellow oil; ^{1}H NMR δ 2.03 (m, 4H), 2.85 (t, J = 7.6 Hz, 4H), 3.50 (t, J = 6.5 Hz, 4 H), 3.62 (m, 8H), 7.11 (m, 4H), 7.56 (td, J = 7.7 Hz, J = 1.9 Hz, 2 H), 8.50 (d, J = 4.9 Hz, 2H); ^{13}C NMR δ 29.5(t), 34.8 (t); 70.1 (t), 70.5 (t), 70.6 (t), 121.0 (d), 122.9 (d), 136.3 (d), 149.2 (d), 161.7 (s). MS (FAB) *m/e* 345 (M + H^+, 100%), 288 (26%). Anal. Calcd for $C_{20}H_{28}N_2O_3$ (344.45): C, 69.74; H, 8.19; N, 8.13. Found: C, 69.97; H, 8.37; N, 8.29.

Syntheses of the Bridged Indolizines 1a−d. General Procedure. A mixture of the crude bridged pyridines (ca. 40 mmol) and some crystals of KI in acetone (100 mL) was refluxed under stirring and an acetone (50 mL) solution of the bromo ketone (50 mmol) was added slowly (2 h). The mixture was refluxed for an additional 4 h. After removing the solvent at a rotary evaporator, the pyridinium bromide was obtained as a semisolid compound. The crude bromide was suspended in 150 mL water containing $NaHCO_3$ (13 g, 155 mmol) and refluxed under stirring for 2 h. The reaction mixture was cooled and extracted with toluene (3 × 30 mL). The organic layer was washed with water (3 × 10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The oily residue was purified by flash chromatography on silica gel with toluene (**1c**) or hexane/EtOAc 1:1 (**1a**, **1b**, **1d**) as eluents.

1,12-Bis(2-methylindolizin-1-yl)dodecane (1a): yield 18%, brown oil; ^{1}H NMR δ 1.24 (m, 16 H), 1.53 (quintet, J = 7.5 Hz, 4 H), 2.24 (s, 6 H), 2.66 (t, J = 7.5 Hz, 4 H), 6.29 (m, 2 H), 6.52 (m, 2 H), 7.02 (s, 2 H), 7.20 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 6.9 Hz, 2 H); ^{13}C NMR δ 10.6, 23.9, 29.6, 29.6, 29.6, 29.6, 31.4, 108.9, 110.3, 112.4, 115.0, 116.8, 123.2, 124.5, 130.0; MS (FAB) *m/e* 429 (M + H^+, 20%), 144 (100%) for $C_{30}H_{40}N_2$ (428).

1,11-Bis(2-methylindolizin-1-yl)-3,6,9-trioxaundecane (1b): yield 27%, orange oil; ^{1}H NMR δ 2.25 (s, 6 H), 3.01 (t, J = 7.7 Hz, 4 H), 3.56 (t, J = 7.7 Hz, 4H), 3.64 (m, 8 H), 6.31 (td, J = 6.8 Hz, J = 1.3 Hz, 2 H), 6.53 (ddd, J = 9.0 Hz, J = 6.5 Hz, J = 1.1 Hz, 2 H), 7.05 (s, 2 H), 7.25 (d, J = 8.7 Hz, 2 H), 7.73 (dt, J = 7.0 Hz, J = 1.1 Hz, 2 H); ^{13}C NMR δ 10.6 (q), 24.7 (t), 70.2 (t), 70,7 (t), 71.9 (t), 107.6 (s), 109.2 (d), 110.5 (d), 115.6 (d), 116.6 (d), 123.6 (s), 124.5 (d), 130.6 (s); MS (MALDI) *m/e* 421 ((M + H^+, 100%) for $C_{26}H_{32}N_2O_3$ (420).

