Controlled Synthesis of Substituted Benzobasketene Derivatives

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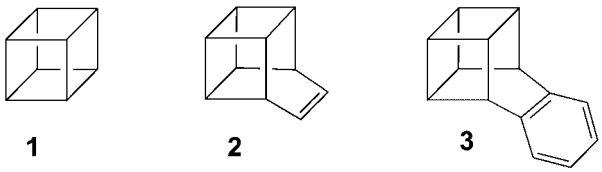
The addition of benzyne to *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (**6**) led to the formation of dibromide **7**. The dehydrobromination of **7** followed by replacement of the Br-atom with a CN substituent gave **9**. Photolysis of **9** in acetone at 254 nm yielded the desired monosubstituted benzobasketene derivative **10**. Bromination of monobromide **8** followed by dehydrobromination furnished the symmetrically substituted dibromo compound **15**. Further bromination of **7** followed by dehydrobromination resulted in the formation of the dibromides **20** and **21**. Substitution of the Br-atoms in **15**, **20**, and **21** with CN substituents and photolysis of the formed dicarbonitriles **16**, **23**, and **24** gave the target benzobasketene-dicarbonitriles **17**, **25**, and **26**, respectively.

Introduction. – The discovery of the intramolecular photochemical [2 + 2] cycloaddition reaction has initiated the synthesis of polycarbocyclic 'cage' compounds, which possess rigid, compact, and often highly strained structures. These compounds are often valuable for discovering and testing concepts of bonding ⇄ and reactivity [1]. Many polycyclic molecules are appealing objects for study because of their actual or anticipated chemical and physical properties as well as because of their aesthetically unusual symmetry characteristics that make them very attractive as synthetic targets.

Cubane **1** [2] and its derivatives, basketene **2** [3], and benzobasketene **3** [4] serve as an important class of these cage molecules. It has been pointed out that some cubane derivatives can be important explosives due to the exceptionally high density [5] and very high heat of formation. Furthermore, a number of cubane derivatives have shown interesting activity in anti-AIDS and antitumor screens [2b].



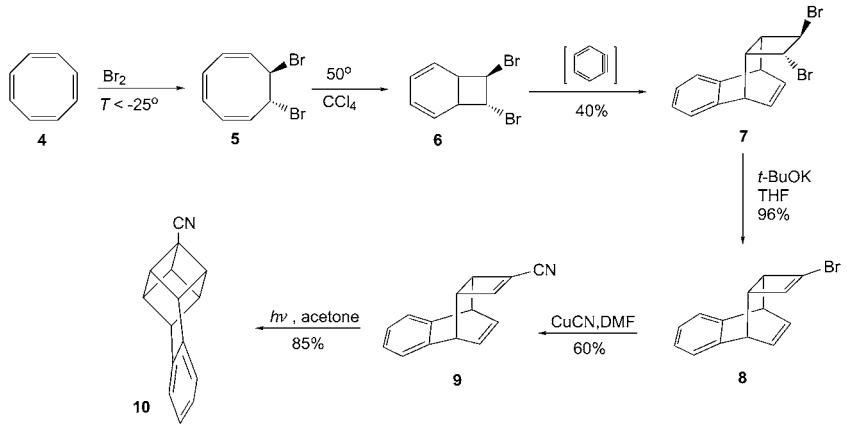
Basketene [4], which is a $(CH)_{10}$ hydrocarbon, has evolved as a result of its fascinating propensity for thermal and photochemical interconversion. The benzobasketene **3** has been synthesized by acetone-sensitized photolysis [4b][6] of the benzo derivative of *Nenitzescu*'s hydrocarbon [7]. Because of the wide interest directed at the

[1]) Author responsible for the X-ray crystal-structure analysis.

synthesis of substituted cubane derivatives, we were interested in the synthesis of benzobasketene derivatives substituted at various positions. In this paper, we describe a general controlled-substitution methodology leading to the synthesis of substituted benzobasketene derivatives.

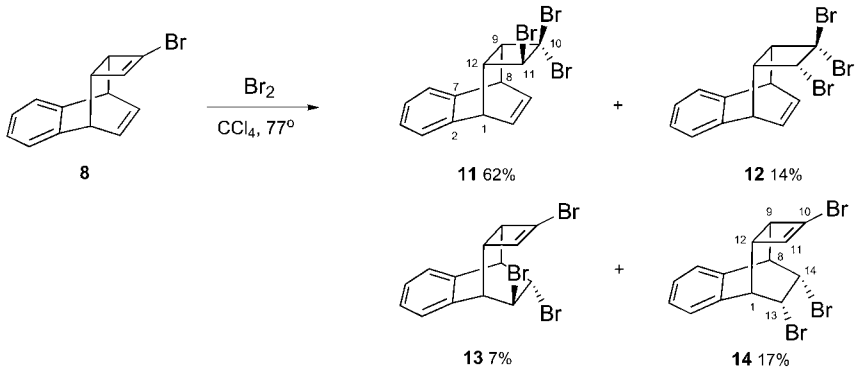
Results and Discussion. – Entry to the skeleton of *Nenitzescu*'s hydrocarbon was performed by cycloaddition of benzyne to the readily available *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (**6**) [8] (obtained from **4** *via* **5**, see *Scheme 1*). Treatment of the isolated **7** with *t*-BuOK gave bromoalkene **8** as the sole product. The compound was characterized by means of ^{1}H- and ^{13}C-NMR data. Irradiation of a soln. of **8** in acetone did not result in the formation of the cage compound, *i.e.*, bromobenzobasketene. We assume that the initially formed excited state of **8** is quenched by the Br-atom. Therefore, we decided to replace the Br-atom with a CN substituent and then to submit the product to photolysis. When **8** was treated with CuCN at 130° in DMF, the expected substitution product **9** was formed in 60% yield. Photolysis of **9** in acetone at 254 nm gave the desired benzobasketene derivative **10** in 85% yield. The symmetrical ^{1}H- and ^{13}C-NMR spectra were in agreement with the proposed structure. Especially, the presence of six absorption lines in the sp^3 region shows the presence of a symmetry element and definitively establishes the position of the substituent.

