Transannular Reactions of Two Non-Parallel 1,3-Butadiyne Units − Syntheses, Structures and Protonation Reactions of 1-Isopropyl-1-azacyclopentadeca-3,5,11,13-tetrayne and 1-Isopropyl-1-azacyclohexadeca-3,5,12,14-tetrayne

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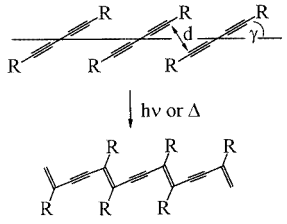
The syntheses of 1-isopropyl-1-azacyclopentadeca-3,5,11,13-tetrayne (**15a**) and 1-isopropyl-1-azacyclohexadeca-3,5,12,14-tetrayne (**15b**) were accomplished in a stepwise approach. The key intermediates were 1,14-dibromotetradeca-2,4,10,12-tetrayne (**14a**) and 1,15-dibromopentadeca-2,4,11,13-tetrayne (**14b**). The ring closure to **15a** and **15b** was achieved by reaction with isopropylamine. X-ray investigations on single crystals of **15a** and **15b** revealed a non-parallel orientation of the 1,3-butadiyne units. The reaction of **15b** with concd. HCl in ethanol yielded 5,12-dichloro-2-isopropyl-1,2,3,6,7,8,9,10-octahydrocyclonona[*e*]isoindole (**16c**) and 5-chloro-2-isopropyl-2,3,6,7,8,9,10,11-octahydrocyclonona[*e*]isoindol-12(1*H*)-one (**17c**). A mechanism for the reaction of **15b** with HCl is proposed. The reaction of **15a** with concd. HCl in ethanol gives 5-chloro-2-isopropyl-2,3,7,8,9,10-hexahydrocycloocta[*e*]isoindol-11(6*H*)-one (**24c**).

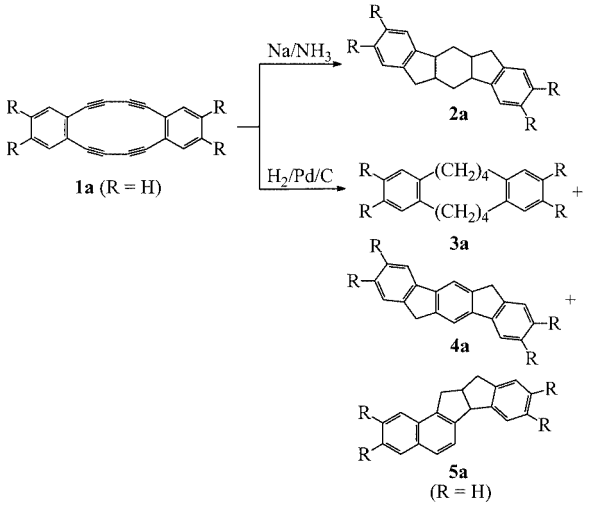
Introduction

The polymerization of 1,3-butadiyne units in the solid state produces a conjugated system, as shown in Scheme 1.[1,2] Essential for the polymerization process is a minimum distance, *d*, between the alkyne units of less than 4.3 Å and an angle, γ, close to 45°.



Scheme 1. Polymerization of 1,3-butadiynes in the solid state

When two 1,3-butadiyne fragments were fixed in medium-sized ring systems transannular reactions are observed. A prominent example is the reduction of 1,2:7,8-dibenzocyclododeca-1,7-diene-3,5,7,11-tetrayne (**1a**)[3] with sodium in liquid ammonia. This process affords the pentacyclic system **2a** as the main product and **4a** and **5a** as side products (Scheme 2).[3] The catalytic hydrogenation of **1a** with palladium on charcoal yields **3a** as the main product, with **4a** and **5a** as side products. Analogous results have been reported for 5,6:11,12-bis(tetramethylene)-1,3,7,9-tetradehydro[12]annulene.[4]



Scheme 2. Reduction of **1a**

Treatment of the tetra-*n*-butyl-substituted congener **1b** of **1a** with iodine at room temperature in benzene yields the fully conjugated pentacyclic compound **6b** (Scheme 3),[5] which contains the same 6-5-6-5-6 fused ring system as encountered in **2a** and **4a**.

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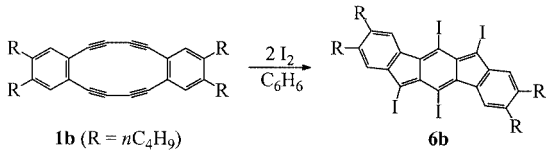
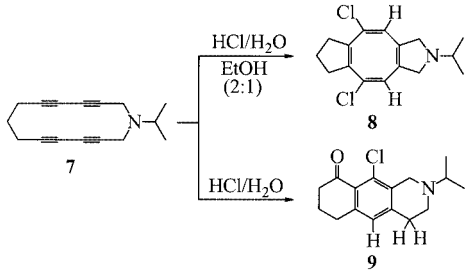


Scheme 3. Reaction of **1b** with iodine

When two 1,3-butadiyne units are embedded in a 14-membered ring a transannular ring-closing reaction occurs. In the presence of ethanol the two parallel 1,3-butadiyne units undergo a ring closure and a twofold HCl addition to give the 5-8-5 tricyclic system **8**. However, when only concentrated hydrochloric acid is present a 6-6-6 tricyclic system (**9** in Scheme 4) is formed.[6] This latter ring closure is somewhat reminiscent of the reactions shown in Schemes 2 and 3.



Scheme 4. The reaction of **7** with HCl leads to the tricyclic products **8** and **9**

In continuation of this work we have also investigated medium-sized rings in which the two butadiyne units are not oriented in a parallel fashion. Examples of such an orientation are 1-isopropyl-1-azacyclopentadeca-3,5,11,13-tetrayne (**15a**) and 1-isopropyl-1-azacyclohexadeca-3,5,12,14-tetrayne (**15b**). The results of these studies are presented here.