1,12-Bis(2-phenylindolizin-1-yl)dodecane (1c): yield 26%, greenish crystals mp 81−85 °C; ^{1}H NMR δ 1.24 (m, 16 H), 1.55 (quintet, J = 7.7 Hz, 4 H), 2.83 (t, J = 7.7 Hz, 4 H),

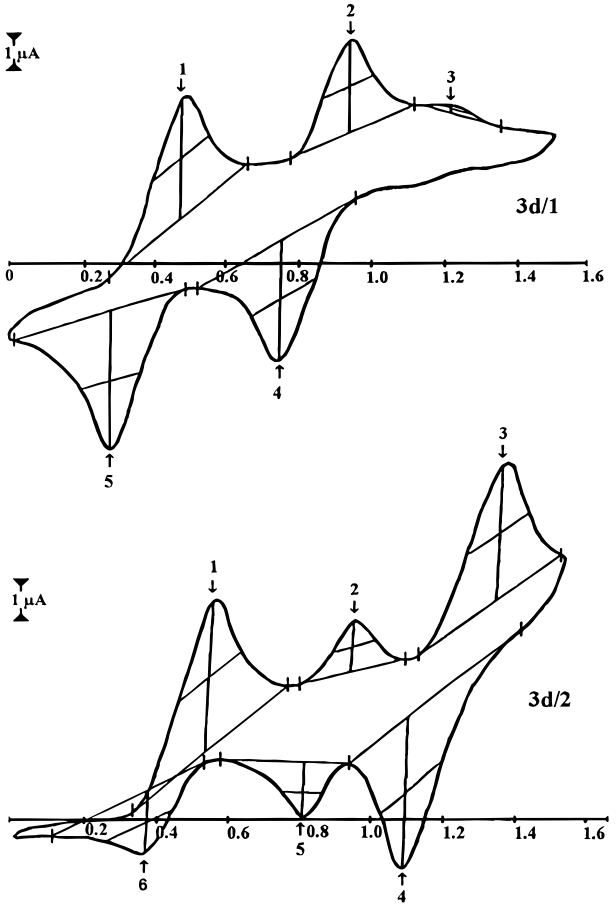
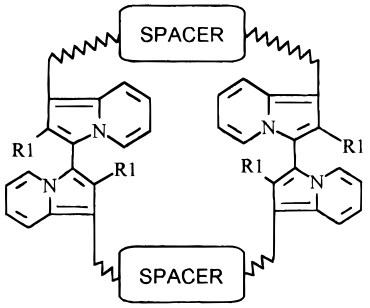


Figure 5. Cyclic voltammograms of **3d/1** and **3d/2** in CH_2Cl_2 containing 0.01 M $TBAPF_6$.



4a: Spacer = -$(CH_2)_{10}$- , R^1 = Me; **4b**: Spacer = -$(CH_2)_{10}$- , R^1 = Ph

Figure 6. Cyclophanes obtained by dimerization of bridged indolizines.

6.40 (td, J = 7.0 Hz, J = 1.6 Hz, 2 H), 6.58 (ddd, J = 9.0 Hz, J = 7.0 Hz, J = 1.4 Hz, 2 H), 7.24 - 7.49 (m, 14 H), 7.82 (d, J = 7.0 Hz, 2 H); ^{13}C NMR δ 24.1 (t), 29.4 (t), 29.60 (t), 29.62 (t), 29.7 (t), 31.6 (t), 110.1 (d), 110.1 (d), 111.5 (s), 115.3 (d), 117.7 (d), 124.8 (d), 126.3 (d), 128.4 (d), 128.8 (d), 128.9 (s), 130.6 (s), 136.2 (s); MS (MALDI) 554 ((M + H)$^+$, 100%), 309.2 (40%). Anal. Calcd for $C_{40}H_{44}N_2$ (552.80): C, 86.91; H, 8.02; N, 5.07. Found: C, 86.79; H, 7.81; N, 4.72.

1,11-Bis(2-phenylindolizin-1-yl)-3,6,9-trioxaundecane (1d): yield 24%, yellow-brown oil; ^{1}H NMR δ 3.09 (t, J = 7.5 Hz, 4 H), 3.49 (m, 12 H), 6.34 (td, J = 7.0 Hz, J = 1.2 Hz, 2 H), 6.53 (ddd, J = 9.0 Hz, J = 6.5 Hz, J = 1.0 Hz, 2 H), 7.19 −7.42 (m, 14 H), 7.75 (dt, J = 7.0 Hz, J = 1.1 Hz, 2 H); ^{13}C NMR δ 24.7 (t), 70.1 (t), 70.6 (t), 71.9 (t), 106.6 (s), 110.3 (d), 116.1 (d), 117.6 (d), 124.8 (d), 126.4 (d), 128.2 (d), 128.4 (d), 128.8 (d), 129.3 (s), 131.2 (s), 135.8 (s); MS (EI) m/e 544 (M$^+$, 24%), 206 (100%) for $C_{36}H_{36}N_2O_3$ (544).