Scheme 1

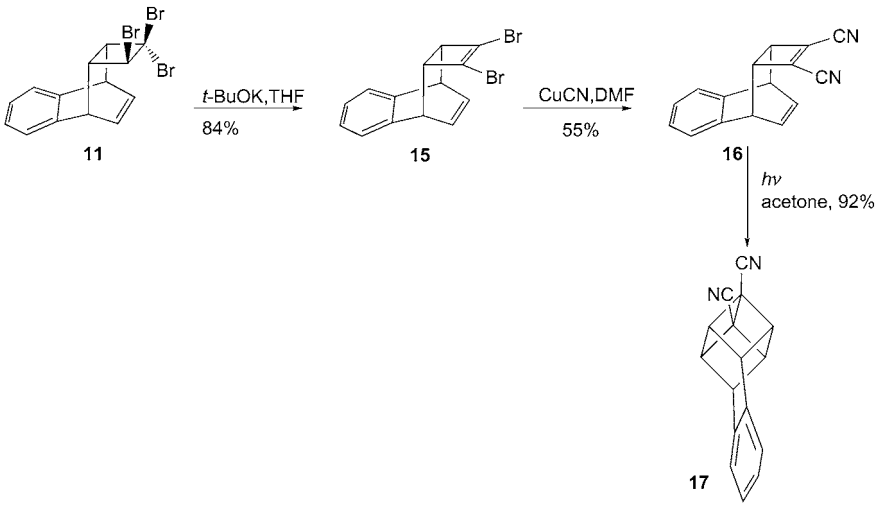


After the successful introduction of a substituent at C(4), we turned our attention to the synthesis of benzobasketene derivatives disubstituted at various positions. For that reason, we submitted monobromide **8** to further bromination (*Scheme 2*). Monobromide **8** was treated with a hot solution of Br_2 at the reflux temperature of CCl_4 to prevent skeletal rearrangements (for high-temperature bromination, see [9]). The ^{1}H-NMR spectroscopic analysis indicated the formation of a mixture consisting of the addition products **11**, **12**, **13**, and **14** in a ratio 62 : 14 : 7 : 17.

Scheme 2



Scheme 3



From the disappearance of the *s* arising from the four-membered-ring olefinic proton in the ^{1}H-NMR spectrum of **8**, it was easily established that Br_2 added mainly to the four-membered ring. The ^{1}H-NMR spectra of **11** and **12** were very similar. The configurational assignments to **11** and **12** were made on the basis of the ^{1}H-NMR chemical shift of H–C(11), which is shifted by *ca.* 0.75 ppm to higher field in **11** because of the location of that proton in the shielding cone of the C=C bond. The correct configurational assignments to the isomers **13** and **14** were made on the basis of the measured coupling constants between the protons H–C(13) and H–C(14). In the case of **14**, the corresponding coupling constant was $J(13,14) = 7.9$ Hz (*cis* coupling), whereas the coupling constant of **13** was $J(13,14) = 4.9$ Hz, indicating the *trans* configuration of the Br-atoms. These values are well in agreement with those reported for a similar skeleton [10].

Subsequently, the desired isomers **11**/**12** (or pure **11**), which have the requisite skeletal arrangement and the functionality to permit the easy introduction of the second C=C bond, were submitted to dehydrobromination reactions with *t*-BuOK, and

15 was isolated as the sole product in 84% yield (from pure **11**; see *Scheme 3*). Replacement of the Br-atoms with CN substituents as described above followed by photolysis gave the desired benzobasketene-dicarbonitrile **17** in 92% yield (*Scheme 3*). The ^{13}C-NMR spectrum of **17** showed 7 C-signals (3 sp^2-C, 1 sp-C and 3 sp^3-C) in accordance with the proposed structure, and the symmetric ^{1}H-NMR spectrum supported the expected position of the CN groups.

We then turned our attention to the synthesis of unsymmetrically substituted benzobasketene derivatives. For this, we had to introduce the substituents at the stage of *Nenitzescu*'s benzohydrocarbon. Thus, dibromide **7** was treated with Br_2 at the reflux temperature of CCl_4 to give a mixture of the two tetrabromides **18** and **19** in 70 and 15% yield, respectively (*Scheme 4*). The NMR spectra showed in both cases the addition of Br_2 to the C=C bond without molecular rearrangement. To distinguish the structures of **18** and **19**, a single-crystal X-ray analysis of **18** was performed that established the *trans*,*cis* configuration of its Br-atoms (see *Fig.* and *Table*). Studies concerning the mechanism of the *cis* addition show that the *cis* adduct can arise in the rigid skeleton directly by *cis* collapse of an ion pair [11]. The configuration of the Br-atoms in **19** was assigned as *trans*,*trans*.

The pure isomers **18** and **19**, or a mixture **18**/**19**, were submitted to dehydrobromination with *t*-BuOK, and a mixture consisting of the dibromides **20** and **21** and bromo ketone **22** was isolated (*Scheme 4*). Bromo ketone **22** was formed during column chromatography; it is likely that part of isomer **21** can be attacked by the H_2O molecule present in silica gel yielding **22**, thus releasing the strain caused by the Br-atoms in **21**. The positions of the Br-atoms in **20** and **21** were determined by NMR data and, especially, HMBC (heteronuclear multi-bond-correlation) spectra. Again, replacement