Results and Discussion

Our synthesis of **15a** and **15b** follows the path for the synthesis of the congener 1-isopropyl-1-azacyclotetradeca-3,5,10,12-tetrayne (**7**).[6] The synthesis commenced by constructing the tetradeca-2,4,10,12-tetrayne and pentadeca-2,4,11,13-tetrayne units **12a** and **12b** from 1,7-octadiyne (**10a**)[7] and 1,8-nonadiyne (**10b**),[7] respectively. These terminal diynes were treated with THP-protected 1-bromoprop-1-yn-3-ol (**11**)[8] (Scheme 6) in a Cadiot−Chodkiewicz coupling reaction[9] with copper(I) iodide and pyrrolidine to yield **12a** and **12b**. The free diols **13a** and **13b**, respectively, were obtained by hydrolyzing **12a** and **12b** with dilute sulfuric acid. The diols were converted into the dibromides **14a** and **14b** by reaction with PBr_3 in pyridine. The reaction of the dibromides with isopropylamine in the presence of potassium carbonate afforded the target molecules **15a** and **15b**. We used isopropylamine because our previous studies on similar ring-closing reactions showed that the yields are highest with this amine.[6,10]

Structural Investigations

The assigned structures of **15a** and **15b** follow from their analytical properties, especially from NMR spectroscopic and mass spectrometric investigations. We were also able to grow single crystals which allowed an X-ray study. The molecular structures of **15a** and **15b** are shown in Figure 1, where it can be seen that the molecules have a chair-like conformation. The isopropyl group prefers the axial position and the tetra- and pentamethylene chains adopt zigzag arrangements.

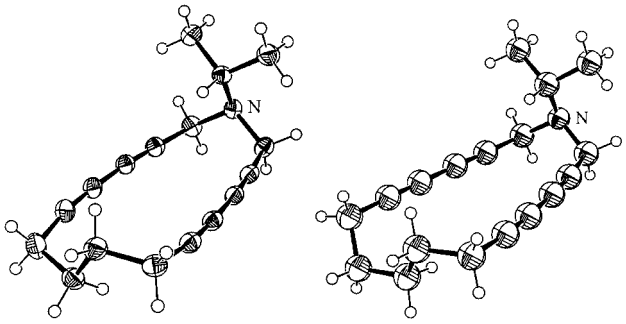
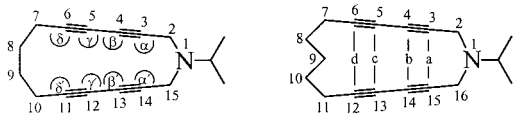


Figure 1. Molecular structure of compounds **15a** and **15b** (50% ellipsoid probability); the hetero atoms are indicated

Table 1. Comparison between selected bond lengths [Å] and bond angles [°] of **7**, **15a** and **15b**; for the definition of *a*, *b*, *c*, *d*, *α*, *β*, *γ* and *δ* as well as the numbering, see Scheme 5

	7	**15a**	**15b**
α[a]	175.7(4)	176.1(1)	176.8(1)
β[a]	173.7(4)	175.7(1)	177.4(1)
γ[a]	171.9(4)	176.7(1)	178.1(1)
δ[a]	174.9(4)	171.7(1)	175.7(1)
a	3.103(6)	3.129(2)	3.117(2)
b	3.413(6)	3.562(2)	3.604(2)
c	3.392(6)	3.863(2)	4.043(2)
d	3.113(6)	3.999(2)	4.355(2)
C3−C4[a]	1.201(6)	1.197(2)	1.199(2)
C4−C5[a]	1.384(5)	1.382(2)	1.381(2)
C5−C6[a]	1.202(6)	1.198(2)	1.197(2)

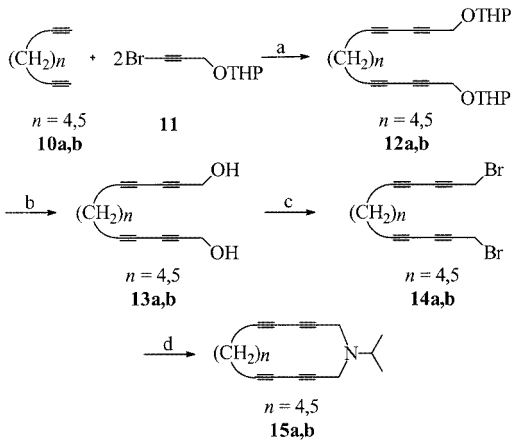
[a] Mean values for **15a** and **15b**.



Scheme 5

In Table 1 we compare the most relevant bond lengths, transannular distances and bond angles of **15a** and **15b** with the values reported for **7**. Due to the different lengths of

the bridges between the 1,3-butadiyne units the geometry varies considerably, especially the transannular distances *b*−*d* (Scheme 6), although the distance at the heterobridge, *a*, remains essentially constant.

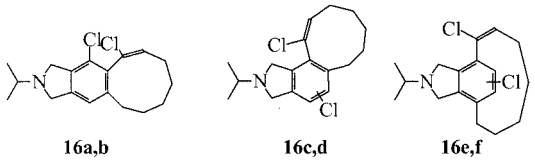


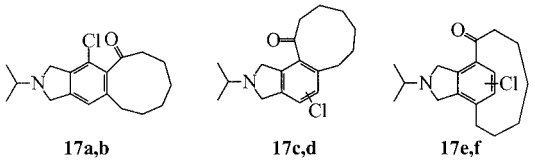
Scheme 6. Syntheses of **15a** and **15b**: a) CuI, pyrrolidine; b) H_2SO_4, H_2O/MeOH; c) PBr_3, pyridine/Et_2O; d) isopropylamine, K_2CO_3, acetonitrile

The angles at the triple bonds in **15a** and **15b**, with one exception (δ in **15a**), are larger than in **7**, indicating less ring-strain for the larger rings. The bond lengths for the 1,3-butadiyne units remain almost constant for all three examples, underlining the rigidity of this part of the molecules.

