Synthesis and X-ray Analysis of New [5]Helicenes – HMO Calculations on the Photocyclization of the Stilbene Precursors[1]

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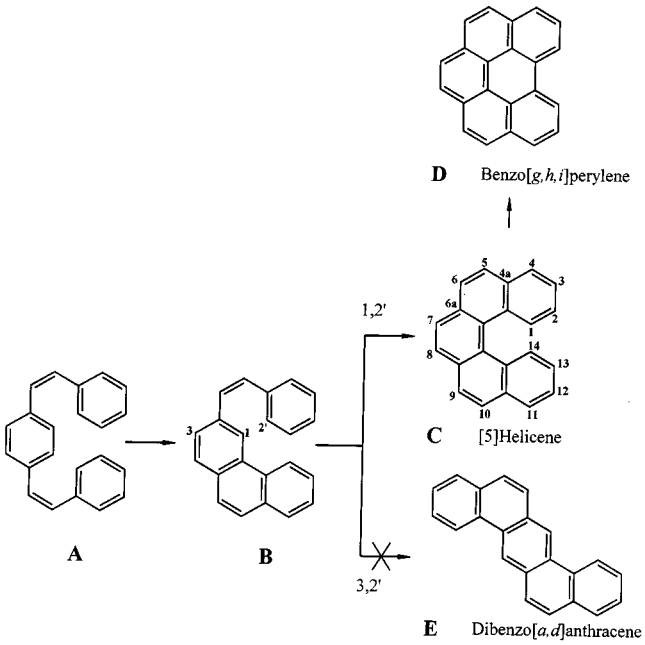
The syntheses of the new pentahelicenes **5**, **11**, **17**, **21**, and **28** with various substituents are described. In the case of 2,13-dicyano-[5]helicene (**11**) optical resolution was achieved by HPLC using a column packed with γ-cyclodextrin. However, the enantiomers racemized within a few hours. On the other hand, the enantiomers of **28** turned out to be stable after separation on triacetylcellulose using MPLC. The crystal structures of **11**, **17**, and **21** were solved and indicated the typical distortions which are expected for helicenes. The model of the sum of free valence numbers was applied in order to rationalize the reactivity pattern of the photochemical phenanthrene cyclization.

The first enantiomerically pure helicene was synthesized in 1956 by Newman and Lednicer in 12 steps involving the resolution of a charge-transfer complex.[2] The authors also suggested the helicene nomenclature which is still used today. In the 1960s and the following years helicenes were intensively studied and interest was especially promoted by the new synthetic procedure of the photochemical phenanthrene formation, developed by Martin and co-workers in 1967.[3] According to this method, suitable stilbene precursors can be cyclized to helicenes in the presence of an oxidant (e.g. iodine). For example, [5]helicene is the product of a twofold cyclization of 1,4-distyrylbenzene (Scheme 1: **A** → **B** → **C**). Surprisingly, it is often the case that only the helicene is formed upon photolysis (**C** by 1,2′-cyclization), rather than the isomeric planar aromatic compound (**E** by 3,2′-cyclization). Scholz, Mühlstedt, and Dietz rationalized this unique reactivity pattern in terms of the highest free valence ($F^*_{r,s}$) or the lowest localization energy ($L^*_{r,s}$) in the excited state, respectively.[4] Later Laarhoven and coworkers deduced some rules from a variety of examples which may be summarized as follows:[5] (i) Photocyclizations only take place if $\Sigma F^*_{r,s} > 1$, and (ii) only one product is formed if $\Delta\Sigma\ F^*_{r,s} > 0.1$. Indicated by these rules, the exclusive formation of [5]helicene **C** from **B** is obviously subject to the condition of a low concentration of the starting material since the free valence of stilbene would support dimerization to a cyclobutane rather than cyclization to a phenanthrene. In some cases the overall yield of helicene formation is decreased due to a second cyclization in the presence of iodine leading to the benzo[*g*,*h*,*i*]perylenes **D**, even if substituents are present at a carbon atom involved in the reaction.[6]



Scheme 1. Oxidative photocyclization of stilbenes

From earlier studies by Martin[7] and by Lindner[8] it is known that [5]helicene readily racemizes via a planar transition state. Haufe et al.[9] recently confirmed this mechanism by means of quantum chemical calculations (AM1 and ab initio using B3LYP/3-21G). They also predicted the racemization barrier of 1-methyl-substituted [5]- and [6]helicene to be at least as high as that of the next (higher) unsubstituted helicene.

In the course of our work into photoinduced electron transfer (PET) reactions[10] we investigated helicenes, and their potential, given their inherent chirality, as possible new chiral PET sensitizers. In particular [5]helicenes, with a suitable substitution pattern, might be of interest as elec-

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tron-acceptor sensitizers. Despite Katz′ recent report on an alternative synthesis of helicenebis(quinones) by the Diels−Alder methodology[11] we followed the classical route by phenanthrene cyclization. Since a variety of general methods of chiral resolution[2][12] or even enantioselective synthesis[13] are available, these [5]helicenes might be useful as chiral sensitizers in asymmetric photoreactions in general.[14]

Results and Discussion

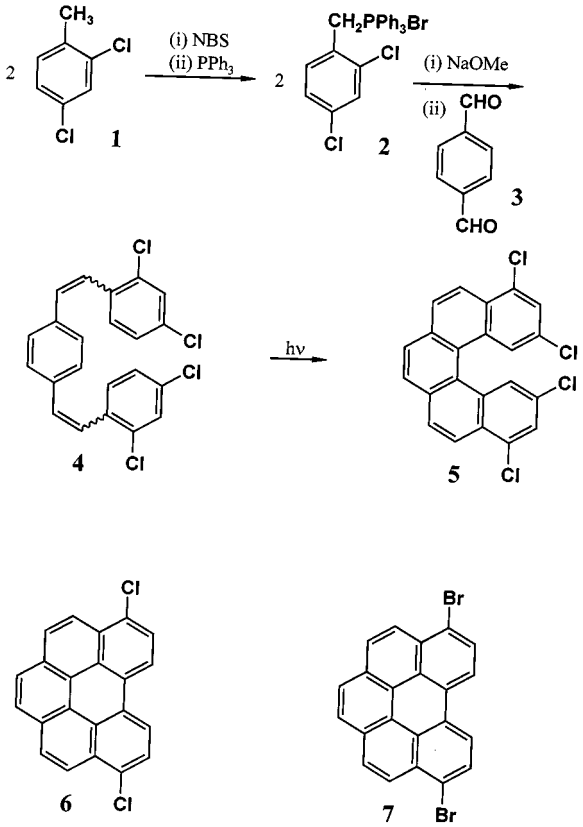
Synthesis

The synthesis of helicenes is based on the well-known photochemical reaction of stilbene to phenanthrene.[15] Most of the [5]helicenes were prepared by photocyclodehydrogenation of bis(arylvinyl)-substituted aromatic compounds.[16][17] These helicene precursors (Scheme 1, **A**) are more accessible than the analogous 1,2-dinaphthylethenes. To prevent dimerization and polymerization occurring as side reactions the irradiations were performed in dilute solutions using a falling-film photoreactor. Following the method of Katz we used propylene oxide as scavenger for HI.[18] The aryl-substituted olefins were obtained by twofold, or two subsequent, Wittig reactions, depending on the symmetry of the target molecule.

Halogen-Substituted [5]Helicenes

The synthesis of halogen-substituted [5]helicenes was performed as shown in Scheme 2. After radical bromination of 2,4-dichlorotoluene (**1**) with NBS, the resulting bromide was treated with PPh_3, resulting in the phosphonium salt **2**. Then two equiv. of the salt were condensed with terephthaldialdehyde (**3**) with NaOMe as a base in dry methanol. The resulting mixture of *cis,cis*-, *cis,trans*-, and *trans,trans*-**4** was directly converted into 2,4,11,13-tetrachloro[5]helicene (**5**) by irradiation with a high-pressure mercury lamp. No dependence was observed on the configuration of the bis(olefin) **4** because of the preceding fast photochemical isomerization processes.

Analogously, but starting with 2,5-dichloro- or 2,5-dibromotoluene, we prepared the precursors which should lead to [5]helicenes with substituents at the carbon atoms 1, 4, 11, and 14. The Wittig reactions of terephthaldialdehyde (**3**) with (2,5-dichlorobenzyl)- and (2,5-dibromobenzyl)triphenylphosphonium bromides gave the corresponding bis(stilbenes) in reasonable yields which, upon irradiation, resulted in formation of a single product in each case. Although the ^{1}H-NMR spectra of the cyclization products show one AB and one AX system ($\delta\nu/J$ = 8.7 and 17.3, respectively) as well as one singlet, as expected for the desired 1,4,11,14-tetrahalo[5]helicenes, the elemental analysis supported a stoichiometric formula with two halogen atoms missing ($C_{22}H_{10}X_2$ rather than $C_{22}H_{10}X_4$). Probably bromine and chlorine was eliminated during the cyclization process under formation of the benzo[*g,h,i*]perylenes **6** and **7**.