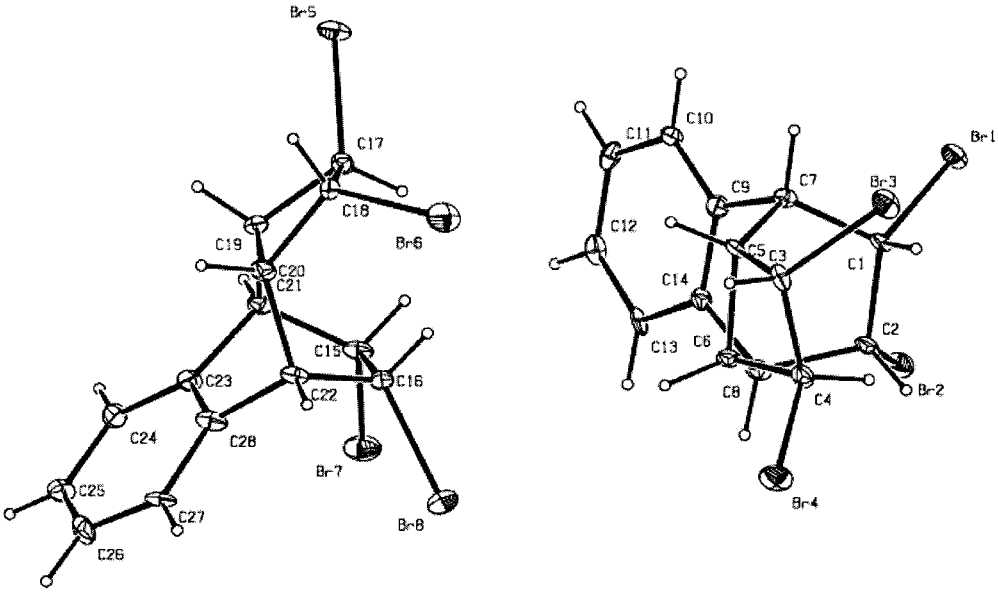
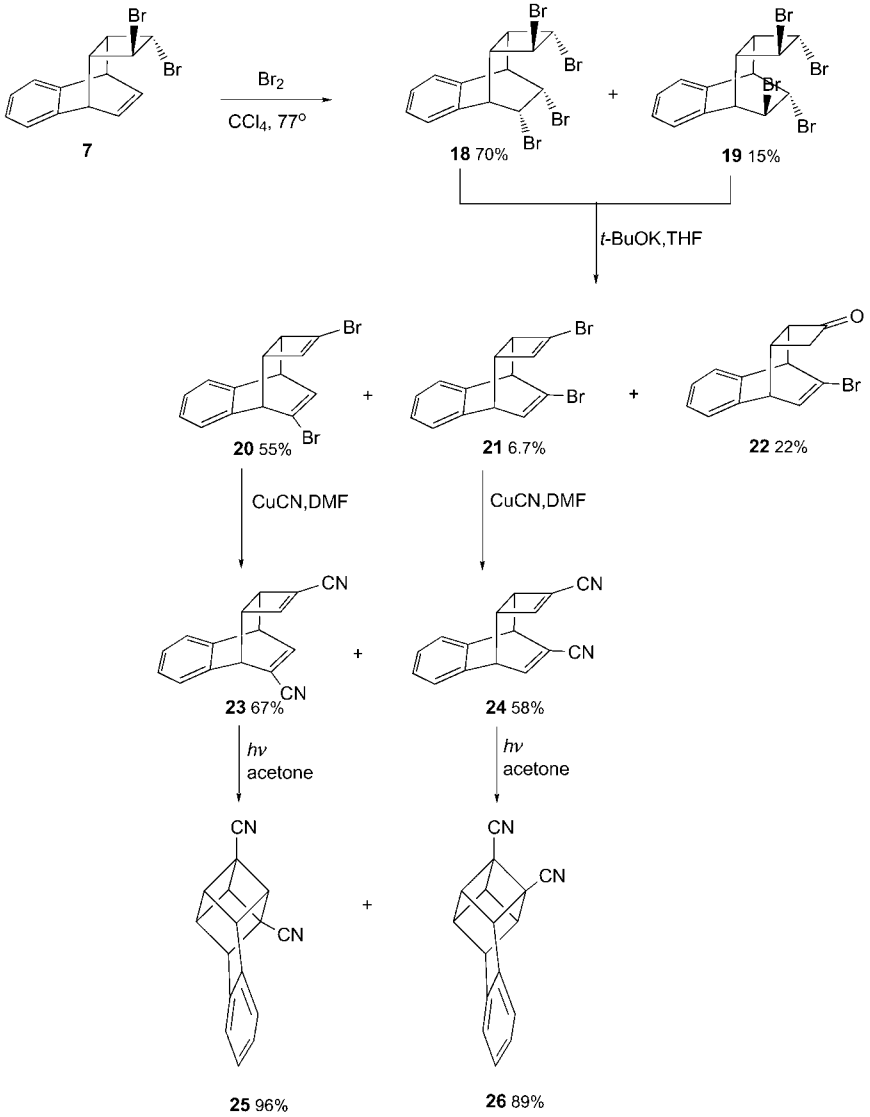


Figure. *X-Ray crystal structure of* **18**

Scheme 4



of the Br-atoms in **20** and **21** with CN substituents ($\rightarrow$ **23** and **24**, resp.) followed by photolysis gave the desired benzobasketene-dicarbonitriles **25** and **26** in 96 and 89% yield, respectively. The ^{13}C-NMR spectra of **25** and **26** (6 sp^2 C, 2 sp-C and 8 sp^3-C) were completely in accordance with the proposed unsymmetric structures.

The described synthetic procedures show that introduction of suitable substituents at the stage of *Nenitzescu*'s benzohydrocarbon opens up a new entry to basketene derivatives substituted at various positions.

Table. *Crystallographic Data of* **18**[a])

Crystallized from	hexane	Scan width [°]	$(1.31 + 0.35 \tan\theta)$
Chemical formula	$C_{14}H_{12}Br_4$	Max θ value for data collection [°]	2.25
Formula weight [g·mol^{-1}]	499.86		
Crystal color	colorless, prism	Min θ value for data collection [°]	30.00
Crystal dimensions	$0.40 \times 0.20 \times 0.40$ mm		
Crystal system	monoclinic	Number of reflections measured	total: 6192
Lattice type	primitive		unique: 5654
Cell determination (2θ range)	25 (20.2–25.8°)		$F_o > 4\sigma(F_o)$: 2262
		Corrections	*Lorentz* polarization
Unit-cell dimensions: a [Å]	8.459(9)		absorption
b [Å]	21.960(3)		(trans. factors: 0.3521–0.9979)
c [Å]	15.990(2)		no decay correction was applied
β [°]	94.2741	Structure solution	direct methods (SIR92)
Cell volume [Å^3]	2962(2)	Refinement	full-matrix least-squares on F^2
Space group	$P2_1/n$ (#14)	Function minimized	$\sum w (F_o^2 - F_c^2)^2$
Number of molecules per unit-cell (Z value)	8	Least squares weights	1
		p-Factor	0.0031
Calc. density D_x [g/cm^3]	2.242	Anomalous dispersion	all non-H-atoms
Linear absorption coeff. μ(Mo$K\alpha$) [cm^{-1}]	10.849	No. observations ($I > 0.00\sigma(I)$)	6016
Diffractometer	*Rigaku AFC7S*	Residuals: R_1; wR_2	0.0838; 0.220
Radiation	Mo$K\alpha$ (λ 0.71069 Å)	Maximum peak in final diff. map	1.59 e$^-$/Å^3
Attenuator	Zr foil (factor = 8.49)		
Data collection temperature [K]	293	Minimum peak in final diff. map	-1.48 e$^-$/Å^3
Scan type	$\omega - 2\theta$	$R_1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.314
		$wR_2 = [\Sigma(w (F_o^2 - F_c^2)^2) / \Sigma w (F_o^2)^2]^{1/2}$	0.220

[a]) Crystallographic data (excluding structure factors) for the structure **18** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-206821. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

Experimental Part

General. All substances reported in this paper are racemic. *Caution.* It has been reported [12] that, of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders, which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of dibromide derived from benzonorbornadiene, there is no report in the literature about the toxicological effect; however, *we recommend that the compounds must be handled only with extreme caution.* TLC: *Merck* 0.2-mm silica gel *60 F_{254}* anal. aluminium plates. Column chromatography (CC): silica gel (60 mesh, *Merck*). M.p.: uncorrected. IR Spectra: from solns. in 0.1-mm cells or KBr pellets; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: 200- and 400-MHz spectrometers; apparent splitting is given in all cases; δ in ppm, J in Hz.