Reaction of 15a and 15b with HCl

The reaction of **15b** with concd. hydrochloric acid in the presence of ethanol (2:1) yielded two products, tentatively assigned as **I** and **II**. Mass spectrometric investigation of **I** revealed that 2 equiv. of HCl have been added. In the case of **II** it was found that 1 equiv. of HCl and 1 equiv. of H_2O have been added. The NMR investigations on both species revealed an aromatic ring with five substituents. For **I** we found a pentamethylene chain on a vinylic group, and for **II** a hexamethylene bridge with a CO group at the aromatic ring. These investigations led us to the structures **16a**−**f** and **17a**−**f**. An important step forward was the reaction of **15b** with concd. hydrobromic acid in the presence of ethanol. In analogy to the reaction with hydrochloric acid we isolated two products: in the first compound 2 equiv. of HBr were added. In the second, 1 equiv. of HBr and 1 equiv. of H_2O were added to the starting material. In the case of the first product we were able to grow crystals which allowed a structural investigation by X-ray diffraction. The resulting structure (Figure 2) allowed us to formulate the reaction as shown in Scheme 7.





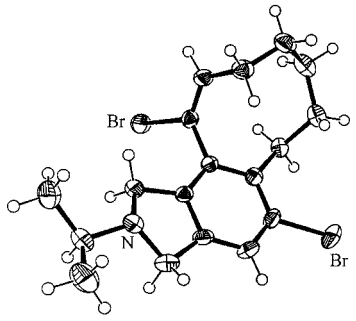
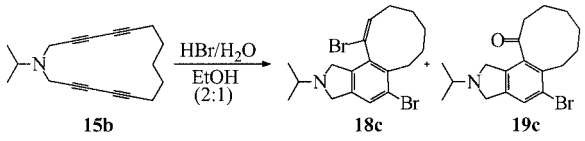
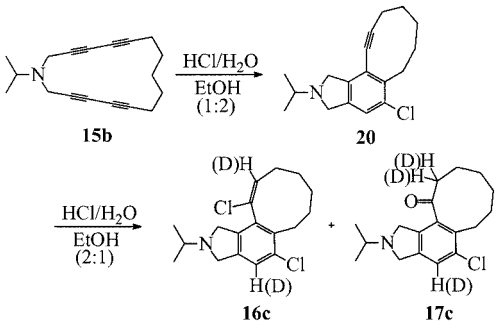


Figure 2. Molecular structure of compound **18c** (50% ellipsoid probability); the hetero atoms are indicated



Scheme 7. Generation of **18c** and **19c** from **15b**

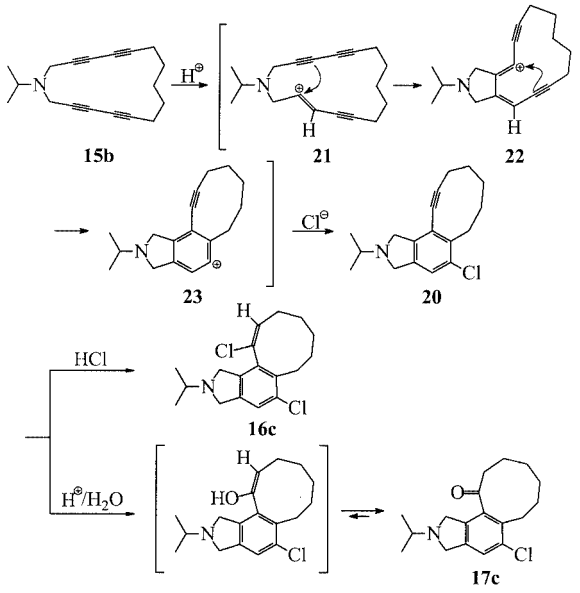
To elucidate the reaction mechanism of the addition of HCl to **15b** further we treated this substance with concd. hydrochloric acid in ethanol in the ratio of 1:2. This afforded a substance in which only 1 equiv. HCl had been added. The NMR investigations of the product revealed a tricylic structure (**20**; Scheme 8) with one 2,5-dihydropyrrole ring, an aromatic ring substituted with an alkyne unit, tethered to a pentamethylene chain. When **20** was treated with concd. HCl/EtOH in the ratio of 2:1 **16c** and **17c** were isolated (Scheme 8).



Scheme 8. The formation of **16c** and **17c** proceeds via compound **20**

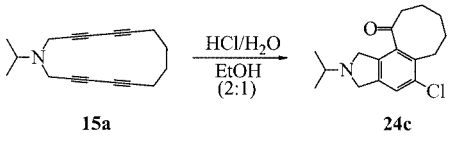
The reaction of **15b** with DCl/D_2O in EtOD (2:1) instead of HCl/H_2O in EtOH afforded the corresponding deuterated products **[D$_2$]16c** and **[D$_3$]17c** as shown in Scheme 8. **[D$_3$]17c** readily loses the two deuterium nuclei adjacent to the carbonyl group in the presence of water and a catalyst; the chromatographic separation on neutral aluminium oxide deactivated with water led to **[D]17c**.

The possible mechanism for this reaction is given in Scheme 9. As a first step we assume protonation at one alkyne unit in **15b** to yield **21**, which rearranges to the vinylic cation **22**. The latter is further stabilized by ring closure to give **23**, which is trapped by a chloride anion to give **20**. The addition of HCl or water to the remaining triple bond leads to **16c** and **17c**, respectively.