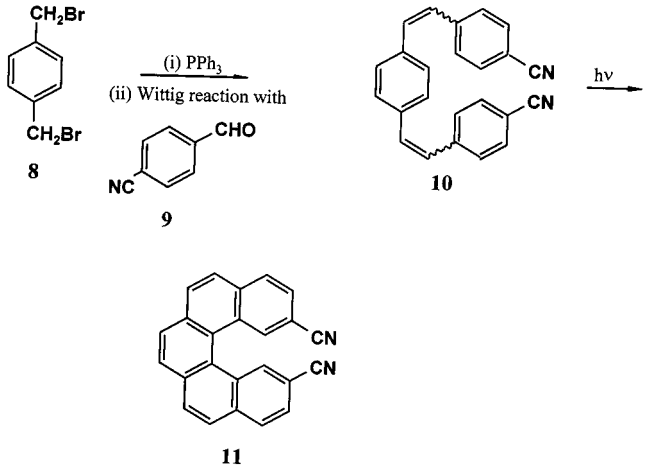
Scheme 2. Synthesis of 2,4,11,13-tetrachloro[5]helicene and benzo[*g,h,i*]perylene side products

Similar results were obtained in experiments designed to yield 1,4-dichloro[5]helicene and 1,4-dibromo[5]helicene from the corresponding bis(stilbenes). In those cases only 4-chloro- and 4-bromobenzo[*g,h,i*]perylenes could be isolated after irradiation. The details of the synthesis of the starting materials and of the irradiation procedures are described elsewhere.[1]

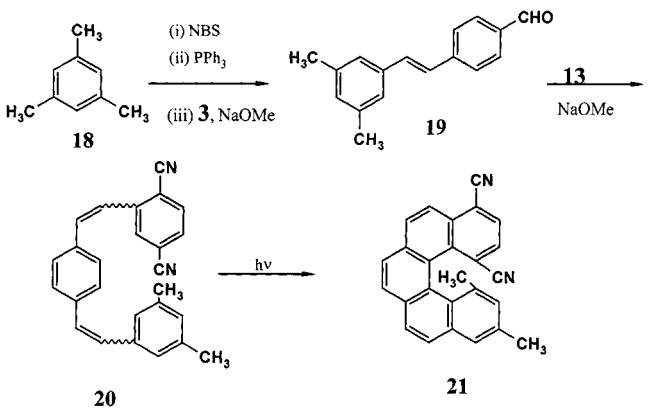
Cyano-Substituted [5]Helicenes

An easy route to 2,13-dicyano[5]helicene (**11**) is shown in Scheme 3. *p*-Xylyl-α,α′-bis(triphenylphosphonium) dibromide, prepared from **8**, was heated with sodium methoxide in the presence of two equiv. of *p*-cyanobenzaldehyde (**9**). Whereas the Wittig reaction gave **10** almost quantitatively, the photochemical cyclization yielded the [5]helicene **11** in a yield of only 30%. According to sterical compression the signals of the protons at C-1 and C-14 show the strongest low-field shift (δ = 8.73). In addition, the coupling pattern comfirms the helicene structure as does its X-ray crystallographic analysis (see below).

The synthesis of 1,4-dicyano-13-methyl[5]helicene (**17**) is shown in Scheme 4. We found that it is possible to synthesize the bis(olefin) **16** in two subsequent Wittig reactions by controlling the condensation of the first phosphonium salt with terephthaldialdehyde (**3**).The dicyanobenzene subunit was introduced in the second step. The corresponding phosphonium salt **13** was obtained in three steps, starting from

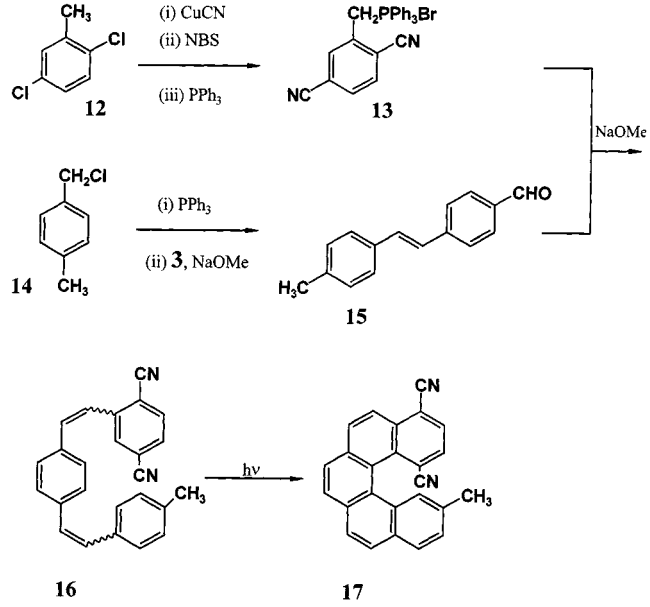


Scheme 3. Synthesis of 2,13-dicyano[5]helicene



Scheme 5. Synthesis of 11,14-dicyano-1,3-dimethyl[5]helicene

2,5-dichlorotoluene by a Rosenmund−von-Braun reaction, followed by bromination of the methyl group and phosphonium salt formation. In a very similar way we prepared 11,14-dicyano-1,3-dimethyl[5]helicene (**21**) starting from mesitylene (Scheme 5). All spectroscopic data, as well as the X-ray crystallographic analysis, confirm the helicene structure.



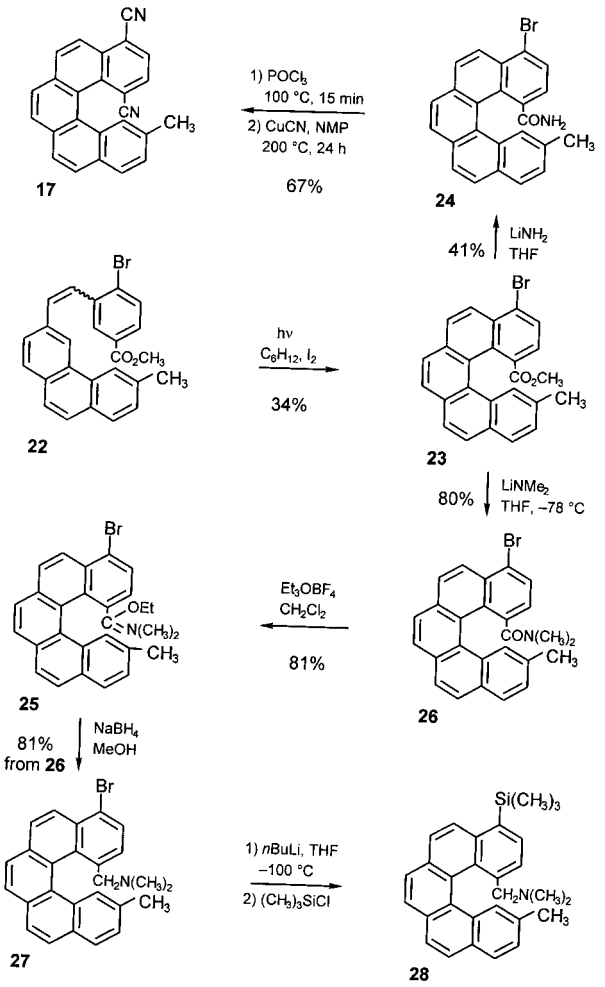
Scheme 4. Synthesis of 1,4-dicyano-13-methyl[5]helicene by oxidative photocyclization of the non-symmetric bis(stilbene) **16**

Compounds **17** and **21** are very interesting when one considers the deformation of the molecules caused by the sterical interference of substituents at the terminal rings (position 1 and/or 14). On the other hand this feature might be the reason for the low yields of the final phenanthrene cyclizations (3% and 8%, respectively). However, it should be noted that the synthesis of **21** in particular is one of the very few successful examples furnishing a 1-methyl-substituted [5]helicene.[19]

A significantly better overall yield of racemic 1,4-dicyano-13-methyl[5]helicene (**17**) was obtained from methyl 4-bromo-13-methyl[5]helicene-1-carboxylate (**23**) prepared by photocyclization/dehydrogenation of 1-(2′-bromo-5′-methoxycarbonylphenyl)-2-(6′′-methyl-3′′-phenanthrenyl)ethene (**22**) as described before.[20] The ester **23** was transformed to the amide **24** by treatment with lithium amide in tetrahydrofuran, dehydration of **24** with $POCl_3$ gave a bromonitrile which was converted into the dicyano derivative **17** without purification (Scheme 6).

In an attempt to prepare an enantiomerically pure [5]helicene derivative with a tertiary amine side chain, the ester **23** was converted into the *N*,*N*-dimethylcarboxamide **26**, which could be reduced via the ethoxyiminium salt **25** to 4-bromo-1-(dimethylamino)-13-methyl[5]helicene (**27**). However, **27** was too poorly soluble for chromatographic enantiomer separation. It was therefore transformed to the more soluble 4-trimethylsilyl derivative **28** by halogen/metal exchange followed by silylation. The latter could indeed be partially separated into its enantiomers by medium-pressure liquid chromatography (MPLC) on triacetylcellulose eluting with ethanol. Two fractions were isolated, the second of which had an enantiomeric excess of 51.3% according to analytical MPLC, and the first eluting one was enantiomerically pure with $[\alpha]_{436}^{20} = -4750$ ($c = 0.19$, ethanol).

The separation of enantiomers was also achieved for **11** by HPLC using a column packed with γ-cyclodextrin and H_2O/acetonitrile (1:1) as eluent. Due to its low solubility in H_2O/acetonitrile **11** was applied to the column as a solution in THF. In order to isolate the enantiomers the aqueous eluates were extracted with toluene followed by concentration of the extracts. For both enantiomers the absolute values of $[\alpha]_D^{20}$ were similar, provided they were measured directly after elution. However, being only 100 these values are too small for helicenes, indicating a rather rapid race-



Scheme 6. Synthesis of various [5]helicenes by controlled substitution of **22**

mization of **11**, which was complete after ca. 5 h at room temperature.

X-ray Crystallography

The first X-ray structure of a helicene was solved for a complex of [6]helicene with 4-bromo-2,5,7-trinitrofluorene[21] in 1969 and in the same year for a sulfur-containing heterohelicene.[22] To our knowledge X-ray structures of substituted [5]helicenes and even [5]helicene itself have not been reported so far. In this study we were able to solve the X-ray crystallographic structures for substituted [5]helicenes. Crystals of proper quality were obtained from acetonitrile solutions of **11**, **17**, and **21**.

In Figures 1−3 the structures are shown and Table 1 summarizes the crystallographic data.

The average lengths of corresponding bonds are equal in all helicenes. Compared with benzene (1.39 Å) the inner bonds of the helicenes are lengthened (ca. 1.44 Å) whereas the outer bonds are almost uninfluenced. As expected, the torsional angle (C14a−C14d) increases with increasing sterical interaction. A similar effect is observed for the angle between the terminal rings and the distance between the centers of these rings. The deviations from the calculated values are within the acceptable limits.