*(1*RS*,8*SR*,9*RS*,10*RS*,11*RS*,12*RS*)-10,11-Dibromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,13-tetraene* (**7**). A soln. of anthranilic acid (= 2-aminobenzoic acid; 11.45 g, 83.6 mmol) in acetone (50 ml) was added within 3 h to a refluxing soln. of *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (**6**) [8] (5.52 g, 20.9 mmol) and isopentyl nitrite (9.78 g, 89.6 mmol) in CH_2Cl_2 (100 ml). After the addition, the mixture was refluxed an additional hour and then evaporated to give a black residue of tarry appearance. The residue was chromatographed (silica gel (200 g), hexane): **7** (2.84 g, 40%). Colorless crystals from AcOEt. M.p. 163–164°. IR: 3061*w*, 2948*m*, 1465*s*, 1348*m*, 1263*m*, 1138*m*, 1060*m*, 966*m*, 886*m*, 785*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.14–7.02 (*m*, 4 arom. H); 6.9

('*t*', H–C(13) or H–C(14)); 6.6 ('*t*', H–C(13) or H–C(14)); 4.62 (*t*, H–C(10)); 4.24 (*dd*, H–C(11)); 4.13 (br. *t*, *J* = 4.5, H–C(1)); 4.09 (*m*, H–C(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.0; 142.4; 137.1; 135.3; 126.2; 126.0; 124.2; 123.5; 52.5; 50.9; 49.0; 48.0; 43.9; 42.9. Anal. calc. for $C_{14}H_{12}Br_2$: C 49.45, H 3.56; found: C 49.63, H 3.60.

*(1*RS*,8*SR*,9*RS*,12*RS*)-10-Bromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene* (**8**). To a stirred soln. of **7** (1.88 g, 5.53 mmol) in dry and freshly distilled THF (50 ml), *t*-BuOK (1.24 g, 11.06 mmol) in THF (20 ml) was added. The resulting mixture was stirred for 3 h at the reflux temp. of THF. After cooling to r.t., the solvent was evaporated, the mixture diluted with H_2O, and the aq. soln. extracted with hexane (2 × 50 ml). The extract was washed with H_2O, dried ($MgSO_4$), and evaporated: **8** (1.37 g, 96%). Colorless crystals from hexane/AcOEt. M.p. 86–87°. IR: 3058*w*, 2948*m*, 1562*w*, 1455*m*, 1350*w*, 1228*m*, 1207*m*, 1114*m*, 1105*w*, 969*m*, 878*m*, 803*m*, 775*m*, 704*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.18 (*m*, 1 arom. H); 7.12 (*m*, 1 arom. H); 7.04 (*m*, 2 arom. H); 6.15–6.33 (*m*, H–C(13), H–C(14)); 6.15 (*s*, H–C(11)); 3.87 (*m*, H–C(8)); 3.75 (*m*, H–C(1)); 2.94 (*t*, *J*(8,9) = *J*(9,12) = 3.8, H–C(9)); 2.74 (*t*, *J*(1,12) = *J*(9,12) = 3.6, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.8; 142.5; 137.8; 131.8; 131.1; 125.9; 125.8; 124.5; 124.2; 121.6; 54.4; 46.4; 44.0; 43.7. Anal. calc. for $C_{14}H_{11}Br$: C 64.89, H 4.28; found: C 64.65, H 4.09.

*(1*RS*,8*SR*,9*RS*,12*RS*)-Tetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene-10-carbonitrile* (**9**). A soln. of **8** (1.05 g, 4.04 mmol) and CuCN (1.08 g, 12.12 mmol) in dry DMF (50 ml) was stirred under N_2 at 130° for 4 h. The mixture was cooled to r.t., diluted with $CHCl_3$ (100 ml) and extracted with 10% aq. $FeCl_3$ soln. (2 × 50 ml), then with 10% aq. NaOH soln. (2 × 50 ml), and finally with H_2O. The org. layer was dried ($MgSO_4$) and evaporated and the crude product (0.58 g, 70%) submitted to CC (silica gel (40 g), hexane/AcOEt 5:1): **9** (0.5 g, 60%). Colorless crystals from hexane/CH_2Cl_2. M.p. 101–102°. IR: 3059*m*, 3020*m*, 2960*s*, 2210*s*, 1634*w*, 1580*w*, 1467*m*, 1349*m*, 1249*w*, 1157*m*, 1076*w*, 943*w*, 870*m*, 786*m*, 759*s*, 705*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.16–7.24 (*m*, 2 arom. H); 7.08 (*m*, 2 arom. H); 6.76 (*s*, H–C(11)); 6.36 (*t*, *J*(8,14) = *J*(13,14) = 6.8, H–C(14)); 6.25 (*t*, *J*(1,13) = *J*(13,14) = 6.8, H–C(13)); 3.98 (*m*, H–C(8)); 3.86 (*m*, H–C(1)); 2.95 (*t*, *J*(8,9) = *J*(9,12) = 3.8, H–C(9)); 2.76 (*t*, *J*(9,12) = *J*(11,12) = 3.8, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 153.4; 142.7; 142.1; 131.6; 131.5; 126.3; 126.2; 124.7; 124.4; 121.0; 113.5; 48.4; 46.2; 43.9; 43.4. Anal. calc. for $C_{15}H_{11}N$: C 87.77, H 5.40, N 6.82; found: C 87.63, H 5.32, N 6.72.