Cyclization of the Bridged Indolizines. $K_3[Fe(CN)_6]$ (493 mg, 1.5 mmol) was added to a solution of $N(Et)_3 \times HClO_4$ (0.1 g, 0.5 mmol) in 100 mL of ethanol. The suspension was stirred for 10 min and then treated with a solution of the bridged indolizine (0.7 mmol) in 50 mL of toluene. After stirring at rt for 20 h the solvent was evaporated under reduced pressure. The mixture was taken up with toluene and water. The organic layer was separated and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. Purification by column chromatography (hexane/ethyl acetate 6:1) yielded the pure cyclophanes.

1,1′-Dodecamethylene-2,2′-dimethyl-3,3′-biindolizine (3a): yield 14%, yellow oil; ^{1}H NMR δ 0.54−1.50 (m, 16 H), 1.71 (s, 6 H), 2.46 (s, 2 H), 2.65 (m, 2 H), 2.96 (m, 2H), 3.25 (m, 2 H), 6.42 (m, 2 H), 6.60 (m, 2 H), 7.38 (d, J = 7.1 Hz, 2 H), 7.61 (d, J = 8.9 Hz, 2 H); ^{13}C NMR δ 10.6, 23.3, 28.1, 28.1, 28.3, 28.7, 29.7, 109.7, 111.8, 112.0, 115.6, 116.9, 123.0, 124.6, 130.1; MS (FAB) m/e 427 (M + H$^+$, 100%). Anal. Calcd for $C_{30}H_{38}N_2$ (426.65): C, 84.46; H, 8.89; N, 6.57. Found: C, 84.13; H, 8.59; N, 6.02.

1,1′-(3,6,9-Trioxaundecamethylene)-2,2′-dimethyl-3,3′-biindolizine (3b): yield 44%, yellow crystals mp 164−70 °C; ^{1}H NMR δ 1.86 (s, 6 H), 2.68 (t, J = 8.1 Hz, 2 H), 3.07 (m, 12 H), 4.08 (m, 2 H), 6.40 (t, J = 6.6 Hz, 2 H), 6.63 (t, J = 6.6 Hz, 2 H), 7.31 (d, J = 8.7 Hz, 2 H), 7.80 (d, J = 7.0 Hz, 2 H); ^{13}C NMR δ 10.8, 25.2, 71.2, 72.0, 72.7, 109.2, 110.1, 113.0, 115.4, 116.1, 123.3, 129.6, 129.7; MS (FAB) m/e 419 (M + H$^+$, 100%). Anal. Calcd for $C_{26}H_{30}N_2O_3$ (418.54): C, 74.61; H, 7.22; N, 6.69. Found: 74.51; H, 7.44; N 6.23.

1,1′-Dodecamethylene-2,2′-diphenyl-3,3′-biindolizine (3c): yield 22%, yellow crystals mp 214−25 °C; ^{1}H NMR (DMSO-d_6, 100 °C) δ 0.72 −0.97 (m, 16 H), 1.42 (m, 4 H), 3.04 (m, 4 H), 5.95 (td, J = 6.8 Hz, J = 1.3 Hz, 2H), 6.46 (ddd, J = 9.0 Hz, J = 6.7 Hz, J = 1.0 Hz, 2 H), 6.84 (m, 4 H), 7.03 (m, 6 H), 7.25 (d, J = 7.2 Hz, 2 H), 7.37 (dt, J = 9.0 Hz, J = 1.3 Hz, 2 H); ^{13}C NMR (DMSO-d_6, 100 °C) δ 22.3, 26.6, 28.2, 28.4, 28.5, 28.5, 109.0, 110.7, 111.0, 115.6, 116.2, 122.3, 125.5, 127.1, 127.8, 127.9, 130.7, 135.2; MS (CI) m/e 551 (M$^+$ + 1, 100%). Anal. Calcd for $C_{40}H_{42}N_2$ (550.79): C, 87.23; H, 7.69; N, 5.09. Found: C, 86.94; H, 7.50; N, 4.71.