Table 1. Crystallographic data of **11**, **17**, and **21**

Helicene	Space group	Angle$_{tors}$ [°] C(14a−d) Exp.	Angle$_{tors}$ [°] C(14a−d) AM1	Angle$_{tors}$ [°] Ring A, E	Distance [Å] Ring A, E
11	*Pbcn*	25.5	28.7	44.3	4.92
17	*C2/c*	27.5	29.2	47.1	4.94
21	$P2_1/n$	30.8	30.9	47.2	4.97

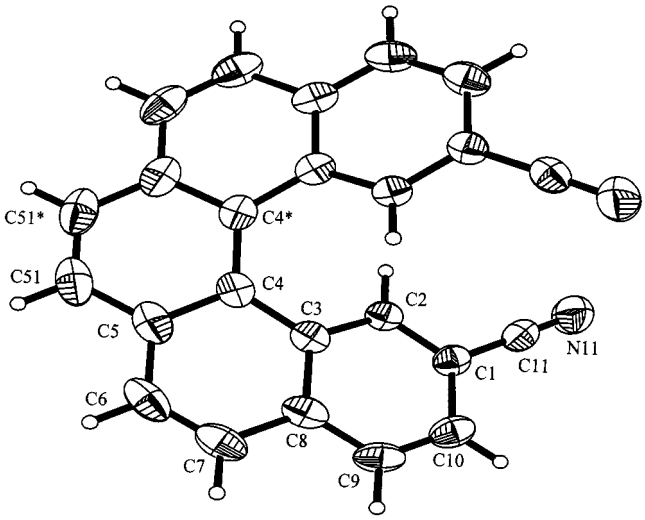


Figure 1. Molecular structure of **11** as determined by X-ray diffraction

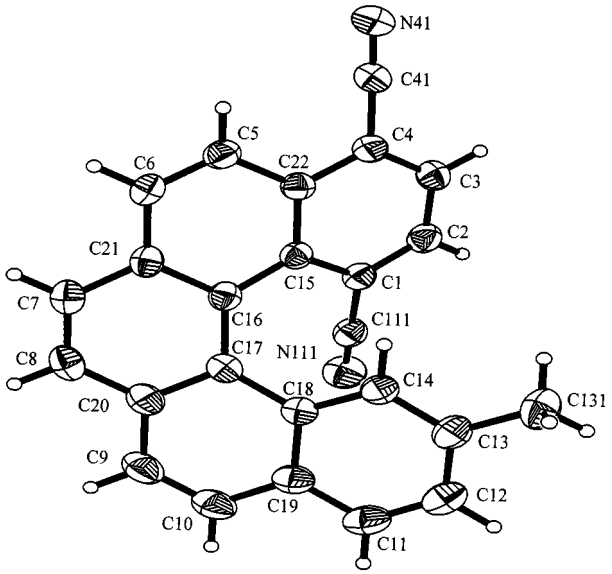


Figure 2. Molecular structure of **17** as determined by X-ray diffraction

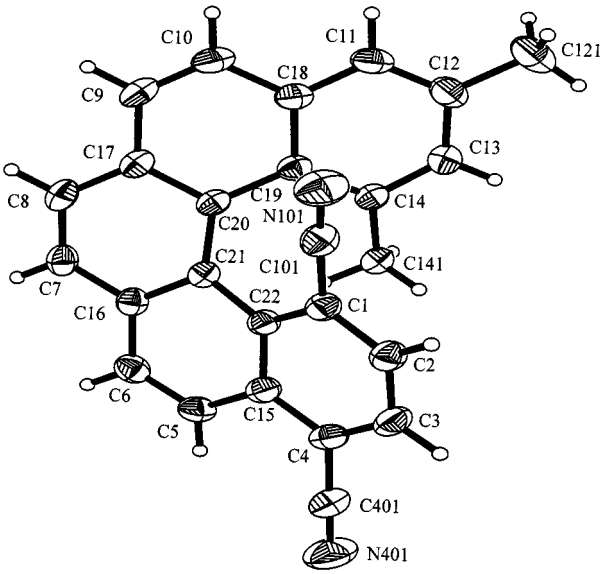
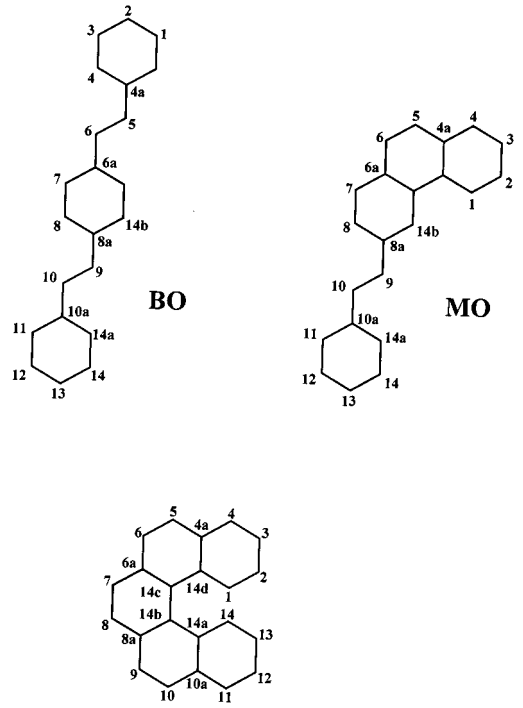


Figure 3. Molecular structure of **21** as determined by X-ray diffraction

HMO Calculations

Depending on the symmetry of the helicene precursor several cyclization products might be formed (cf. Scheme 1). Obviously, as pointed out in the introduction, the high selectivity observed in this study is caused by the electron distribution in the excited styrylanthracenes. There are several parameters for the photocyclization which appear to be valuable when rationalizing the reactivity pattern. The most simple one is the sum of free valence numbers of the atoms r and s involved in the cyclization step in the excited state ($\Sigma F^*_{r,s}$) ($F_r = \sqrt{3} - \Sigma P_r$, P = bond order).[4] Numerous examples lead to the conclusion that photocyclization only proceeds if $\Sigma F^*_{r,s} > 1.0$.[5] The HMO procedure turned out to be suitable to obtain the free valence number. For our systems we established two structures for the calculations (Scheme 7). The first structure (**BO**) represents the bis(olefin), the second one (**MO**) the product of the cyclization of one double bond. The protons, the localization of double bonds, the configuration and the conformation are omitted as these parameters are not considered in HMO calculations. The numbering of the carbon atoms follows the IUPAC rules of the corresponding helicene.



Scheme 7. Bis(olefin) (BO) and mono(olefin) (MO) framework as model systems for HMO calculations

F^*_{10} represents the value for carbon atoms of olefinic double bonds. Each of these atoms has a higher free valence number than any other carbon atom which should be involved in the cyclization process. For that reason dimerization rather than cyclization should be the favoured reaction. That, in conclusion, is the theoretical background for the highly diluted solutions required in the photoreaction.

According to the calculations obviously none of the cyano-substituted precursors should result in the desired product. Only the value of **10-MO** and the halogen-containing systems satisfy the rule. Nevertheless, cyclization is observed resembling *p*-distyrylbenzene, which for a long time stands as the only exception to the rule of the sum of the free valence number. Irradiation of *p*-distyrylbenzene leads to [5]helicene although $\Sigma F^* = 0.95$ for the first cycli-

Table 2. Results of the HMO calculations

System	F^*14a	F^*8	F^*14b	ΣF^*14a,8	ΣF^*14a,14b	F^*10
10-BO	0.469	0.463	0.463	0.932	0.932	0.556
10-MO	0.477	0.460	0.556	0.937	1.033	0.571
F-BO[a]	0.612	0.491	0.491	1.103	1.103	0.621
F-MO[a]	0.507	0.609	0.685	1.116	1.192	0.634
4-BO	0.613	0.489	0.489	1.102	1.102	0.612
4-MO	0.506	0.607	0.685	1.113	1.191	0.612
G-MO[b]	0.508	0.609	0.685	1.193		0.635
				ΣF^*14c,14d	ΣF^*8,11	F^*10
20-BO				0.917	0.989	0.503
20-MO				0.986	0.929	0.509

[a] **F**: 4-(2′,5′-dichlorostyryl)stilbene. – [b] **G**: 4-(2′,5′-dibromostyryl)stilbene.

zation. Laarhoven was able to prove that dimerizations occur giving rise to a cyclobutane derivative, in which the ΣF^* value of the remaining stilbene units is larger and therefore allows a cyclization. Subsequently, photolytic cleavage of the cyclobutane system leads to a 3-styrylphenanthrene which finally cyclizes to [5]helicene.[17]

Conclusion

In this paper the syntheses of the new [5]helicenes **5**, **11**, **17**, **21**, and **28** are reported. Attempts to synthesize [5]helicenes substituted with halogen at C-1 and/or C-14 have so far failed since benzo[*g*,*h*,*i*]perylenes were formed as the major products due to elimination processes. The crystal structures of **11**, **17**, and **21** were solved. The AM1-calculated structures are in good accordance with the experimental results. HMO calculations concerning the reactivity pattern of the cyclization are in accordance with the experimental data earlier reported by Laarhoven for pentahelicene itself. Photophysical studies of these substituted pentahelicenes regarding fluorescence and phosphorescence, quenching behaviour, and exciplex formation are reported elsewhere.[23]

Experimental Section

General Procedures: Unless otherwise noted, solvents of a purity greater than 99% were used without purification. Methanol was distilled from magnesia. Solvents for irradiation and propylene oxide were purchased from Aldrich Chemical Co., Inc. in 99%+ purity. Phosphonium salts were commercially available or synthesized from benzyl halides using general literature procedures. − ^{1}H-NMR spectroscopy: Bruker WM 300 (300 MHz) or Varian Unity-Plus (600 MHz) with internal standards TMS (δ = 0), $CHCl_3$ (δ = 7.24), and [D_5]DMSO (δ = 2.49). − ^{13}C-NMR spectroscopy: Bruker WM 300 (75 MHz) or Bruker AM 360 (90 MHz) with internal standards $CDCl_3$ (δ = 77.0) and [D_6]DMSO (δ = 39.7). − Mass spectrometry: Finnigan MAT 312; GC-MS using MAT CH 7A; TOF on Lazarus using MALDI or LDI technique (no matrix or 9-nitroanthracene as matrix, UV laser: 337 nm). − Infrared spectroscopy: Shimadzu IR-408, Perkin−Elmer 298 and Nicolet 5DXC FT-IR. − UV/Vis spectroscopy: Shimadzu UV 2100 spectrometer. − Emission spectroscopy: Perkin−Elmer LS 5 luminescence spectrometer. − Elemental analysis: Perkin−Elmer DIA CHN 240 and Heraeus CHN-O-Rapid. − Polarimeter: Perkin−Elmer polarimeter 241 using a micrometer cell (l = 9.998 cm).