Hexacyclo[8.4.0.0^{2,5}.0^{3,8}.0^{4,7}.0^{6,9}]tetradeca-1(10),11,13-triene-4-carbonitrile (**10**). A soln. of **9** (200 mg, 0.98 mmol) in dist. acetone (350 ml) was placed into a quarz phototube and irradiated with a Hg-vapor lamp (180–254 nm) for 3.5 h at r.t. under N_2. The solvent was carefully evaporated and the brown residual oil submitted to CC (silica gel (15 g), CH_2Cl_2/hexane 1:2): **10** (170 mg, 85%). Colorless crystals from hexane/CH_2Cl_2. M.p. 116–117°. IR: 3068*w*, 3000*m*, 2968*m*, 2209*m*, 1482*w*, 1256*m*, 1019*w*, 754*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.25–7.29 (*m*, 4 arom. H); 4.44 (*t*, *J*(2,3) = *J*(2,5) = 5.6, H–C(2)); 4.16 (*t*, *J*(9,8) = *J*(9,6) = 5.6, H–C(9)); 3.71 (br. *t*, *J*(5,2) = *J*(5,6) = 4.5, H–C(5)); 3.36 (*t*, *J*(3,8) = *J*(3,2) = *J*(7,8) = *J*(7,6) = 5.8, H–C(3), H–C(7)); 3.10 (*q*, *J*(8,3) = *J*(8,7) = *J*(8,9) = 5.8, H–C(8), H–C(6)). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.4; 136.4; 127.4; 127.3; 126.0; 125.7; 118.1; 44.1; 44.0; 40.4; 39.7; 39.0; 35.8. Anal. calc. for $C_{15}H_{11}N$: C 87.77, H 5.40, N 6.82; found: C 87.55, H 5.27, N 6.65.

Bromination of **8** *at 77°*. A soln. of **8** (0.9 g, 3.47 mmol) in CCl_4 (20 ml) was heated while stirring magnetically until CCl_4 started to reflux. To the refluxing soln. (77°) was added dropwise a hot soln. of Br_2 (0.6 g, 3.82 mmol) in CCl_4 (5 ml) over 5 min. After cooling to r.t., the solvent was evaporated and the yellow oily residue submitted to CC (silica gel (150 g), hexane). **11**/**12** (800 mg), followed by **13** (51.0 mg, 5%) and **14** (180 mg, 17%; after crystallization from CCl_4). The major product **11** was isolated by crystallization of **11**/**12** from CCl_4: **11** (0.65 g, 62%). Isomer **12** could not be isolated as pure compound.

*(1*RS*,8*SR*,9*RS*,11*SR*,12*RS*)-10,10,11-Tribromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,13-tetraene* (**11**): Colorless crystals. M.p. 141–142°. IR: 3020*m*, 2962*m*, 1468*m*, 1458*w*, 1351*m*, 1247*w*, 1159*w*, 1062*m*, 1034*m*, 937, 894, 881*m*, 794*m*, 781*s*, 711*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.10–7.17 (*m*, 2 arom. H); 7.02–7.08 (*m*, 2 arom. H); 6.87 (br. *t*, *J* = 6.7, H–C(14)); 6.60 (br. *t*, *J* = 7.0, H–C(13)); 4.64 (*dd*, *J*(11,12) = 7.1, *J*(9,11) = 1.4, H–C(11)); 4.28 ('*t*', *J*(8,9) = *J*(8,14) = 3.9, H–C(8)); 4.09 (*t*, *J*(1,13) = *J*(1,12) = 4.7, H–C(1)); 3.46 (br. *d*, *J*(9,12) = 9.3, H–C(9)); 3.11 (*m*, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.5; 141.3; 135.2; 135.1; 125.8; 125.7; 123.8; 123.2; 62.7; 61.8; 56.8; 49.7; 44.9; 41.3. Anal. calc. for $C_{14}H_{11}Br_3$: C 40.14, H 2.65; found: C 40.01, H 2.73.

*(1*RS*,8*SR*,9*RS*,11*RS*,12*RS*)-10,10,11-Tribromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,13-tetraene* (**12**): ^{1}H-NMR (400 MHz, $CDCl_3$; data from **11**/**12**): 7.0–7.2 (*m*, 4 arom. H); 6.69 (*m*, H–C(13), H–C(14)); 5.39 (*dd*, *J*(11,12) = 8.8, *J*(9,11) = 1.5, H–C(11)); 4.22 ('*t*', *J*(8,9) = *J*(8,14) = 5.6, H–C(8)); 4.00 (*t*, *J*(1,13) = *J*(1,12) = 4.6, H–C(1)); 3.75 (*dd*, *J*(9,12) = 8.7, *J*(9,8) = 2.2, H–C(9)); 3.38 (*dt*, *J*(12,9) = *J*(12,8) = 8.8, *J*(12,1) = 4.6, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.8; 142.3; 134.3; 133.6; 125.6; 125.5; 123.3; 123.1; 65.2; 62.5; 59.9; 45.5; 44.83; 42.9.

*(1*SR,*8*RS,*9*RS,*12*RS,*13*SR,*14*SR*)-10,13,14-Tribromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10-tetraene* (**13**): Colorless powder, purity > 90%. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.16–7.24 (*m*, 3 arom. H); 7.07 (*dd*, J_o = 7.4, J_m = 1.5, 1 arom. H); 6.39 (*s*, H–C(11)); 4.75 (*dd*, *J*(13,14) = 4.9, *J*(8,14) = 2.5, H–C(14)); 3.95 (*m*, H–C(13)); 3.51 ('*t*', *J*(8,9) = *J*(8,14) = 2.5, H–C(8)); 3.45 (*m*, H–C(1)); 2.94 ('*t*', *J* = 3.8, H–C(9)); 2.86 ('*t*', *J* = 4.3, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.8; 142.3; 134.3; 133.6; 125.6; 125.5; 123.3; 123.1; 65.2; 62.5; 59.9; 45.5; 44.83; 42.9.

*(1*SR,*8*RS,*9*RS,*12*RS,*13*RS,*14*SR*)-10,13,14-Tribromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10-tetraene* (**14**): Colorless crystals from CCl_4. M.p. 174–175°. IR: 3067*w*, 2936*m*, 1633*w*, 1567*m*, 1460*s*, 1315*m*, 1260*m*, 1017*w*, 990*m*, 865*m*, 824*m*, 775*s*, 753*s*, 728*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33–7.29 (*m*, 2 arom. H); 7.19–7.26 (*m*, 2 arom. H): 6.55 (*s*, H–C(11)); 4.83 (*AB*, *J*(13,14) = 7.8, H–C(13), H–C(14)); 3.71 (br. *d*, *J*(8,9) = 4.2, H–C(8)); 3.63 (br. *d*, *J*(1,12) = 4.2, H–C(1)); 3.05 (*t*, *J*(12,9) = *J*(12,1) = 4.2, H–C(12)); 2.90 (*t*, *J*(9,8) = *J*(9,12) = 4.2, H–C(9)). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.3; 136.3; 134.8; 126.6; 126.5; 126.0; 125.9; 122.7; 52.5; 48.7; 48.2; 48.1; 47.7; 45.0. Anal. calc. for $C_{14}H_{11}Br_3$: C 40.14, H 2.65; found: C 39.94, H 2.61.