Scheme 9. Proposed reaction mechanism to generate **16c** and **17c** from **15b**

When we carried out analogous experiments with **15a** we obtained mixtures which only allowed the separation of 5-chloro-2-isopropyl-2,3,7,8,9,10-hexahydro-1*H*-cyclooct[*e*]isoindol-11(6*H*)-one (**24c**; Scheme 10).



Scheme 10. Generation of **24c** from **15a**

Conclusion

We have achieved the syntheses of two cyclic compounds in which two 1,3-butadiyne units are oriented in a non-parallel arrangement by applying a short and a longer tether. The protonation studies with **15a** and **15b** showed that only three of the four alkyne units are involved in a transannular ring-closing process giving rise to a fivefold substituted benzene ring in the center of the resulting tricyclic product. The transannular ring closure observed for **7**, which leads to a central cyclooctatetraene ring, seems to be the exception due to the close proximity of the 1,3-butadiyne units at both ends.

Experimental Section

General: Starting compounds and solvents used in the syntheses were of reagent grade. Diethyl ether and tetrahydrofuran were dried by standard drying techniques and degassed by distillation under argon. Reactions were performed under argon in standard glassware. For column chromatography, neutral aluminium oxide was deactivated with 6% (weight) of water prior to use. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance 300 (300 and 75 MHz, respectively) or Bruker Avance 500 spectrometers (500 and 125 MHz, respectively). Chemical shifts are quoted in ppm on the δ scale, using the residual protonated solvent as the internal standard. IR spectra were measured with a Bruker Vector 22 FT-IR spectrometer, UV/Vis spectra were obtained from a Hewlett−Packard HP 8452A spectrometer using CH_2Cl_2 as solvent. Absorption maxima of IR spectra are quoted in cm^{-1} and those of UV/Vis spectra in nm, with log ε values quoted in 1000 $cm^2 \cdot mol^{-1}$. Elemental analyses were carried out by the Mikroanalytisches Labor der Chemischen Institute der Universität Heidelberg. Mass spectrometry was performed with a JEOL JMS-700 spectrometer. Melting points were obtained with a melting point determination apparatus as described by Dr. Tottoli (Büchi) and are uncorrected.

1,14-Bis(tetrahydro-2-pyranyloxy)tetradeca-2,4,10,12-tetrayne (12a): Copper(I) iodide (0.76 g, 4 mmol) was dissolved in pyrrolidine (50 mL) with magnetic stirring. At 0 °C compound **10a**[7] (2.12 g, 20 mmol) was added to the solution and compound **11**[8] (8.60 g, 40 mmol) was then added dropwise to the reaction mixture with a syringe over a period of 2 h. After stirring at 0 °C for 30 min, the resulting solution was poured into a stirred mixture of ice (250 g) and diethyl ether (100 mL). The resulting mixture was separated and the aqueous solution was extracted with diethyl ether (2 × 100 mL). The combined organic layers were washed with a saturated aqueous solution of ammonium chloride (3 × 50 mL) and a saturated aqueous solution of sodium hydrogencarbonate, and dried with sodium sulfate. After filtration, the solvent was evaporated and the crude product was purified by column chromatography (Alox III, petroleum ether/diethyl ether, 5:1; R_f = 0.25) to yield 2.71 g (7.1 mmol, 35%) of **12a** as a pale-yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.80 (t, $^3J_{H\text{-}15,H\text{-}16/H\text{-}20,H\text{-}21}$ = 3.1 Hz, 2 H, H-15/20), 4.32, 4.26 (2 d, $^2J_{H,H}$ = 16.8 Hz, 4 H, H-1^a/14^a, H-1^b/14^b), 3.84−3.79 (m, 2 H, H-19^a/24^a), 3.54−3.51 (m, 2 H, H-19^b/24^b), 2.30 (br., 4 H, H-6/9), 1.84−1.49 (m, 16 H, H-7/8, 16/21, 17/22, 18/23) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 97.0 (C-15/20), 80.2 (C-5/10), 72.2 (C-2/13), 70.9 (C-3/12), 65.3 (C-4/11), 62.2 (C-19/24), 54.6 (C-1/14), 30.3 (C-6/21), 27.2 (C-7/8), 25.4 (C-17/22), 19.1 (C-18/23), 18.9 (C-6/9) ppm. IR (film): $\tilde{\nu}$ = 2944 (s), 2868 (m), 2256 (w), 1440 (m), 1345 (m), 1201 (m), 1120 (s), 1026 (vs), 902 cm^{-1} (m). UV/Vis: λ_{max} (log ε) = 244 (2.97), 258 (2.75), 272 (2.00), 288 nm (1.73). HRMS (FAB+): *m*/*z* calcd. 383.2217 [M$^+$ + H]; found 383.2222.

Tetradeca-2,4,10,12-tetrayne-1,14-diol (13a): A solution of concentrated H_2SO_4 (0.2 mL) in water (2.5 mL) was added dropwise to a magnetically stirred solution of **12a** (7.1 mmol) in methanol (50 mL). Stirring was continued at room temperature overnight.