X-ray Crystal Analyses: All data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELS-86, structure refinement SHELXL-93, graphics XP: Siemens 1900, Interactive Molecular Graphics Program, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. The XP plots of Figures 1−3 exhibit 50% probability. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101630 (**11**), -101631 (**21**), and -101632 (**17**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure A (Wittig Reaction): Among various procedures the following was the most favourable for our purpose. To prevent the hydrolysis of sodium methoxide the reactions were carried out in a dry apparatus and under an inert gas. − A concentrated solution of the phosphonium salt in methanol was added to a solution of the aldehyde and sodium methoxide in dry methanol. After 1−2 h of stirring, 1 equiv. of water was added and the solution extracted with ether or toluene. Concentration of the dried organic layers followed by filtration with toluene through silica gel yielded a mixture of *cis*,*cis*, *cis*,*trans* and *trans*,*trans* products. The pure *trans*,*trans* product was obtained by recrystallization from toluene in the presence of some crystals of iodine following a procedure described by Campbell and McDonald[26].

General Procedure B (Photocyclizations): 2 equiv. of iodine were added to a solution of the bis(olefin) in benzene, toluene, or cyclohexane (about 10^{-5} M). The solution was degassed for 15−30 min and an excess of propylene oxide added. Irradiation was performed using a falling-film photoreactor and a TQ718 high-pressure Hg-vapor lamp (700 W, Heraeus). The argon flow was maintained throughout the irradiation. The reaction was monitored by either TLC or HPLC or by disappearance of the iodine color. Then the reaction mixture was concentrated in vacuo and the crude product was purified by chromatography using Alox N and toluene. After removing the solvent under reduced pressure, the product was isolated by HPLC (Si 60, toluene or ethyl acetate/cyclohexane mixtures).

(2,4-Dichlorobenzyl)triphenylphosphonium Bromide (2): 20.0 g (0.124 mol) of 2,4-dichlorotoluene (**1**) was brominated using NBS in tetrachloromethane and AIBN as a radical starter by simultaneously refluxing and irradiating (300-W UV lamp, Ultra-Vitalux, Osram). The reaction was stopped at ca. 60% conversion (control by gas chromatography) and the bromide was isolated in the usual way (filtration of succinimide and distillation). The bromide was dissolved in ca. 200 mL of toluene, the appropriate amount of triphenylphosphane was added and the solution was heated under reflux for 2 h. After cooling, the precipitate was collected by filtration and recrystallized from ethanol to give **2** in a yield of nearly 60% (referring to **1**), mp 239−240°C. − ^{1}H NMR ([D_6]DMSO): δ = 5.20 (d, $J_{H,P}$ = 15.1 Hz, 2 H, CH_2), 7.18 (dd, J = 8.4/2.3 Hz, 1 H, 5-H), 7.37 (dd, J = 8.4/2.3 Hz, 1 H, 6-H), 7.56 (d, J = 2.3 Hz, 1 H, 3-H), 7.65−7.78 (m, 12 H, phenyl), 7.89−7.95 (m, 3 H, phenyl). − ^{13}C NMR ([D_6]DMSO): δ = 26.6 (d, $J_{C,P}$ = 49.6 Hz, CH_2), 117.9 (d, $J_{C,P}$ = 86.5 Hz, C_{quat} of phenyl), 126.2 (d, $J_{C,P}$ = 8.9 Hz, C_{quat} of aryl), 129.0 (d, $J_{C,P}$ = 2.5 Hz, CH), 130.5 (d, $J_{C,P}$ = 2.5 Hz, CH), 131.2 (d, $J_{C,P}$ = 12.7 Hz, CH), 134.6 (d, $J_{C,P}$ = 5.1 Hz, CH), 135.0 (d, $J_{C,P}$ = 12.7 Hz, CH), 135.4 (d, $J_{C,P}$ = 5.1 Hz, C_{quat}), 136.4 (d, $J_{C,P}$ = 2.5 Hz, CH), 136.9 (d, $J_{C,P}$ = 5.1 Hz, C_{quat}). − MS (70 eV); *m*/*z* (%): 420 (38), 384 (32), 262 (78), 183 (82), 108 (86), 81 (100). − $C_{25}H_{20}BrCl_2P$ (502.2): calcd. C 59.79, H 4.01; found C 60.02, H 4.48.

(*E*,*E*)-1,4-Bis(2′,4′-dichlorostyryl)benzene (4): The olefination (General Procedure A) of 2.55 g (5.1 mmol) of (2,4-dichlorobenzyl)-triphenylphosphonium bromide (**2**) with 0.34 g (2.5 mmol) of terephthaldialdehyde (**3**) yielded 0.64 g (60%) of the product, after crystalliziation from toluene (in the presence of few crystals of iodine), mp 239−241°C. − ^{1}H NMR ([D_8]THF): δ = 7.14 (d, J = 16.2 Hz, 2 H, olefinic H), 7.26 (dd, J = 8.3/2.0 Hz, 2 H, 5′-H), 7.41 (d, J = 1.9 Hz, 2 H, 3′-H), 7.44 (d, J = 16.2 Hz, 2 H, olefinic H), 7.53 (s, 4 H, CH), 7.70 (d, J = 8.3 Hz, 2 H, 6′-H). − MS (70 eV); *m*/*z* (%): 420 (3) [M^+], 418 (3), 349 (3), 348 (5), 330 (6), 278 (6), 173 (22), 149 (22), 71 (100). − UV/Vis (cyclohexane): λ_{max} (lg ε) = 355 nm (4.35). − $C_{22}H_{14}Cl_4$ (420.2): calcd. C 62.89, H 3.36; found C 62.20, H 3.33.

2,4,11,13-Tetrachloro[5]helicene (5): The photocyclization reaction of 0.64 g (1.5 mmol) of 1,4-bis(2′,4′-dichlorostyryl)benzene (**4**), 0.774 g (3 mmol) of iodine, and 42.4 mL (0.61 mol) of propylene oxide in 2.5 L of cyclohexane was monitored by TLC (5% acetic ester/cyclohexane) and was terminated after 6 h. The usual workup and recrystallization from toluene yielded 70 mg (11%) of **5** as a fluffy yellow solid. − IR (KBr): $\tilde{\nu}$ = 1605 cm^{-1}, 1590, 1550, 1470, 1390, 1370, 1290, 1190, 1130, 1070, 970, 860, 840, 730. − ^{1}H NMR ($CDCl_3$): δ = 7.65 (d, *J* = 1.9 Hz, 2 H, 3-H), 7.94 (s, 2 H, 7-H), 7.99 (d, *J* = 8.9 Hz, 2 H, 5/6-H), 8.32 (d, *J* = 1.9 Hz, 2 H, 1-H), 8.40 (d, *J* = 8.9 Hz, 2 H, 5/6-H). − ^{13}C NMR ($CDCl_3$): δ = 133.15 (C_{quat}), 133.0 (C_{quat}), 132.0 (C_{quat}), 130.4 (C_{quat}), 128.6 (C_{quat}), 128.3 (CH), 127.8 (CH), 127.3 (CH), 127.0 (CH), 125.8 (C_{quat}), 123.6 (CH). − MS (70 eV); *m*/*z* (%): 416 (52) [M$^+$], 380 (46), 344 (100), 308 (42), 274 (59), 154 (53), 137 (72).

4,11-Dichlorobenzo[*g*,*h*,*i*]perylene (6) and 4,11-Dibromobenzo[*g*,*h*,*i*]-perylene (7). − Experiments Aiming at the Synthesis of 1,4,11,14-Tetrahalogeno[5]helicenes: The starting materials 2,5-dichlorobenzyl bromide and 2,5-dibromobenzyl bromide were synthesized following the procedure described for the bromination of **1**. Then the bromides were converted into the corresponding triphenylphosphonium salts, the ylides of which were condensed with terephthaldialdehyde (**3**) to yield the bis(stilbenes) in a Wittig reaction similar to the synthesis of **4**.[24]

(*E*,*E*)-1,4-Bis(2,5-dichlorostyryl)benzene: Yield 13%, mp 245°C. − ^{1}H NMR ([D$_8$]THF): δ = 7.20 (dd, *J* = 8.7/2.6 Hz, 2 H, 4′-H), 7.22 (d, *J* = 16.4 Hz, 2 H, olefin-H), 7.35 (d, *J* = 8.7 Hz, 2 H, 3′-H), 7.45 (d, *J* = 16.4 Hz, 2 H, olefin-H), 7.58 (s, 4 H, CH), 7.77 (d, *J* = 2.6 Hz, 2 H, 6′-H). − $C_{22}H_{14}Cl_4$ (420.2): calcd. C 62.89, H 3.36; found C 63.00, H 3.53.

(*E*,*E*)-1,4-Bis(2,5-dibromostyryl)benzene: Yield 31%, mp 246−248°C. − ^{1}H NMR ([D$_8$]THF): δ = 7.27 (d, *J* = 16.2 Hz, 2 H, olefinic H), 7.31 (dd, *J* = 8.7/2.6 Hz, 2 H, 4′-H), 7.46 (d, *J* = 16.2 Hz, 2 H, olefinic H), 7.53 (d, *J* = 8.7 Hz, 2 H, 3′-H), 7.63 (s, 4 H, CH), 7.79 (d, *J* = 2.3 Hz, 2 H, 6′-H). − ^{13}C NMR ([D$_8$]THF): δ 122.4 (C_{quat}), 123.3 (C_{quat}), 127.0 (CH), 128.2 (CH), 130.4 (CH), 132.5 (CH), 133.5 (CH), 135.4 (CH), 138.0 (C_{quat}), 140.3 (C_{quat}). − UV/Vis (toluene): λ_{max} (lg ε) = 348 nm (4.58). − $C_{22}H_{14}Br_4$ (598.0): calcd. C 44.19, H 2.36; found C 43.92, H 2.40.