*rel-(1*R,*8*S,*9*R,*12*S*)-10,11-Dibromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene* (**15**). As described for **8**, with **11** (590 mg, 1.41 mmol) (or with **11**/**12**), and *t*-BuOK (315 mg, 2.8 mmol), and THF (30 ml). Colorless crystals from CH_2Cl_2 (0.400 g, 84%). M.p. 97–98°. IR: 3058*w*, 2960*m*, 2942*m*, 1601*m*, 1469*m*, 1251*m*, 966*m*, 759*s*, 713*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.14–7.18 (*AA′* of *AA′BB′*, H–C(3), H–C(6)); 7.03–7.07 (*BB′* of *AA′BB′*, H–C(4), H–C(5)); 6.35 (*AA′* of *AA′XX′*, H–C(13), H–C(14)); 3.86 (*XX′* of *AA′XX′*, H–C(1), H–C(8)); 3.03 (*m*, H–C(9), H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.5; 131.7; 126.1; 124.6; 121.8; 53.7; 42.9. Anal. calc. for $C_{14}H_{10}Br_2$: C 49.74, H 2.98; found: C 49.63, H 2.81.

*rel-(1*R,*8*S,*9*R,*12*S*)-Tetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,10,13-pentaene-10,11-dicarbonitrile* (**16**). As described for **9**, with **15** (500 mg, 1.48 mmol), CuCN (0.79 g, 8.88 mmol), and DMF CC (silica gel (30 g), hexane/CH_2Cl_2 1:2) gave **16** (0.18 g, 55%). Colorless crystals from hexane/CH_2Cl_2. M.p. 204–205°. IR: 3070*w*, 2969*m*, 2218*m*, 1469*s*, 1353*m*, 1217*m*, 1158*m*, 819*m*, 770*s*, 716*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.28 (*AA′* of *AA′BB′*, H–C(3), H–C(6)); 7.16 (*BB′* of *AA′BB′*, H–C(4), H–C(5)); 6.42 (*AA′* of *AA′XX′*, H–C(13), H–C(14)); 4.08 (*XX′* of *AA′XX′*, H–C(1), H–C(8)); 3.05 (*m*, H–C(9), H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.0; 131.86; 131.83; 126.9; 125.0; 111.1; 48.3; 42.8. Anal. calc. for $C_{16}H_{10}N_2$: C 83.46, H 4.38, N 12.17; found: C 83.10, H 4.28, N 12.01.

Hexacyclo[8.4.0.0^{2,5}.0^{3,8}.0^{4,7}.0^{6,9}]tetradeca-1(10),11,13-triene-4,7-dicarbonitrile (**17**). A soln. of **16** (100 mg, 0.43 mmol) in dist. acetone (350 ml) was irradiated at 180–254 nm for 3.5 h at r.t. under N_2. The solvent was carefully evaporated and the brown residual oil submitted to CC (silica gel (15 g) AcOEt/hexane 1:5): **17** (92 mg, 92%). Colorless crystals from hexane/CH_2Cl_2. M.p. 132–133°. IR: 3013*m*, 2974*m*, 2935*w*, 2231*s*, 1645*w*, 1625*m*, 1605*w*, 1468*m*, 1390*s*, 1273*s*, 1253*s*, 1194*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.25–7.29 (br. *s*, 4 arom. H); 4.48 (*AA′* of *AA′XX′*, H–C(2), H–C(9)); 3.50 (*XX′* of *AA′XX′*, H–C(3), H–C(5), H–C(6), H–C(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 135.4; 128.2; 126.3; 115.0; 43.0; 39.2; 37.7. Anal. calc. for $C_{16}H_{10}N_2$: C 83.46, H 4.38, N 12.17; found: C 83.27, H 4.42, N 12.06.

Bromination of **7** *at 77°*. A soln. of **7** (2.0 g, 5.88 mmol) was brominated at 77° with Br_2 (1.0 g, 6.49 mmol) as described for the bromination of **8**. After cooling to r.t., the solvent was evaporated and the yellow oily residue submitted to CC (silica gel (100 g), hexane): **19** and then **18**.

*(1*SR,*8*RS,*9*RS,*10*SR,*11*SR,*12*SR,*13*SR,*14*SR*)-10,11,13,14-Tetrabromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6-triene* (**19**): Colorless crystals from hexane (450 mg, 15%). M.p. 174–175°. IR: 3064*w*, 3041*w*, 2956*m*, 1474*m*, 1458*w*, 1342*m*, 1261*w*, 1164*w*, 977*m*, 855*m*, 796*s*, 724*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.33 (*m*, 3 arom. H): 7.12 (*dd*, *J* = 7.1, 1.5, 1 arom. H): 5.81 (*t*, *J*(9,10) = *J*(10,11) = 8.6, H–C(10)); 5.35 (*dd*, *J*(13,14) = 6.4, *J*(8,14) = 1.5, H–C(14)); 4.67 (*t*, *J*(11,12) = *J*(10,11) = 8.6, H–C(11)); 4.03 (br. *d*, *J*(13,14) = 6.4, H–C(13)); 3.67 (*dd*, *J*(8,9) = 4.5, *J*(8,14) = 1.5, H–C(8)); 3.62 (br. *s*, H–C(1)); 2.90 (*dt*, *J*(9,8) = *J*(9,10) = 4.5, *J*(9,12) = 9.9, H–C(9)); 2.85 (*dt*, *BB′* of *AA′BB′*, *J*(9,12) = *J*(11,12) = 9.9, *J*(1,12) = 3.2, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.9; 136.9; 128.8; 128.7; 126.7; 124.4; 56.0; 49.8; 47.6; 46.8; 46.6; 46.2; 44.9; 44.7. Anal. calc. for $C_{14}H_{12}Br_4$: C 33.64, H 2.42; found: C 33.84, H 2.50.