The solvent was evaporated and the residue dissolved in ethyl acetate. The organic solution was washed with a saturated aqueous solution of sodium hydrogencarbonate (2 × 50 mL) and brine (1 × 50 mL), and dried with anhydrous sodium sulfate. After filtration, the ethyl acetate was partly removed, leaving approximately 50 mL of solution. Petroleum ether (150 mL) was added dropwise to the resulting solution and the initial crystallisation was completed at −30 °C overnight. The crystals were filtered off and dried in vacuo yielding **13a** (1.25 g, 5.8 mmol, 82%) as a colorless solid [m.p. 98−99 °C; R_f(Al_2O_3, Et_2O) = 0.5], which turns purple on exposure to light. ^{1}H NMR (500 MHz, CD_3OD): δ = 4.21 (s, 4 H, H-1/14), 2.33 (m, 4 H, H-6/9, $^3J_{H\text{-}6/9,H\text{-}7/8}$ = 5.3 Hz), 1.63 (m, 4 H, H-7/8) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 80.9 (C-5/10), 75.6 (C-2/13), 70.3 (C-3/12), 65.9 (C-4/11), 51.0 (C-1/14), 28.4 (C-7/8), 19.2 (C-6/9) ppm. IR (KBr): $\tilde{\nu}$ = 2937 (s), 2864 (m), 2255 (w), 1463 (m), 1339 (m), 1211 (w), 1030 (vs), 918 (w), 686 cm^{-1} (m). UV/Vis: λ_{max} (log ε) = 220 (2.75), 230 (2.87), 242 (2.87), 256 nm (2.65). HRMS (EI+): *m*/*z* calcd. 214.0993 [M$^+$]; found 214.0988.

1,14-Dibromotetradeca-2,4,10,12-tetrayne (14a): Diol **13a** (1.25 g, 5.8 mmol) was suspended in diethyl ether (150 mL) and tetrahydrofuran (8 mL) was added for better solvation. Pyridine (0.1 mL) was added and the reaction mixture was cooled to 0 °C. Under magnetic stirring a solution of phosphorus(III) bromide (0.63 mL, 8.7 mmol) in diethyl ether (20 mL) was added dropwise within 1.5 h. The reaction mixture was then stirred at room temperature for 24 h. The polyphosphorus acid was neutralized by addition of a saturated aqueous solution of sodium hydrogencarbonate. The organic layer was separated, and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with a saturated aqueous solution of sodium hydrogencarbonate and water and dried with anhydrous sodium sulfate. After filtration, the solvent was removed and the crude product was purified by column chromatography (Alox III, petroleum ether/diethyl ether, 50:1; R_f = 0.3) to yield **14a** (0.77 g, 2.2 mmol, 38%) as a colorless solid, that turns lavender very quickly on exposure to light. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.96 (s, 4 H, H-1/14), 2.33 (br., 4 H, H-6/9), 1.65 (m, 4 H, H-7/8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 92.4 (C-5/10), 71.8 (C-2/13), 70.4 (C-3/12), 65.1 (C-4/11), 27.1 (C-7/8), 20.0 (C-6/9), 14.8 (C-1/14) ppm. IR (KBr): $\tilde{\nu}$ = 2947 (m), 2252 (s), 1628 (w), 1421 (m), 1259 (s), 1198 (vs), 607 cm^{-1} (s). UV/Vis: λ_{max} (log ε) = 242 (3.78), 256 (3.89), 270 nm (3.78). HRMS (EI+): *m*/*z* calcd. 261.0102 [$C_{14}H_{12}{}^{81}Br^+$], 259.0122 [$C_{14}H_{12}{}^{79}Br^+$]; found 261.0110, 259.0137.

1-Isopropyl-1-azacyclopentadeca-3,5,11,13-tetrayne (15a): Freshly ground potassium carbonate (2.76 g) and isopropylamine (0.17 mL, 2.2 mmol) were added to a solution of **14a** (0.77 g, 2.2 mmol) in acetonitrile (260 mL). The mixture was heated to reflux and the reaction monitored by TLC. After the starting material had disappeared, the reaction mixture was allowed to cool to room temperature. The solvent was evaporated and the residue was dissolved in a mixture of dichloromethane and water. The organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried with anhydrous sodium sulfate and filtered. After evaporation of the solvent, the crude product was purified by column chromatography (Alox III, petroleum ether/diethyl ether, 10:1; R_f = 0.24) to yield **15a** (100 mg, 0.4 mmol, 20%) as colorless, powdery solid [m.p. > 105 °C (decomp.)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.60 (s, 4 H, H-2/15), 3.29 (sept, $^3J_{H\text{-}16,H\text{-}17/18}$ = 6.3 Hz, 1 H, H-16), 2.20 (br., 4 H, H-7/10), 1.72 (m, 4 H, H-8/9), 1.11 (d, $^3J_{H\text{-}17/18,H\text{-}16}$ = 6.3 Hz, 6 H, H-17/18) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 80.3 (C-6/11), 72.9 (C-3/14), 71.8 (C-4/13), 66.0 (C-5/12), 47.9 (C-16), 43.5 (C-2/15), 27.4 (C-8/9), 21.4 (C-17/18), 20.2 (C-7/10) ppm. IR (KBr): $\tilde{\nu}$ = 2980 (s), 2934 (s), 2866 (m), 2246 (w), 1628 (m), 1432 (m), 1334 (m), 1262 (w), 1223 (w), 1153 (w), 1081 (w), 920 (w), 680 cm^{-1} (w). UV/Vis: λ_{max} (log ε) = 248 (3.14), 262 nm (2.84). HRMS (EI+): *m*/*z* calcd. 237.1517 [M$^+$]; found 237.1506.