Irradiation of the Bis(stilbenes): Both bis(stilbenes) were irradiated according to the General Procedure B. In case of the tetrachlorobis(stilbene) 60 mg of yellow fluffy crystals were obtained after recrystallization from toluene, which contained 1,4,11,14-tetrachloro[5]helicene and the perylene **6** in a 1:2 ratio according to ^{1}H-NMR and TOF-MS analysis.[24] − In case of the tetrabromobis(stilbene) only the perylene **7** was obtained in a yield of 36%, mp 265−273°C after filtration through Alox N (toluene) and recrystallization from toluene. − ^{1}H NMR ($CDCl_3$): δ = 8.21 (d, *J* = 9.0 Hz, 2 H, 5-H/6-H), 8.23 (d, *J* = 8.5 Hz, 2 H, 2-H/3-H), 8.37 (s, 2 H, 7-H/8-H), 8.47 (d, *J* = 9.0 Hz, 2 H, 6-H/5-H), 8.72 (d, *J* = 8.5 Hz, 2 H, 3-H/2-H). − MS (70 eV); *m*/*z* (%): 434 (44, M$^+$), 355 (24), 274 (62), 137 (63), 110 (66), 99 (80), 98 (86), 85 (100), 69 (88), 56 (72). − UV/Vis (toluene): λ_{max} (lg ε) = 403 nm (4.15), 380 (4.09), 361 (3.77), 338 (3.53), 308 (4.35), 296 (4.27), 284 (4.14). − UV/Vis (acetonitrile): λ_{max} (lg ε) = 396 (4.11), 376 (4.03), 356 (3.70), 337 (3.49), 304 (4.31), 293 (4.23), 281 (4.10), 255 (3.86). − $C_{22}H_{10}Br_2$ (434.1): calcd. C 60.87, H 2.32; found C 60.43, H 2.40.

1,4-Bis(4′-cyanostyryl)benzene (10): The olefination (General Procedure A) of 0.75 g (5.7 mmol) of 4-cyanobenzaldehyde and of 2.25 g (2.8 mmol) of *p*-xylylenebis(triphenylphosphonium dibromide) yielded 0.9 g (95%) of the crude yellow product **10**, mp 295°C. − Spectroscopic data of the all-*trans* isomer: IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 3016, 2227, 1601, 1511, 1503, 1421, 1410, 1184, 891, 867, 837, 827. − ^{1}H NMR ($CDCl_3$): δ = 7.13 (d, *J* = 16.3 Hz, 2 H, olefinic H), 7.22 (d, *J* = 16.3 Hz, 2 H, olefinic H), 7.56 (s, 4 H, aryl-H), 7.60 (d, *J* = 8.5 Hz, 4 H, 2′-H/6′-H), 7.65 (d, *J* = 8.5 Hz, 4 H, 3′-H/5′-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 109.5 (C_{quat}), 118.0 (C_{quat}), 127.2 (CH), 127.5 (CH), 131.7 (CH), 132.6 (CH), 133.2 (CH), 136.5 (C_{quat}), 141.8 (C_{quat}). − MS (70 eV); *m*/*z* (%): 332 (100) [M$^+$], 315 (30), 228 (36), 216 (35), 204 (38), 203 (78), 111 (47), 99 (49), 85 (41), 57 (47). − UV/Vis (acetonitrile): λ_{max} (lg ε) = 367 nm (4.73). − $C_{24}H_{16}N_2$ (332.4): calcd. C 86.72, H 4.85, N 8.43; found C 86.45, H 4.81, N 8.24.

2,13-Dicyano[5]helicene (11): The photocyclization reaction (General Procedure B) of 540 mg (1.6 mmol) of the 1,4-bis(4′-cyanostyryl)benzene (**10**) in 3.5 L of benzene yielded 170 mg (32%) of a yellow solid (mp > 300°C after recrystallization from acetonitrile), showing a violet fluorescence when dissolved. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2221, 1268, 1256, 918, 859, 629. − ^{1}H NMR ($CDCl_3$): δ = 7.71 (dd, *J* = 8.3/1.2 Hz, 2 H, 3-H), 7.96 (s, 2 H, 7-H), 7.98 (d, *J* = 8.6 Hz, 2 H, 5-H/6-H), 8.04 (d, *J* = 8.6 Hz, 2 H, 6-H/5-H), 8.06 (d, *J* = 8.3 Hz, 2 H, 4-H), 8.73 (d, *J* = 1.2 Hz, 2 H, 1-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 107.5 (C_{quat}), 117.8 (C_{quat}), 125.0 (C_{quat}), 126.6 (CH), 126.9 (CH), 127.3 (CH), 128.4 (CH), 128.5 (CH), 128.7 (C_{quat}), 132.1 (C_{quat}), 132.2 (CH), 133.5 (C_{quat}). − MS (70 eV); *m*/*z* (%): 328 (100) [M$^+$], 327 (95), 301 (87), 300 (66), 299 (72), 248 (20), 136 (52), 71 (54), 57 (70). − UV/Vis (acetonitrile): λ_{max} (lg ε) = 346 nm (4.06), 319 (4.45), 300 (4.52), 290 (4.59), 278 (4.6). − UV/Vis (toluene): λ_{max} (lg ε) = 354 nm (4.65), 320 (5.11), 303 (5.13), 292 (5.25). − UV/Vis (ethanol): λ_{max} (lg ε) = 345 nm (3.98), 318 (4.44), 300 (4.50), 290 (4.58), 279 (4.60). − UV/Vis (methylcyclohexane): λ_{max} (lg ε) = 349 nm (3.68), 317 (4.16), 304 (4.17), 289 (4.3), 278 (4.34), 235 (4.71). − Fluorescence (acetonitrile, λ_{ex} = 335 nm): λ_{em} = 414 nm, 433, 462, 487 (shoulder); (toluene, λ_{ex} = 310 nm): λ_{em} = 415 nm, 433, 457, 485 (shoulder), 560 (weak exciplex emission); (ethanol, λ_{ex} = 360 nm): λ_{em} = 439 nm, 431, 387, 484 (shoulder); (methylcyclohexane, λ_{ex} = 340 nm): λ_{em} = 424 nm, 431, 454 (shoulder), 488 (shoulder), 540 (small exciplex emission). − $C_{24}H_{12}N_2$ (328.4): calcd. C 87.79, H 3.68, N 8.53; found C 87.86, H 3.85, 8.59.

X-ray Crystal Structure Analysis of 11: $C_{24}H_{12}N_2$, *M* = 328.36, 1.5 × 0.15 × 0.05 mm, *a* = 5.705(1), *b* = 20.101(1), *c* = 14.657(1) Å, *V* = 1680.8(3) Å^3, $\rho_{calcd.}$ = 1.298 g cm^{-3}, μ = 5.98 cm^{-1}, empirical absorption correction by φ scan data (0.865 ≤ *C* ≤ 0.999) *Z* = 4, orthorhombic, space group *Pbcn* (No. 60), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 1711 reflections collected (−*h*, −*k*, +*l*), (sinθ)/λ = 0.62 Å^{-1}, 1711 independent and 1373 observed reflections [*I* ≤ 2 σ(*I*)], 119 refined parameters, *R* = 0.056, wR^2 = 0.154, max. residual electron density 0.34 (−0.24) e Å^{-3}, hydrogen atoms calculated and riding.

2,5-Dicyanotoluene: Analogous to a procedure described by Anzalore[25] 23.3 g (0.151 mol) of 2,5-dichlorotoluene (**12**) and 49.3 g (0.55 mol) of CuCN in 130 mL of *N*-methylpyrrolidone were heated under reflux at 220°C for 72 h. The solution was allowed to cool to ca. 110°C and was poured into a mixture of 130 mL of concentrated ammonia, 130 mL of water, and 100 mL of toluene. After cooling to room temp., 100 mL of ether was added and the mixture was filtered followed by a further addition of 100 mL of ether. The organic layer was washed with 10% aqueous ammonia (until the aqueous extracts no longer turned blue) followed by washing with water, 10% aqueous HCl, and again water and saturated NaCl solution. Drying with $MgSO_4$ and evaporation of the solvent resulted in 11.3 g (53%) of 2,5-dicyanotoluene, mp 148°C. − ^{1}H NMR ($CDCl_3$): δ = 2.62 (s, 3 H, CH_3), 7.61 (d, *J* = 7.8 Hz,

1 H, 4-H), 7.64 (s, 1 H, 6-H), 7.74 (d, J = 7.8 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 20.3 (CH_3), 116.16 (C_{quat}), 116.17 (C_{quat}), 116.9 (C_{quat}), 117.0 (C_{quat}), 129.7 (CH), 133.0 (CH), 133.5 (CH), 143.1 (C_{quat}). − MS (70 eV); *m/z* (%): 143 (14), 142 (100) [M^+], 141 (18), 115 (66), 114 (22), 88 (11). − $C_9H_6N_2$ (142.2): calcd. C 76.04, H 4.25, N 19.71; found C 76.15, H 4.07, N 19.84.

2,5-Dicyanobenzyl Bromide: Bromination of 6.0 g (0.04 mol) of 2,5-dicyanotoluene with NBS analogous to the procedure described for **2** yielded 3.5 g (40%) of 2,5-dicyanobenzyl bromide after recrystallization from ethanol, mp 175−180°C. − ^{1}H NMR ($CDCl_3$): δ = 4.64 (s, 2 H, CH_2), 7.72 (dd, J = 8.0/1.5 Hz, 1 H, 4-H), 7.81 (d, J = 8.0 Hz, 1 H, 3-H), 7.88 (d, J = 1.5 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 27.6 (CH_2), 115.1 (C_{quat}), 116.4 (C_{quat}), 116.5 (C_{quat}), 117.1 (C_{quat}), 132.1 (CH), 133.7 (CH), 133.8 (CH), 142.5 (C_{quat}. − MS (70 eV); *m/z* (%): 222 (2), 220 (4), 142 (13), 141 (100), 115 (4), 114 (20). − $C_9H_5BrN_2$ (221.1): calcd. C 48.90, H 2.28, N 12.67; found C 48.91, H 2.34, N 12.44.

(2,5-Dicyanobenzyl)triphenylphosphonium Bromide (13): 3.5 g (16 mmol) of 2,5-dicyanobenzyl bromide was treated with triphenylphosphane to yield 3.0 g (46%) of the phosphonium salt, mp 265−270°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 5.36 (d, $J_{H,P}$ = 15.3 Hz, 2 H, CH_2), 7.62 (br. s, 1 H), 7.67−7.81 (m, 12 H), 7.91−8.07 (m, 5 H). − ^{13}C NMR ([D$_6$]DMSO): δ = 28.1 (CH_2, d, $J_{C,P}$ = 24.0 Hz), 115.4 (C_{quat}), 115.9 (2 C_{quat}), 116.9 (C_{quat}), 117.0 (C_{quat}), 118.1 (C_{quat}), 130.4 (CH, d, $J_{C,P}$ = 10 Hz), 132.9 (C_{quat}, d, $J_{C,P}$ = 8 Hz), 133.1 (CH), 134.4 (CH), 134.8 (CH), 135.3 (CH, d, $J_{C,P}$ = 5 Hz), 135.8 (CH, d, $J_{C,P}$ = 2 Hz). − $C_{27}H_{20}BrN_2P$ (483.4): calcd. C 67.09, H 4.17, N 5.80; found C 67.13, H 4.28, N 5.78.