*(1*SR,*8*RS,*9*RS,*10*SR,*11*SR,*12*SR,*13*RS,*14*SR*)-10,11,13,14-Tetrabromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6-triene* (**18**): Colorless crystals from hexane (2050 mg, 70%). M.p. 149–150°. IR: 3037*w*, 2948*m*, 1475*m*, 1293*w*, 1160*w*, 974*m*, 946*m*, 877*m*, 829*s*, 796*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.18–7.35 (*m*, 4 arom. H); 5.53 (*dd*, *J*(13,14) = 8.6, *J*(13,1) = 1.3, H–C(13)); 5.1 (*dd*, *J*(13,14) = 8.6, *J*(14,8) = 3.2, H–C(14)); 4.62–4.68 (*m*, H–C(10), H–C(11)); 3.75 (*dd*, *J*(8,9) = 5.0, *J*(8,14) = 3.2, H–C(8)); 3.61 (br. *d*, *J* = 2.4, H–C(1)); 2.90–2.97 (*m*, H–C(9)); 2.69–2.78 (*m*, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.5; 136.3; 127.8; 127.5; 127.1; 125.9; 50.6; 46.6 (2C); 46.5; 46.2; 45.8; 45.0; 44.4. Anal. calc. for $C_{14}H_{12}Br_4$: C 33.64, H 2.42; found: C 33.81, H 2.37.

Elimination Reaction with **18** *in Refluxing THF.* As described for **8**, with **18** (2.167 g, 4.33 mmol) (or **18**/**19**), *t*-BuOK (2.42 g, 21.7 mmol), and THF (50 ml). After cooling to r.t., the solvent was evaporated and the oily residue submitted to CC (silica gel (30 g), hexane): **20**, followed by **21** and **22**.

*(1*SR,*8*RS,*9*RS,*12*SR*)-10,13-Dibromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene* (**20**): Colorless crystals from hexane/CH_2Cl_2 (805 mg, 55%). M.p. 81–83°. IR: 3080*m*, 3055*m*, 3029*w*, 2978*m*, 2927*w*, 1625*m*, 1574*s*, 1472*m*, 1319*w*, 1165*m*, 1140*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.16 (*m*, 2 arom. H); 7.05 (*m*, 2 arom. H); 6.41 (*dd*, *J*(8,14) = 6.6, *J*(1,14) = 2.0, H–C(14)); 6.26 (*s*, H–C(11)); 3.87 (*t*, H–C(1)); 3.82 (*dd*, *J*(8,9) = 3.8, *J*(8,14) = 6.6, H–C(8)); 2.84 (*t*, *J*(8,9) = *J*(9,12) = 3.8, H–C(9)); 2.77 (*t*, *J*(9,12) = *J*(1,12) = 3.7, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.3; 140.8; 137.9; 130.3; 126.9; 126.4; 124.8; 124.6; 123.6; 122.4; 54.3 (2C); 46.9; 45.26. Anal. calc. for $C_{14}H_{10}Br_2$: C 49.74, H 2.98; found: C 49.55, H 2.88.

*(1*RS,*8*RS,*9*RS,*12*SR*)-10,14-Dibromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene* (**21**): Colorless crystals from hexane/CH_2Cl_2 (97 mg, 6.7%). M.p. 125–127°. IR: 3080*m*, 3029*m*, 2978*s*, 2927*w*, 1625*m*, 1574*s*, 1472*m*, 1329*w*, 1268*m*, 1248*m*, 1158*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.23 (*m*, 1 arom. H); 7.06 (*m*, 3 arom. H); 6.36 (*dd*, *J*(1,13) = 6.6, *J*(8,13) = 2.1, H–C(13)); 6.18 (*s*, H–C(11)); 3.99 (br. *s*, H–C(1)); 3.75 (*dd*, *J*(8,9) = 3.7, *J*(8,14) = 6.6, H–C(8)); 2.96 (*t*, *J*(8,9) = *J*(9,12) = 3.7, H–C(9)); 2.66 (*t*, *J*(9,12) = *J*(1,12) = 3.7, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.2; 141.0; 138.1; 130.5; 126.7; 126.3; 124.8; 124.6; 124.3; 122.7; 54.6; 53.9; 46.0; 45.7. Anal. calc. for $C_{14}H_{10}Br_2$: C 49.74, H 2.98; found: C 49.98, H 3.03.

*(1*RS,*8*RS,*9*RS,*12*RS*)-14-Bromotetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,13-tetraen-10-one* (**22**): 263 mg (22%). M.p. 138–140°. IR: 3079*m*, 2986*m*, 2968*w*, 1731*s*, 1583*m*, 1509*w*, 1380*w*, 1324*m*, 1250*m*, 1177*w*, 1140*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.28 (*m*, 1 arom. H): 7.12 (*m*, 3 arom. H); 6.62 (*dd*, *J*(1,13) = 6.8, *J*(8,13) = 2.1, H–C(13)); 4.26 (*dd*, *J*(8,9) = 2.7, *J*(8,13) = 2.1, H–C(8)); 4.24 (*dd*, *J*(1,13) = 6.5, *J*(1,12) = 4.5, H–C(1)); 3.39 (*m*, H–C(12)); 2.85–2.93 (*m*, $H_{exo'}$–C(11)); 2.63–2.72 (*m*, H–C(9), $H_{endo'}$–C(11)). ^{13}C-NMR (100 MHz, $CDCl_3$): 207.24; 143.5; 140.3; 133.0; 126.9; 126.4; 124.1; 124.0; 123.9; 65.8; 53.0; 45.6; 43.9; 29.7. Anal. calc. for $C_{14}H_{11}BrO$: C 61.11, H 4.03; found: C 61.25, H 4.09.

*(1*RS,*8*SR,*9*SR,*12*RS*)-Tetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene-10,13-dicarbonitrile* (**23**). As described for **9**, with **20** (297 mg, 0.88 mmol), CuCN (470 g; 5.27 mmol), and DMF (6 h). CC (silica gel (50 g), hexane/CH_2Cl_2 1:3 gave **23** (135 mg, 67%). Colorless crystals from hexane/CH_2Cl_2. M.p. 181–182°. IR: 3074*m*, 3026*w*, 2980*m*, 2220*s*, 1472*m*, 1460*m*, 1264*m*, 863*m*, 752*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.18–7.24 (*m*, 2 arom. H); 7.11–7.15 (*m*, 2 arom. H, H–C(14)); 6.82 (*s*, H–C(11)); 4.13 (*dd*, *J*(8,14) = 6.7, *J*(8,9) = 3.7, H–C(8)); 4.06 (br. *s*, H–C(1)); 3.00 (*t*, *J*(8,9) = *J*(9,12) = 3.8, H–C(9)); 2.84 (*t*, *J*(1,12) = *J*(9,12) = 3.8, H–C(12)). ^{13}C-NMR (100 MHz, $CDCl_3$): 152.7; 147.3; 139.7; 138.8; 127.6; 127.3; 125.3; 125.0; 121.5; 117.3; 116.9; 112.7; 48.0; 46.6; 45.4; 43.6. Anal. calc. for $C_{16}H_{10}N_2$: C 83.46, H 4.38, N 12.17; found: C 83.15, H 4.50, N 12.12.