1,1′-(3,6,9-Trioxaundecamethylene)-2,2′-diphenyl-3,3′-biindolizines (3d/1 and 3d/2). **3d/1**: yield 26%, yellow crystals mp 260−70 °C; ^{1}H NMR (DMSO d$_6$, 80 °C) δ 2.83 (m, 4 H), 2.99−3.17 (m, 12 H), 5.85 (td, J = 7.3 Hz, J = 1.3 Hz, 2 H), 6.33 (m, 2 H), 6.75−6.89 (m, 10 H), 7.24 (m, 4 H); ^{13}C NMR (DMSO-d_6, 80 °C) δ 24.0, 69.9, 70.2, 70.4, 108.7, 109.0, 111.9, 115.5, 116.5, 122.8, 125.2, 126.8, 129.2, 130.5, 132.2, 136.1; MS (MALDI) 543 ((M + H)$^+$, 100%). Anal. Calcd for $C_{36}H_{34}N_2O_3$ (542.68): C, 79.68; H, 6.31; N, 5.16. Found: C, 79.39; H, 6.33; N 4.83. CD for (+)-**3d/1** (n-hexane) λ ($\Delta\theta$) 405 (5.426 x 10^4), 350 (−3.061 x 10^4), 302 (1.413 x 10^5), 266 (1.519 x 10^5), 223 (−3.948 x 10^5).

3d/2: yield 5%, yellow crystals mp 222−27 °C; ^{1}H NMR δ 2.02 (m, 1H), 2.46−2.98 (m, 10 H), 3.24 (m, 2 H), 3.37 (m, 1 H), 3.51 (m, 1 H), 4.00 (m, 1 H), 6.26 (td, J = 6.7 Hz, J = 1.2 Hz, 1 H), 6.46 (d, J = 6.7 Hz, 1 H), 6.59 (m, 1 H), 6.64 (t, J = 6.4 Hz, 1 H), 6.71 (m, 1 H), 6.78−6.96 (m, 10 H), 7.40 (d, J = 8.9 Hz, 1 H), 7.44 (d, J = 8.8 Hz, 1 H), 7.67 (d, J = 5.8 Hz, 1 H); ^{13}C NMR 24.9 (t), 25.5 (t), 69.4 (t), 71.0 (t), 71.4 (t), 71.6 (t), 71.8 (t), 72.4(t), 109.1 (s), 110.2 (d), 111.1(d), 111.2(s), 111.5 (s), 115.3 (d), 115.6 (s), 115.7 (d), 115.8 (d), 119.7 (d), 124.4(d), 124.6(d), 125.2 (d), 125.5 (d), 126.6(d), 127.7 (d), 128.5 (s), 129.5 (s), 130.0 (d), 131.6 (d), 134.6 (s), 135.3 (s), 136.0 (s), 136.2 (s); MS (FAB) 543 (M + H$^+$, 12%), 485 (20%), 261 (100%). Anal. Calcd for $C_{36}H_{34}N_2O_3$ (542.68): C, 79.68; H, 6.31; N, 5.16. Found: C, 79.55; H, 6.27; N, 4.85. CD for (−)-**3d/2** (n-hexane) λ ($\Delta\theta$) 390 (−4.125 x 10^4), 329 (−9.965 x 10^3), 301 (2.874 x 10^4), 280 (2.029 x 10^4), 256 (−4.339 x 10^4), 228 (1.531 x 10^5), 202 (2.595 x 10^5).