4-(4′-Methylstyryl)benzaldehyde (15): The Wittig olefination (General Prodcedure A) of 1.58 g (3.9 mmol) of (4-methylbenzyl)triphenylphosphonium chloride and of terephthaldialdehyde (**3**) yielded 500 mg (58%) of a yellow solid after extraction with diethyl ether and crystallization from toluene, mp 182−187°C. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2822, 2821, 2731, 1700 (CO), 1598, 1166, 974, 827, 795. − ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 7.07 (d, J = 16.6 Hz, 1 H, olefinic H), 7.18 (d, J = 8.8 Hz, 2 H), 7.22 (d, J = 16.6 Hz, 1 H, olefinic H), 7.43 (d, J = 8.1 Hz, 2 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H), 9.97 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 20.3 (CH_3), 126.7 (CH), 127.2 (CH), 127.3 (CH), 130.0 (CH), 130.7 (CH), 132.6 (CH), 132.7 (C_{quat}), 134.1 (C_{quat}), 137.6 (C_{quat}), 142.6 (C_{quat}), 192.1 (CH). − MS (70 eV); *m/z* (%): 222 (100) [M^+], 207 (7), 193 (24), 178 (51), 91 (5). − $C_{16}H_{14}O$ (222.3): calcd. C 86.45, H 6.35; found C 86.36, H 6.43.

1-(2′,5′-Dicyanostyryl)-4-(4′′-methylstyryl)benzene (16): The Wittig olefination (General Procedure A) of 0.78 g (3.5 mmol) of 4-(4′-methylstyryl)benzaldehyde (**15**) and (2,5-dicyanobenzyl)triphenylphosphonium bromide (**13**) yielded 0.5 g (41%) of a yellow solid after extraction with toluene and crystallization from toluene, mp 245°C. − Spectroscopic data refer to the all-*trans* isomer: IR (KBr): $\tilde{\nu}$ = 3021 cm^{-1}, 2900, 2234 (CN), 1595, 1515, 1179, 965, 823, 542. − ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 7.05 (d, J = 16.6 Hz, 1 H, olefinic H), 7.14 (d, J = 16.6 Hz, 1 H, olefinic H), 7.17 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 16.1 Hz, 1 H, olefinic H), 7.38 (d, J = 16.1 Hz, 1 H, olefinic H), 7.42 (d, J = 8.0 Hz, 2 H), 7.52 (d, J = 8.6 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 1 H), 7.57 (d, J = 8.6 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 1 H), 8.05 (d, J < 1 Hz, 1 H). − MS LDI (no matrix); *m/z*: 346 [M^+]. − UV/Vis (toluene): λ_{max} (lg ε) = 380 nm (4.32). − HRMS ($C_{25}H_{18}N_2$): calcd. 346.147; found 346.146.

1,4-Dicyano-13-methyl[5]helicene (17): The photocyclization reaction (General Procedure B) of 253 mg (0.73 mmol) of 1-(2′,5′-dicyanostyryl)-4-(4′′-methylstyryl)benzene (**16**) in 2.5 L of toluene yielded 8 mg (3%) of a yellow solid after 20 h of irradiation, the usual workup and subsequent HPLC on silica gel (eluent: toluene). For details see ref.[1] Here we report an alternative procedure leading to a significantly better overall yield based on earlier results.[20]

4-Bromo-13-methyl[5]helicene-1-carboxamide (24): Into a solution of 100 mg (0.23 mmol) of the ester **23** in 10 mL of anhydrous THF was condensed 2 mL of NH_3. To this solution was subsequently added dropwise at −78°C 437 μL (0.70 mmol) of *n*BuLi (1.6 M solution in hexane). The mixture was stirred at −78 °C for 30 min, warmed up to room temperature and stirred for an additional 60 min, then poured into 20 mL of 2 N hydrochloric acid. The aqueous mixture was extracted with ether (3 × 10 mL), the combined organic phases were washed with H_2O (3 × 10 mL), brine (15 mL), and dried with $MgSO_4$. After evaporation of the solvents in a rotatory evaporator, chromatography of the residue on 20 g of silica gel, eluting with ether, gave three fractions: I (R_f = 0.85): 27 mg (27%) of starting material **23**. − II (R_f = 0.60): 32 mg (51%, based on reacted starting material) of methyl 3- and 4-amino-13-methyl[5]helicene-1-carboxylate, ratio 2:3. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.29 and 2.31 (s, 3 H, Ar-CH_3), 2.71 and 2.73 (s, 3 H, CO_2CH_3), 4.00 (br. s, 1 H, NH), 4.55 (br. s, 1 H, NH), 6.82 (d, 1 H, Ar-H), 7.21 (s, 1 H, Ar-H), 7.32 (d, 1 H, Ar-H), 7.65 (d, 1 H, Ar-H), 7.70 (s, 1 H, Ar-H), 7.73−7.98 (m, 6 H, Ar-H). − III (R_f = 0.2): 30 mg (41%, based on reacted starting material) of **24** as a yellow solid. − IR (KBr): $\tilde{\nu}$ = 3494 cm^{-1}, 3371 (NH), 3043, 2927, 1671, 1652 (CO), 1597, 1381, 1365, 847, 769. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, Ar-CH_3), 4.39 (br. s, 2 H, NH_2), 7.31 (dd, ^3J = 8.1, ^4J = 1.6 Hz, 1 H, Ar-H), 7.41 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 7.67 (d, ^4J = 0.8 Hz, 1 H, Ar-H), 7.75−7.93 (m, 5 H, Ar-H), 7.96 (d, ^3J = 8.1 Hz, 1 H, Ar-H), AB system (δ_A = 8.02, δ_B = 8.39, $^3J_{AB}$ = 8.9 Hz, 2 H, Ar-H).

1,4-Dicyano-13-methyl[5]helicene (17): A solution of 30 mg (0.07 mmol) of the amide **24** in 5 mL of phosphoryl chloride was stirred at 100 °C for 15 min, at which time the thin-layer-chromatographic monitoring indicated complete conversion of the starting material [R_f = 0.20 (ether)]. The reaction mixture was poured into 30 mL of ice-cold water, and the aqueous mixture was extracted with ether (3 × 5 mL). The combined organic phases were washed with H_2O (8 mL), saturated $NaHCO_3$ solution (8 mL), H_2O (8 mL) again, and brine (8 mL). The solution was dried with $MgSO_4$, and the solvents removed in a rotatory evaporator. The crude product was taken up in 3 mL of *N*-methylpyrrolidone, 20 mg of anhydrous CuCN [dried under reduced pressure (10^{-3} Torr) at 90°C], and the mixture was stirred at 200 °C for 24 h, at which time the thin-layer-chromatographic monitoring indicated complete conversion of the starting material [R_f = 0.65 (ether/light petroleum ether, 1:1)] to product (R_f = 0.5). The reaction mixture was poured into H_2O (10 mL), the aqueous mixture extracted with ether (3 × 2 mL), the combined organic phases were washed with H_2O (4 × 2 mL), brine (2 mL), and dried with $MgSO_4$. After evaporation of the solvents in a rotatory evaporator, column chromatography of the residue on 15 g of silica gel eluting with ether/light petroleum ether (1:1) gave 16 mg (67%, based on **24**) of **17** as a yellow-green solid. − IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 2231 (CN), 2217 (CN), 1608, 1492, 1354, 1148, 1097, 848, 808. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, Ar-CH_3), 7.41 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1 H, Ar-H), 7.50 (s, 2 H, Ar-H), 7.72 (d, ^3J = 7.6 Hz, 1 H, Ar-H), 7.85−8.08 (m, 5 H, Ar-H), 8.12 (d, ^3J = 8.2 Hz, 1 H, Ar-H), AB system (δ_A = 8.19, δ_B = 8.38, $^3J_{AB}$ = 8.7 Hz, 2 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$: δ = 21.8 (+, Ar-CH_3), 114.4 (C_{quat}), 116.2 (C_{quat}), 116.9 (C_{quat}), 117.3 (C_{quat}), 123.0 (+), 123.4 (C_{quat}), 124.7 (+), 125.4 (+), 125.5 (+), 126.0 (+), 126.4 (C_{quat}), 128.8 (+), 129.1 (+), 129.3 (+), 130.2 (C_{quat}), 130.6 (+), 130.9 (+), 131.2 (+), 131.5 (C_{quat}), 132.4

(C_{quat}), 132.5 (C_{quat}), 132.9 (C_{quat}), 133.3 (C_{quat}), 135.9 (C_{quat}). − HR-MS: 342.1154 ($C_{25}H_{14}N_2$, M^+; calcd. 342.1154).

X-ray Crystal Structure Analysis of 17: Formula $C_{25}H_{14}N_2$, M = 342.38, 0.6 × 0.5 × 0.2 mm, a = 20.223(4), b = 11.727(2), c = 14.619(2) Å, β = 99.03(2)°, V = 3424.0(10) Å^3, $\rho_{calcd.}$ = 1.328 g cm^{-3}, μ = 6.08 cm^{-1}, no absorption correction (0.979 ≤ C ≤ 0.999), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 3642 reflections collected (+h, +k, ±l), (sinθ)/λ = 0.62 Å^{-1}, 3514 independent and 3157 observed reflections [$I \leq 2\ \sigma(I)$], 246 refined parameters, R = 0.0611, wR_2 = 0.176, max. residual electron density 0.88 (−0.86) e Å^{-3}, hydrogen atoms calculated and riding.