*(1*RS,*8*RS,*9*RS,*12*SR*)-Tetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,10,13-pentaene-10,14-dicarbonitrile* (**24**). As described for **9**, with **21** (594 mg, 1.76 mmol), CuCN (940 mg, 10.54 mmol), and DMF (60 ml) (6 h). CC (silica gel (100 g), AcOEt/hexane 1:3 gave **24** (225 mg, 58%). Colorless crystals from hexane/CH_2Cl_2. M.p. 178–180°. IR: 3080*m*, 3055*w*, 2978*m*, 2238*s*, 1625*m*, 1600*m*, 1472*m*, 1268*m*, 1242*w*, 1165*m*, 987*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.22–7.36 (*m*, 1 arom. H); 7.1–7.2 (*m*, 3 arom. H); 7.07 (*dd*, *J*(1,13) = 6.4, *J*(8,13) = 1.7, H–C(13)); 6.84 (*s*, H–C(11)); 4.24 (*m*, H–C(8)); 4.12 (*dd*, *J*(1,13) = 6.4, *J*(1,12) = 3.9, H–C(1)); 3.09 (*t*, *J*(8,9) = *J*(9,12) = 3.9, H–C(9)); 2.91 (*t*, *J*(1,12) = *J*(9,12) = 3.9, H–C(12)). ^{13}C-NMR (50 MHz, $CDCl_3$): 155.4; 149.6; 141.0; 140.8; 129.2; 128.9; 126.9; 126.8; 122.3; 118.7; 118.6; 114.4; 49.2; 47.7; 47.4; 45.7. Anal. calc. for $C_{16}H_{10}N_2$: C 83.46, H 4.38, N 12.17; found: C 83.66, H 4.52, N 12.24.

Hexacyclo[8.4.0.0^{2,5}.0^{3,8}.0^{4,7}.0^{6,9}]tetradeca-1(10),11,13-triene-3,7-dicarbonitrile (**25**). A soln. of **23** (150 mg, 0.64 mmol) in dist. acetone (350 ml) was irradiated with a Hg-vapor lamp (180–254 nm) for 8 h at r.t. under N_2. The solvent was carefully evaporated and the brown residual oil submitted to CC (silica gel (15 g), AcOEt/hexane 1:5): **17** (145 mg, 96%). Colorless crystals from hexane/CH_2Cl_2. M.p. 126–127°. IR: 3074*w*, 3052*m*, 2965*s*, 2922*m*, 2879*w*, 2250*s*, 1687*w*, 1665*m*, 1622*w*, 1491*w*, 1470*m*, 1361*m*, 1145*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.26–7.50 (*s*, 4 arom. H); 4.54 (*t*, *J*(8,9) = *J*(6,9) = 5.7, H–C(9)); 4.43 (*d*, *J*(2,5) = 6.0, H–C(2)); 4.11 (*dt*, *J* = 5.0, *J* = 1.7, 1 H); 3.62 (*m*, 1 H); 3.41 (*m*, 1 H); 3.16 (*m*, 1 H–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 136.7; 135.5; 130.3; 130.0; 128.2; 128.0; 120.2; 118.2; 50.2; 49.8; 45.5; 45.2; 41.1; 38.9; 37.2; 36.7. Anal. calc. for $C_{16}H_{10}N_2$: C 83.46, H 4.38, N 12.17; found: C 83.33, H 4.46, N 12.01.

Hexacyclo[8.4.0.0^{2,5}.0^{3,8}.0^{4,7}.0^{6,9}]tetradeca-1(10),11,13-triene-3,4-dicarbonitrile (**26**). As described for **25**, with **24** (100 mg, 0.43 mmol), acetone (350 ml), and a Hg-vapor lamp (180–254 nm) (10 h): **26** (89 mg, 89%). Colorless crystals from hexane/CH_2Cl_2. M.p. 120–121°. IR: 3055*w*, 3029*m*, 2953*s*, 2927*m*, 2876*w*, 2238*s*, 1688*w*, 1625*m*, 1497*w*, 1472*m*, 1268*m*, 1217*w*, 1191*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.34–7.23 (*m*, 4 arom. H); 4.65 (*d*, *J*(2,5) = 5.8, H–C(2)); 4.30 (*t*, *J*(8,9) = *J*(6,9) = 5.7, H–C(9)); 3.83 (*dt*, *J* = 4.7, *J* = 1.5, 1 H); 3.48 (*t*, *J* = 6.7, 1 H); 3.37 (*q*, *J* = 5.7, 1 H); 3.14 (*m*, H–C(6)). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.3; 133.0; 128.9; 128.2; 126.8;

126.1; 117.1; 115.0; 44.4; 43.3; 43.1; 42.6; 40.9; 40.8; 40.1; 38.5. Anal. calc. for $C_{16}H_{10}N_2$: C 83.46, H 4.38, N 12.17; found: C 83.49, H 4.32, N 12.25.

X-Ray Measurements. A colorless prism crystal of **18** ($C_{14}H_{12}Br_4$) was mounted on a glass fiber. All measurements were made on a *Rigaku-AFC7S* diffractometer with graphite-monochromated Mo-K_α radiation. Cell-constants and an orientation matrix for data collection, obtained from a least-squares refinement with the setting angles of 25 carefully centered reflections in the range $20.23^\circ < 2\theta < 25.83^\circ$, corresponded to a primitive monoclinic cell with the dimensions given in the *Table*. The data were collected at $20 \pm 1^\circ$ with the ω-2θ scan technique to a maximum 2θ value of 60.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26° with a take-off angle of 6.0°. Scans of $(1.31 + 0.35 \tan\theta)^\circ$ were made at a speed of 0.0°/min (in ω). The weak reflections ($I < 15.0\sigma(I)$) were rescanned (maximum of 2 scans), and the counts were accumulated to ensure good counting statistics. The structure was solved by direct methods [13] and expanded with *Fourier* techniques [14]. The non-H-atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 6016 observed reflections and 146 variable parameters and converged (largest parameter shift was 505.71 times its esd) with unweighted and weighted agreement factors.

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