1,15-Bis(tetrahydro-2-pyranyloxy)pentadeca-2,4,11,13-tetrayne (12b): The synthesis was carried out according to the synthetic procedure of **12a**. At 0 °C compound **11**[8] (17.2 g, 80 mmol) was added dropwise to a solution of copper(I) iodide (1.5 g, 4 mmol) and **10b**[7] (4.80 g, 40 mmol) in pyrrolidine (100 mL). The crude product was purified by column chromatography (Alox III, petroleum ether/diethyl ether, 5:1; R_f = 0.33) to yield **12b** (10.5 g, 26.5 mmol, 66%) as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.81 (t, $^3J_{H\text{-}16,H\text{-}17/H\text{-}21,H\text{-}22}$ = 3.3 Hz, 2 H, H-16/21), 4.32, 4.29 (2 d, $^2J_{H,H}$ = 18.7 Hz, 4 H, H-1^a/15^a, H-1^b/15^b), 3.83−3.79 (m, 2 H, H-20^a/25^a), 3.54−3.51 (m, 2 H, H-20^b/25^b), 2.28 (t, $^3J_{H\text{-}6,H\text{-}7/H\text{-}10,H\text{-}9}$ = 6.5 Hz, 4 H, H-6/10), 1.84−1.46 (m, 18 H, H-7, 8, 9, 17/22, 18/23, 19/24) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 97.0 (C-16/21), 80.7 (C-5/11), 72.1 (C-2/14), 70.9 (C-3/13), 65.0 (C-4/12), 62.1 (C-20/25), 54.6 (C-1/15), 30.3 (C-17/22), 28.1 (C-8), 27.8 (C-7/9), 25.5 (C-18/23), 19.3 (C-6/10), 19.1 (C-19/24) ppm. IR (film): $\tilde{\nu}$ = 2941 (vs), 2863 (s), 2255 (m), 1441 (m), 1345 (m), 1201 (m), 1120 (s), 1025 (vs), 902 cm^{-1} (s). UV/Vis: λ_{max} (log ε) = 244 (3.05), 258 (2.88), 276 (2.35), 288 nm (2.18). HRMS (FAB+): *m*/*z* calcd. 397.2378 [M$^+$ + H]; 397.2354.

Pentadeca-2,4,11,13-tetrayne-1,15-diol (13b): Similar to the synthesis of **13a**, a solution of concentrated H_2SO_4 (0.2 mL) in water (10 mL) was added dropwise to a magnetically stirred solution of **12b** (10.5 g, 26.5 mmol) in methanol (125 mL). Addition of petroleum ether (150 mL) yielded compound **13b** (4.1 g, 17.8 mmol, 67%) as colorless solid [m.p. 82−84 °C; R_f(Al_2O_3, Et_2O) = 0.5], which turns purple on exposure to light. ^{1}H NMR (500 MHz, CD_3OD): δ = 4.21 (s, 4 H, H-1/15), 2.31 (t, $^3J_{H\text{-}6/8,H\text{-}7/9}$ = 6.3 Hz, 4 H, H-6/10), 1.58−1.48 (m, 6 H, H-7/9, 8) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 81.3 (C-5/11), 75.4 (C-2/14), 70.4 (C-3/13), 65.7 (C-4/12), 51.0 (C-1/13), 29.0 (C-8), 28.1 (C-7/9), 19.6 (C-6/10) ppm. IR (KBr): $\tilde{\nu}$ = 2936 (s), 2854 (m), 2255 (m), 1635 (w), 1462 (m), 1351 (m), 1231 (m), 1015 (vs), 727 cm^{-1} (w). UV/Vis: λ_{max} (log ε) = 222 (2.84), 230 (2.93), 242 (2.92), 256 nm (2.72). HRMS (EI+): *m*/*z* calcd. 228.1150 [M$^+$]; found 228.1146. $C_{15}H_{16}O_2$ (228.29): calcd. C 78.92, H 7.06; found C 78.71, H 7.10.

1,15-Dibromopentadeca-2,4,11,13-tetrayne (14b): The reaction was carried out according to the synthesis of **14a**. Pyridine (0.5 mL) and a solution of phosphorus(III) bromide (3.2 mL, 33.9 mmol) in diethyl ether (30 mL) were added to a suspension of diol **13b** (5.16 g, 22.6 mmol) in diethyl ether (300 mL) and tetrahydrofuran (10 mL). After column chromatography (Alox III, petroleum ether/diethyl ether, 10:1; R_f = 0.4), **14b** (4.26 mmol, 12.0 mmol, 53%) was obtained as a slightly yellow oil, that solidified to form an amorphous, pale-pink solid (m.p. 40−42 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.96 (s, 4 H, H-1/15), 2.31 (t, $^3J_{H\text{-}6/10,H\text{-}7/9}$ = 6.3 Hz, 4 H, H-6/10), 1.58−1.47 (m, 6 H, H-7/9, 8) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 82.1 (C-5/11), 71.9 (C-2/14), 70.3 (C-3/13), 64.8 (C-4/12), 28.1 (C-8), 27.6 (C-7/9), 19.3 (C-6/10), 15.2 (C-1/15) ppm. IR (KBr) = $\tilde{\nu}$: 2945 (s), 2253 (vs), 1461 (m), 1421 (m), 1262 (m), 1195 (vs), 605 cm^{-1} (vs). UV/Vis: λ_{max} (log ε) = 242 (3.79), 256 (3.89), 276 nm (3.77). HRMS (EI+): *m*/*z* calcd. 275.0259 [$C_{15}H_{14}{}^{81}Br^+$], 273.0279 [$C_{15}H_{14}{}^{79}Br^+$]; found 275.0252, 273.0293. $C_{15}H_{14}Br_2$ (354.08): calcd. C 50.88, H 3.99, Br 45.13; found C 51.04, H 4.03, Br 45.10.