(3,5-Dimethylbenzyl)triphenylphosphonium Bromide: The phosphonium salt was prepared from 3,5-dimethylbenzyl bromide in 93% yield, mp 325−330°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.05 (s, 6 H, 2 CH_3), 5.05 (d, $J_{H,P}$ = 15.5 Hz, 2 H, CH_2), 6.51 (s, 2 H, 2-H/6-H), 6.92 (s, 1 H, 4-H), 7.60−7.70 (m, 12 H, phenyl), 7.85−7.95 (m, 3 H, phenyl). − ^{13}C NMR ([D$_6$]DMSO): δ = 20.1 (2 CH_3), 27.6 (CH_2, d, $J_{C,P}$ = 48.0 Hz), 117.3 (C_{quat}, d, $J_{C,P}$ = 85.9 Hz), 126.9 (C_{quat}, d, $J_{C,P}$ = 10.1 Hz), 128.2 (CH, d, $J_{C,P}$ = 7.6 Hz), 129.0 (CH, d, $J_{C,P}$ = 7.6 Hz), 129.4 (CH, d, $J_{C,P}$ = 10.1 Hz), 133.5 (CH, d, $J_{C,P}$ = 5.1 Hz), 134.4 (CH), 137.1 (C_{quat}). − MS; *m/z* (%): 380 (23), 379 (23), 263 (23), 262 (71), 261 (23), 184 (45), 183 (100). − $C_{27}H_{26}BrP$ (461.4): calcd. C 70.29, H 5.68; found C 70.32, H 5.79.

(*E*)-4-(3′,5′-Dimethylstyryl)benzaldehyde (19): The Wittig olefination (General Procedure A) of 30 g (66 mmol) of (3,5-dimethylbenzyl)triphenylphosphonium bromide and of terephthaldialdehyde (**3**) yielded 10.0 g (64%) of a white solid after extraction with diethyl ether and filtration through silica gel (eluent: toluene), mp 76−77°C. − IR (KBr): ṽ = 3027 cm^{-1}, 2915, 1686, 1597, 1298, 1160, 967, 845, 803, 686. − ^{1}H NMR (300 MHz; [D$_6$]DMSO): δ = 2.34 (s, 6 H, CH_3), 6.95 (s, 1 H, 4′-H), 7.10 (d, J = 16.4 Hz, 1 H, olefinic H), 7.16 (s, 2 H, 2′-H/6′-H), 7.19 (d, J = 16.4 Hz, 1 H, olefinic H), 7.62 (d, J = 8.3 Hz, 2 H, 3-H/5-H), 7.85 (d, J = 8.3 Hz, 2 H. 2-H/6-H), 9.98 (s, 1 H, CHO). − MS (70 eV); *m/z* (%): 236 (100) [M^+], 207 (23), 192 (70), 178 (49). − UV/Vis (toluene): λ_{max} (lg ε) = 340 nm (4.60). − $C_{17}H_{16}O$ (236.3): calcd. C 86.41, H 6.83; found C 86.13, H 6.82.

1-(2′,5′-Dicyanostyryl)-4-(3′′,5′′-dimethylstyryl)benzene (20): The Wittig olefination (General Procedure A) of 2.45 g (10.4 mmol) of 4-(3′,5′-dimethylstyryl)benzaldehyde (**19**) and (2,5-dicyanobenzyl)-triphenylphosphonium bromide (**13**) yielded 1.7 g (45%) of a crude yellow solid after extraction with toluene and filtration through silica gel (eluent: toluene). − Spectroscopic data of the all-*trans* isomer: IR (KBr): ṽ = 3019 cm^{-1}, 2900, 2221 (CN), 1633, 1598, 1512, 1294, 976, 955, 842, 818, 808, 688. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.33 (s, 6 H, 2 Me), 6.92 (s, 1 H, 4′′-H), 7.08 (d, J = 16.5 Hz, 1 H, $H_{olef.}$), 7.10 (d, J = 16.5 Hz, 1 H, $H_{olef.}$), 7.15 (s, 2 H, 2′′-H/6′′-H), 7.31 (d, J = 16.2 Hz, 1 H, $H_{olef.}$), 7.38 (d, J = 16.5 Hz, 1 H, $H_{olef.}$), 7.53 (d, J = 8.8 Hz, 2 H, 2-H/6-H/3-H/5-H), 7.54 (dd, J = 8.1/1.4 Hz, 1 H, 4′-H), 7.56 (d, J = 8.8 Hz, 2 H, 3-H/5-H/2-H/6-H), 7.73 (d, J = 8.1 Hz, 1 H, 3′-H), 8.05 (d, J = 1.4 Hz, 1 H, 6′-H). − MS (70 eV); *m/z* (%): 361 (20), 360 (60) [M^+], 345 (18), 330 (26), 329 (45), 328 (25), 203 (14), 165 (32), 115 (38), 97 (46), 91 (60), 83 (68), 71 (84), 57 (100). − UV/Vis (toluene): λ_{max} (lg ε) = 380 nm (4.33). − $C_{26}H_{20}N_2$ (360.5): calcd. C 86.64, H 5.59, N 7.77; found C 86.18, H 5.83, N 7.83.

11,14-Dicyano-1,3-dimethyl[5]helicene (21): The photocyclization reaction (General Procedure B) of 600 mg (1.7 mmol) of 1-(2′,5′-dicyanostyryl)-4-(3′′,5′′-dimethylstyryl)benzene (**20**) in 1.4 L of benzene yielded 49 mg (8%) of a yellow solid after 7 d of irradiation, the usual workup and subsequent HPLC on silica gel (eluent: toluene), mp 313°C. − IR (KBr): ṽ = 2957 cm^{-1}, 2225 (CN), 1606, 1444, 1301, 844. − ^{1}H NMR ($CDCl_3$): δ = 1.04 (s, 3 H, Me), 2.56 (s, 3 H, Me), 7.03 (s, 1 H, 2-H/4-H), 7.63 (d, J = 7.6 Hz, 1 H), 7.81 (s, 1 H, 4-H/2-H), 7.89 (d, J = 8.3 Hz, 1 H), 7.93 (d, J = 7.6 Hz, 1 H), 8.01 (d, J = 8.1 Hz, 1 H), 8.02 (d, J = 8.3 Hz, 1 H), 8.16 (d, J = 8.1 Hz, 1 H), 8.23 (d, J = 8.7 Hz, 1 H), 8.34 (d, J = 8.7 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 22.1 (CH_3), 114.1 (C_{quat}), 114.3 (C_{quat}), 116.1 (C_{quat}), 116.9 (C_{quat}), 122.6 (CH), 124.4 (C_{quat}), 124.9 (CH), 125.0 (C_{quat}), 125.6 (CH), 126.9 (CH), 129.8 (C_{quat}), 129.8 (CH), 129.8 (CH), 130.1 (CH), 131.0 (CH), 131.3 (C_{quat}), 131.6 (C_{quat}), 131.8 (CH), 132.1 (C_{quat}), 132.2 (CH), 132.4 (C_{quat}), 132.9 (C_{quat}), 134.3 (C_{quat}), 137.1 (C_{quat}). − MS (70 eV); *m/z* (%): 356 (22) [M^+], 341 (19), 330 (33), 326 (15), 315 (20), 178 (18), 135 (33), 84 (69), 57 (100). − UV/Vis (acetonitrile): λ_{max} (lg ε) = 361 nm (3.88), 295 (4.60), 236 (4.73). − UV/Vis (toluene): λ_{max} (lg ε) = 441 nm (2.38), 367 (2.99), 299 (3.71). − UV/Vis (methylcyclohexane): λ_{max} (lg ε) = 442 nm (3.27), 359 (4.25), 343 (3.94), 298 (4.54), 238 (4.58). − UV/Vis (ethanol): λ_{max} (lg ε) = 443 nm (3.15), 363 (3.83), 297 (4.65), 237 (4.75). − Fluorescence (acetonitrile, λ_{ex} = 360 nm): λ_{em} = 509. − Fluorescence (toluene, λ_{ex} = 380 nm): λ_{em} = 481. − Fluorescence (ethanol, λ_{ex} = 380 nm): λ_{em} = 514. − Fluorescence (methylcyclohexane, λ_{ex} = 380 nm): λ_{em} = 464. − $C_{26}H_{16}N_2$ (356.4): calcd. C 87.62, H 4.53, N 7.86; found C 87.50, H 4.55, N 7.98.

X-ray Crystal Structure Analysis of 21: $C_{26}H_{16}N_2$, M = 356.41, 0.30 × 0.15 × 0.15 mm, a = 7.758(1), b = 22.185(2), c = 10.666(1) Å, β = 101.53(1)°, V = 1798.7(3) Å^3, $\rho_{calcd.}$ = 1.316 g cm^{-3}, μ = 5.99 cm^{-1}, no empirical absorption correction (0.973 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 3869 reflections collected (±h, −k, −l), (sinθ)/λ = 0.62 Å^{-1}, 3676 independent and 2341 observed reflections [$I \leq 2\ \sigma(I)$], 254 refined parameters, R = 0.054, wR_2 = 0.139, max. residual electron density 0.49 (−0.36) e Å^{-3}, hydrogen atoms calculated and riding.

4-Bromo-*N*,*N*,13-trimethyl[5]helicene-1-carboxamide (26): Into a solution of 917 mg (2.14 mmol) of the ester **23** in 50 mL of THF was condensed 4 mL of dimethylamine and subsequently was added dropwise at −78°C 1.6 mL (2.6 mmol) of a 1.6 M solution of *n*BuLi in hexane within 25 min, during which time the reaction mixture changed its color from yellow to red and eventually deep purple. Upon warming to room temperature within 1 h, the color of the mixture lightened up, and it was stirred for an additional 30 min. It was poured into 100 mL of H_2O, and the aqueous mixture was extracted with three portions of ether (40 mL each). The combined ethereal extracts were washed with H_2O (3 × 20 mL) brine (30 mL), and dried with $MgSO_4$. The solvents were removed in a rotatory evaporator, and the crude product chromatographed on 100 g of silica gel, eluting with diethyl ether to give two fractions: I (R_f = 0.85): 77 mg (8%) of starting material **23**. − II (R_f = 0.43): 692 mg (80%, based on reacted starting material) of **26** as a yellow solid. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (s, 3 H, N-CH_3), 1.86 (s, 3 H, N-CH_3), 2.28 (s, 3 H, Ar-CH_3), AB system [δ_A = 7.37, δ_B = 7.95, $^3J_{AB}$ = 8.2 Hz, 2 H, 13(14)-H], AB system (δ_A = 7.45, δ_B = 7.98, $^3J_{AB}$ = 7.8 Hz, 2 H, Ar-H), 7.62 (s, 1 H, 11-H), 7.29−8.00 (m, 4 H, Ar-H), AB system [δ_A = 7.73, δ_B = 8.40, $^3J_{AB}$ = 8.8 Hz, 2 H, 8(9)-H].