1,14(1,1′)-Di(2,2′-dimethyl-3,3′-biindolizino)hexaeicosaphane (4a): yield 3%, oily crystals, decomposition 150−70 °C; ^{1}H NMR δ 1.17 - 1.39 (m, 32 H), 1.63 (m, 8 H), 2.07 (s, 12 H), 2.78 (broadened m, 8 H), 6.27 (broadened t, 4 H), 6.59 (broadened m, 4 H), 7.08 (broadened m, 4 H), 7.35 (d, J = 9.0 Hz, 4 H); ^{13}C NMR δ 10.4, 24.1, 29.1, 29.2, 29.3, 29.4, 31.0, 109.1, 111.8, 112.4, 115.5, 116.8, 123.0, 125.2, 130.7; MS (FAB)

854 ($M + H^+$, 100%), 427 (10%). Anal. Calcd for $C_{60}H_{76}N_4$ (853.29): C, 84.46; H, 8.98; N, 6.57. Found: C, 84.14; H, 8.71; N, 6.39.

1,14(1,1′)-Di(2,2′-diphenyl-3,3′-biindolizino)hexaeicosaphane (4b): yield 7%, bright yellow crystals mp 194−99 °C; ^{1}H NMR ($CDCl_3$, 40 °C) δ 1.11 (broadened m, 32 H), 1.49 (broadened m, 8 H), 2.79 (broadened m, 8 H), 6.29 (broadened t, 4 H), 6.61 (broadened t, 4 H), 6.80 (broadened m, 8 H), 7.03 (broadened m, 12 H), 7.25 (broadened m, 4 H), 7.39 (d, J = 9.2 Hz, 4 H); ^{13}C NMR δ 23.7, 28.7, 29.1, 29.2, 29.3, 30.9, 110.2, 112.1, 116.2, 117.5, 123.0, 125.9, 127.7, 129.2, 129.3, 130.9, 131.0, 135.6; MS (MALDI) 1102 ($(M + H)^+$, 100%). Anal. Calcd for $C_{80}H_{84}N_4$ (1101.57): C, 87.23; H, 7.69; N, 5.09. Found: C, 86.88; H, 7.50; N, 5.04.

X-ray Diffraction Analysis. Suitable crystals for the X-ray study were grown from a toluene/ethyl acetate mixture. Crystal data:

3c ($C_{40}H_{42}N_2$, fw 550.79): The crystals are monoclinic, space group $P2_1/n$; crystal size 0.3 × 0.3 × 0.2 mm, with very poor quality. Unit cell dimensions a = 13.635(4), b = 18.317(12), c = 12.684(6) Å, α = 90.0°, β = 90.64(4)°, γ = 90.0°; V = 3168(3) Å^3; 6201 unique reflections, 3617 < 2σ(F)!; R = 12.9%; Rw 13.9%, some calculated hydrogen atoms are included but not refined.

3d/1 ($C_{36}H_{34}N_2O_3$, fw 542.68): crystals are monoclinic: space group $P2_1/n$; crystal size 0.5 × 0.5 × 0.2 mm, unit cell dimensions a = 13.302(3), b = 17.869(3), c = 12.278 (4) Å; α = 90.0°, β = 91.91(3)°, γ = 90.0°; V = 2921 (1) Å^3; 5127 unique reflections, 1181 < 2σ(F); R = 6.0%; Rw = 6.2%; all hydrogen atoms are included and refined.

3d/2 ($C_{36}H_{34}N_2O_3$, fw 542.68): crystals are triclinic, space group $P1$; crystal size 0.7 × 0.5 × 0.5 mm, unit cell dimensions a = 11.210(5), b = 11.285(4), c = 12.175(3) Å; α = 80.60 (3)°, β = 72.45(4)°, γ = 71.48 (3)°; V = 1388.6 (9) Å^3; 5429 refs, 749 < 2σ(F); R = 4.5%; Rw = 5.0%; all hydrogen atoms are included and refined.

The structures were solved by direct methods with the SHELXS-86 program[7] and refined anisotropically using SHELXL-93[8] and XTAL3.2.[9] The coordinates of structures **3c**, **3d/1**, and **3d/2** have been deposited with the Cambridge Data Centre. The coordinates can be obtained from the Director, Cambridge Data Centre, 12 Union Road, Cambridge, CB2 1 BZ, U.K.

Acknowledgment. We thank Prof. Dr. S. Hünig for helpful discussions and suggestions. This work was supported by the Fonds der Chemischen Industrie.

Supporting Information Available: Plots of **3d/1**, **3d/2**, and **3c** according to the X-ray analysis; stereochemistry of the ansa-compounds **3d** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951419O

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