1-Isopropyl-1-azacyclohexadeca-3,5,12,14-tetrayne (15b): According to the synthesis of **15a** a solution of **14b** (4.26 g, 12.0 mmol) in

acetonitrile (1.5 L) was heated together with freshly ground potassium carbonate (17.8 g) and isopropylamine (1.1 mL, 12.0 mmol). Column chromatography (Alox III, petroleum ether/diethyl ether, 10:1; R_f = 0.18) yielded **15b** (2.10 g, 8.3 mmol, 70%) as colorless, powdery solid [m.p. > 125 °C (decomp.)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.59 (s, 4 H, H-2/16), 3.27 (sept, $^3J_{H\text{-}17,H\text{-}18/19}$ = 6.2 Hz, 1 H, H-17), 2.31 (t, $^3J_{H\text{-}7/11,H\text{-}8/9}$ = 6.1 Hz, 4 H, H-7/11), 1.80 (quint, $^3J_{H\text{-}9,H\text{-}8/10}$ = 7.5 Hz, 2 H, H-9), 1.52 (m, 4 H, H-8/10), 1.11 (d, $^3J_{H\text{-}18/19,H\text{-}17}$ = 6.2 Hz, 6 H, H-18/19) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 78.8 (C-6/12), 72.3 (C-3/15), 71.1 (C-4/14), 66.9 (C-5/13), 47.9 (C-17), 43.6 (C-2/16), 25.9 (C-8/10), 25.6 (C-9), 21.3 (C-18/19), 18.8 (C-7/11) ppm. IR (KBr): $\tilde{\nu}$: 2977 (m), 2929 (s), 2859 (m), 2249 (w), 1628 (m), 1455 (m), 1336 (m), 1224 (w), 1155 (w), 1083 (w), 949 (w), 687 cm^{-1} (w). UV/Vis: λ_{max} (log ε) = 246 (2.94), 260 nm (3.21). HRMS (EI+): *m/z* calcd. 251.1674 [M^+]; found 251.1675. $C_{18}H_{21}N$ (251.37): calcd. C 86.01, H 8.42, N 5.57; found C 85.94, H 8.33, N 5.60.

5,12-Dichloro-2-isopropyl-1,2,3,6,7,8,9,10-octahydrocyclonona-[*e*]isoindole (16c): A suspension of tetrayne **15b** (300 mg, 1.2 mmol) in ethanol (5 mL) and concentrated hydrochloric acid (10 mL) was heated to 80 °C with magnetic stirring for 2 h, until there was no more starting material detectable by TLC (a small quantity was taken from the reaction mixture, treated with sodium hydroxide solution and extracted with diethyl ether). The reaction mixture was allowed to cool to room temperature and added to a stirred and cooled mixture of a solution of sodium hydroxide (10 g) in water (40 mL) and diethyl ether (40 mL). The organic layer was separated and the aqueous layer was extracted with two portions of diethyl ether. The ether layers were combined, washed with brine and dried with anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (Alox III, petroleum ether/diethyl ether, 20:1), yielding **16c** [113 mg, 0.35 mmol, 29%; R_f(petroleum ether/diethyl ether, 20:1) = 0.65] as a yellow, viscous liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.20 (s, 1 H, H-4), 6.05 (dd, $^3J_{H\text{-}11,H\text{-}10a}$ = 11.4, $^3J_{H\text{-}11,H\text{-}10b}$ = 5.4 Hz, 1 H, H-11), 4.04 (d, $^2J_{H\text{-}3a,H\text{-}3b}$ = 12.7 Hz, 1 H, H-3^a), 3.90 (s, 2 H, H-1), 3.83 (d, $^2J_{H\text{-}3b,H\text{-}3a}$ = 12.7 Hz, 1 H, H-3^b), 3.21−3.16 (m, 1 H, H-6^a), 2.73 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.0 Hz, 1 H, H-13), 2.48−2.43 (m, 1 H, H-6^b), 2.04−1.97 (m, 2 H, H-10$^{a/b}$), 1.68−1.37 (m, 6 H, H-7, 8, 9), 1.18, 1.17 (2 d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.0 Hz, 6 H, H-14/15,) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.7 (C-3a), 138.2 (C-5), 137.9 (C-12b), 133.3 (C-12a), 133.0 (C-5a), 132.4 (C-11), 127.6 (C-12), 123.9 (C-4), 57.1 (C-3), 56.0 (C-1), 54.7 (C-13), 32.5 (C-6), 29.4, 29.2, 27.6 (C-7,8,9), 26.5 (C-10), 21.92, 21.89 (C-14/15) ppm. HRMS (EI+): *m/z* calcd. 325.1178 [$C_{18}H_{23}{}^{37}Cl^{35}ClN^+$], 323.1208 [$C_{18}H_{23}{}^{35}Cl_2N^+$]; found 325.1130, 323.1156.

[4,11-D$_2$]-5,12-Dichloro-2-isopropyl-1,2,3,6,7,8,9,10-octahydrocyclonona[*e*]isoindole ([D$_2$]16c): The reaction was carried out according to the synthesis of **16c**. Compound **15b** (300 mg, 1.2 mmol) was suspended in [D_1]ethanol (4.5 mL) and DCl (10 mL) in D_2O yielding **[D$_2$]16c** (145 mg, 0.44 mmol, 37%) as yellow, viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (d, $^2J_{H\text{-}3a,H\text{-}3b}$ = 12.7 Hz,1 H, H-3^a), 3.90 (s, 2 H, H-1), 3.84 (d, $^2J_{H\text{-}3b,H\text{-}3a}$ = 12.7 Hz, 1 H, H-3^b), 3.22−3.15 (m, 1 H, H-6^a), 2.74 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.3 Hz, 1 H, H-13), 2.51−2.43 (m, 1 H, H-6^b), 2.04−1.96 (m, 2 H, H-10$^{a/b}$), 1.66−1.39 (m, 6 H, H-7,8,9), 1.18 (d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.3 Hz, 6 H, H-14/15) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.6 (C-3a), 138.3 (C-5), 138.0 (C-12b), 133.3 (C-12a), 133.0 (C-5a), 127.5 (C-12), 57.0 (C-3), 56.1 (C-1), 54.7 (C-13), 32.5 (C-6), 29.4, 29.1, 27.6 (C-7,8,9), 26.5 (C-10), 21.9 (C-14/15) ppm. HRMS (EI+): *m/z* calcd. 327.1303 [$C_{18}H_{21}{}^{37}Cl^{35}ClD_2N^+$], 325.1333 [$C_{18}H_{21}{}^{35}Cl_2D_2N^+$]; found 327.1269, 325.1286.