4-Bromo-1-(dimethylaminomethyl)-13-methyl[5]helicene (27): To a solution of the amide **26** (690 mg, 1.64 mmol) in 25 mL of anhydrous CH_2Cl_2 was added at room temperature 440 mg (2.23 mmol) of triethyloxonium tetrafluoroborate, and the mixture was stirred for 24 h. The solvent was removed by bulb-to-bulb distillation at room temperature, and the residue was taken up in 20 mL of meth-

anol. To the mixture was added at 0 °C 151 mg (4.00 mmol) of sodium tetrahydroborate, the cooling bath was removed, and the mixture stirred for an additional 12 h. It was poured into H_2O (100 mL), the aqueous mixture was extracted with ether (4 × 10 mL), and the combined ethereal extracts were washed with H_2O (3 × 15 mL), brine (20 mL), and dried with $MgSO_4$. The solvents were removed in a rotatory evaporator, and the residue subjected to column chromatography on 80 g of silica gel, eluting with ether/light petroleum ether (b.p. 40−60°C) within 20 h to yield three fractions: I (R_f = 0.8): 49 mg (8%) of 4-bromo-13-methyl[5]helicene-1-carbaldehyde. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, Ar-CH_3), 7.31 (dd, 1 H, Ar-H), 7.54 (s, 1 H, 14-H), 7.71 (d, 1 H, Ar-H), 7.78−7.81 (m, 7 H, Ar-H), 8.46 (d, 1 H, Ar-H), 9.10 (s, 1 H, CHO). − II (R_f = 0.2): 523 mg (81%, based on reacted starting material) of **27** as a yellow solid. − ^{1}H NMR (250 MHz,$CDCl_3$): δ = 1.39 (s, 6 H, N-CH_3), 2.20 (s, 3 H, Ar-CH_3), AB system (δ_A = 2.45, δ_B = 2.58, $^2J_{AB}$ = −14.2 Hz, 2 H, Ar-CH_2), 7.39 (d, ^3J = 8.0 Hz, 1 H, ArH), 7.45 (s, 1 H, 14-H), 7.49 (d, ^3J = 8.0 Hz, 1 H, Ar-H), 7.78−7.88 (m, 4 H, Ar-H), AB system (δ = 7.92, δ_B = 8.00, $^3J_{AB}$ = 8.0 Hz, 2 H, Ar-H), AB system [δ_A = 7.92, δ_B = 8.38, $^3J_{AB}$ = 8.8 Hz, 2 H, ArH]. − III (R_f = 0.1): 35 mg (5%) of starting material **26**.

1-(Dimethylaminomethyl)-13-methyl-4-(trimethylsilyl)[5]helicene (28): To a solution of 500 mg (1.17 mmol) of **27** in 20 mL of anhydrous THF was added dropwise at −100 °C 934 μL (1.4 mmol) of a 1.5 M solution of *n*BuLi in hexane, and the mixture stirred at this temperature for an additional 15 min. Then 1.76 mL (14.0 mmol) of chlorotrimethylsilane (distilled from CaH_2) was added within 5 min, the mixture was warmed up to room temperature, stirred for an additional 1 h and poured into 100 mL of a 2.5% $NaHCO_3$ solution. After having been shaken vigorously, the aqueous mixture was extracted with ether (3 × 20 mL), the combined ethereal extracts were washed with H_2O (4 × 30 mL), brine (20 mL), and dried with $MgSO_4$. After evaporation of the solvents in a rotatory evaporator, chromatography of the residue on 50 g of silica gel eluting with ether/light petroleum ether (2:1) yielded **28** as a yellow solid, R_f = 0.8. Yield after recrystallization from pentane, 484 mg (98%). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59 (s, 9 H, Si-CH_3), 1.38 (s, 6 H, N-CH_3), 2.19 (s, 3 H, Ar-CH_3), AB system (δ_A = 2.50, δ_B = 2.64, $^2J_{AB}$ = −14.2 Hz, 2 H, Ar-CH_2), 7.28 (d, ^3J = 7.4 Hz, 1 H, Ar-H), 7.46 (s, 1 H, 11-H), 7.54 (d, ^3J = 7.2 Hz, 1 H, Ar-H), 7.78−7.86 (m, 5 H, Ar-H), AB system (δ_A = 7.89, δ_B = 7.98, $^3J_{AB}$ = 8.1 Hz, 2 H, Ar-H), 8.18 (d, ^3J = 8.6 Hz, 1 H, Ar-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.8 (+, Si-CH_3), 21.8 (+, Ar-CH_3), 44.9 (+, N-CH_3), 62.8 (−, CH_2-N), 125.0 (+), 125.3 (+), 125.8 (+), 125.9 (+), 126.2 (+), 126.9 (+), 127.2 (+), 127.5 (+), 127.6 (+), 127.7 (+), 128.9 (C_{quat}), 129.9 (C_{quat}), 130.3 (C_{quat}), 130.7 (C_{quat}), 131.0 (C_{quat}), 131.9 (C_{quat}), 133.4 (+), 134.6 (C_{quat}), 135.7 (C_{quat}), 136.1 (C_{quat}), 137.4 (C_{quat}). − $C_{29}H_{31}NSi$ (421.7): calcd. C 82.61, H 7.41, N 3.32; found C 82.70, H 7.49, N 3.38.

Acknowledgments

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[1] Taken in part from: C. Stammel, Dissertation, Universität Münster, **1995**.
[2] M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78*, 4765−4770.
[3] M. Flammang-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett*. **1967**, 743−744.
[4] M. Scholz, M. Mühlstädt, F. Dietz, *Tetrahedron Lett*. **1967**, 665−668.
[5] W. H. Laarhoven, T. J. H. M. Cuppen, R. J. F. Nivard, *Recl. Trav. Chim. Pay-Bas* **1968**, *87*, 687−698; *Tetrahedron* **1970**, *26*, 4865−4881.
[6] M. Gorsane, R. H. Martin, *Bull. Soc. Chim. Belg*. **1985**, *94*, 205−214.
[7] R. H. Martin, M. J. Marchant, *Tetrahedron* **1974**, *30*, 347−349.
[8] H. J. Lindner, *Tetrahedron* **1975**, *31*, 281−284.
[9] R. H. Janke, G. Haufe, E.-U. Würthwein, J. H. Borkent, *J. Am. Chem. Soc*. **1996**, *118*, 6031−6035.
[10] [10a] G. J. Karvanos, N. J. Turro, *Chem. Rev.* **1986**, *86*, 401−449. − [10b] J. Mattay, *Angew. Chem.* **1987**, *99*, 849−870; *Angew. Chem. Int. Ed. Engl*. **1987**, *26*, 825−845. − [10c] J. Mattay, *Synthesis* **1989**, 233−252. − [10d] J. Mattay, M. Vondenhof, *Top. Curr. Chem*. **1991**, *159*, 219−255. − [10e] F. Müller, J. Mattay, *Chem. Rev.* **1993**, *93*, 99−117. − [10f] S. Hintz, A. Heidbreder, J. Mattay, *Top. Curr. Chem*. **1996**, *177*, 77−124.
[11] [11a] L. Liu, T. J. Katz, *Tetrahedron Lett.* **1990**, *31*, 3983−3986. − [11b] N. D. Willmore, L. Liu, T. J. Katz, *Angew. Chem.* **1992**, *104*, 1081−1082; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1093−1094. − [11c] T. J. Katz, L. Liu, N. D. Willmore, J. M. Fox, A. L. Rheingold, S. Shi, C. Nuckolls, B. H. Rickman, *J. Am. Chem. Soc.* **1997**, *119*, 10054−10063.
[12] [12a] M. S. Newman, C. H. Chen, *J. Org. Chem*. **1972**, *37*, 1312−1314. − [12b] A. J. Lindner, B. Kitschke, *Bull. Soc. Chim. Belg*. **1979**, *88*, 831−839. − [12c] H. J. Teuber, L. Vogel, *Chem. Ber*. **1970**, *103*, 3319−3342. − [12d] M. Nakazaki, K. Yamamoto, M. Maeda, *J. Org. Chem*. **1981**, *46*, 1985−1987; *Chem. Lett*. **1980**, 1553−1554. − [12e] Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, R. Noyori, *J. Am. Chem. Soc*. **1981**, *103*, 6971−6973.
[13] [13a] Y. Cochez, J. Jespers, V. Libert, K. Mislov, R. H. Martin, *Bull. Soc. Chim Belg*. **1975**, *84*, 1033−1036. − [13b] Y. Cochez, R. H. Martin, J. Jespers, *Isr. J. Chem.* **1977**, *15*, 29−32. − [13c] J. Vanest, R. H. Martin, *Recl. Trav. Chim. Pay-Bas* **1979**, *98*, 113.
[14] Y. Inoue, *Chem. Rev.* **1992**, *92*, 741−770.
[15] P. Hugelshofer, J. Kalvoda, K. Schaffner, *Helv. Chim. Acta* **1960**, *43*. 1322−1332.
[16] F. B. Mallory, C. W. Mallory, *Org. React.* **1984**, *30*, 1−456.
[17] J. J. M. Lamberts, W. H. Laarhoven, *Recl. Trav. Chim. Pay-Bas* **1983**, *102*, 185−204.
[18] L. Liu, B. Yang, T. J. Katz, M. K. Pointdexter, *J. Org. Chem*. **1991**, *56*, 3769−3775.
[19] W. H. Laarhoven in *Organic Photochemistry* (Ed.: A. Padwa), M. Dekker, New York, **1989**, vol. 10, chapter 2, p. 163−308.
[20] C. Puls, A. Stolle, A. de Meijere, *Chem. Ber.* **1993**, *126*, 1635−1641.
[21] I. R. Mackay, J. Monteath Robertson, J. G. Sime, *Chem. Commun*. **1969**, 1470−1471.
[22] G. Stulen, G. J. Visser, *Chem. Commun*. **1969**, 965.
[23] H. Görner, C. Stammel, J. Mattay, *J. Photochem. Photobiol., A: Chem*. **1999**, *120*, 171−179.
[24] The experimental details and the analytical data are described in ref.[1]
[25] L. Anzalore, J. A. Hirsch, *J. Org. Chem*. **1985**, *50*, 2128−2133.
[26] T. Campbell, R. McDonald, *J. Org. Chem.* **1959**, *24*, 1246−1251.

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