5-Chloro-2-isopropyl-2,3,6,7,8,9,10,11-octahydrocyclonona-[*e*]isoindol-12(1*H*)-one (17c): According to the synthetic procedure for **16c**, compound **17c** (42 mg, 0.14 mmol, 11%) was isolated as a further product by column chromatography, eluting with petroleum ether/diethyl ether (5:1; R_f = 0.32), as a yellow, viscous liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.21 (s, 1 H, H-4), 3.89 (s, 2 H, H-3), 3.80 (s, 2 H, H-1), 2.85 (t, $^3J_{H\text{-}6,H\text{-}7}$ = 6.4 Hz, 2 H, H-6), 2.77 (m, 2 H, H-11), 2.71 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.3 Hz, 1 H, H-13), 1.86−1.84 (m, 2 H, H-10), 1.69−1.67 (m, 2 H, H-7), 1.52−1.49 (m, 2 H, H-9), 1.33−1.31 (m, 2 H, H-8), 1.14 (d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.5 Hz, 6 H, H-14/15) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 210.9 (C-12), 140.19, 140.17, 134.2, 133.2, 133.1 (C-3a, 5, 5a, 12a, 12b), 124.2 (C-4), 56.4 (C-3), 55.5 (C-1), 54.4 (C-13), 41.9 (C-11), 28.1 (C-6), 26.8 (C-7), 26.1 (C-9), 24.5 (C-10), 22.6 (C-8), 21.8 (C-14/15) ppm. HRMS (EI+): *m/z* calcd. 307.1517 [$C_{18}H_{24}{}^{37}ClNO^+$], 305.1546 [$C_{18}H_{24}{}^{35}ClNO^+$]; found 307.1563, 305.1568.

[4-D]-5-Chloro-2-isopropyl-2,3,6,7,8,9,10,11-octahydrocyclonona-[*e*]isoindol-12(1*H*)-one ([D]17c): The synthesis of **[D$_2$]16c** yielded compound **[D]17c** (46 mg, 0.15 mmol, 13%) as a further product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.90 (s, 2 H, H-3), 3.81 (s, 2 H, H-1), 2.86 (t, $^3J_{H\text{-}6,H\text{-}7}$ = 6.4 Hz, 2 H, H-6), 2.78 (m, 2 H, H-11), 2.72 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.3 Hz, 1 H, H-13), 1.89−1.84 (m, 2 H, H-10), 1.72−1.67 (m, 2 H, H-7), 1.56−1.49 (m, 2 H, H-9), 1.36−1.33 (m, 2 H, H-8), 1.15 (d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.2 Hz, 6 H, H-14/15) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 210.9 (C-12), 140.2, 140.1, 134.2, 133.1, (C-3a/5/5a/12a/12b), 56.4 (C-3), 55.5 (C-1), 54.4 (C-13), 41.9 (C-11), 28.1 (C-6), 26.8 (C-7), 26.1 (C-9), 24.5 (C-10), 22.6 (C-8), 21.8 (C-14/15) ppm. HRMS (EI+): *m/z* calcd. 308.1580 [$C_{18}H_{23}{}^{37}ClDNO^+$], 306.1609 [$C_{18}H_{23}{}^{35}ClDNO^+$]; found 308.1608, 306.1609.

[4,11,11-D$_3$]-5-Chloro-2-isopropyl-2,3,6,7,8,9,10,11-octahydrocyclonona[*e*]isoindol-12(1*H*)-one ([D$_3$]17c): When the products from the reaction of **15b** with DCl/D_2O in [D_1]ethanol (c.f. [D$_2$]**16c**) were separated on an Alox column deactivated with D_2O we isolated [D$_3$]**17c**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.91 (s, 2 H, H-3), 3.81 (s, 2 H, H-1), 2.87 (t, $^3J_{H\text{-}6,H\text{-}7}$ = 6.4 Hz, 2 H, H-6), 2.73 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.3 Hz, 1 H, H-13), 1.88−1.85 (m, 2 H, H-10), 1.73−1.67 (m, 2 H, H-7), 1.56−1.50 (m, 2 H, H-9), 1.36−1.32 (m, 2 H, H-8), 1.15 (d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.3 Hz, 6 H, H-14/15) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 211.1 (C-12), 140.4, 140.3, 140.1, 134.2, 133.1 (C-3a/5/5a/12a/12b), 56.4 (C-3), 55.6 (C-1), 54.5 (C-13), 28.1 (C-6), 26.8 (C-7), 26.0 (C-9), 24.4 (C-10), 22.6 (C-8), 21.8 (C-14/15) ppm. HRMS (EI+): *m/z* calcd. 308.1735 [$C_{18}H_{21}{}^{35}ClD_3NO^+$]; found 308.1688.

5,12-Dibromo-2-isopropyl-1,2,3,6,7,8,9,10-octahydrocyclonona-[*e*]isoindole (18c): Compound **18c** (164 mg, 0.40 mmol, 36%) was isolated as brown-green oily liquid when tetrayne **15b** (300 mg, 1.2 mmol) was heated in ethanol (5 mL) and concentrated hydrobromic acid (5 mL) according to the synthesis of compound **16c**. Indole **18c** was purified by column chromatography [Alox III, petroleum ether/diethyl ether, 20:1; R_f(petroleum ether/diethyl ether, 5:1) = 0.55]. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38 (s, 1 H, H-4), 6.27 (dd, 1 H, $^3J_{H\text{-}11,H\text{-}10a}$ = 11.4, $^3J_{H\text{-}11,H\text{-}10b}$ = 5.4 Hz, H-11), 4.04 (d, 1 H, $^2J_{H\text{-}3a,H\text{-}3b}$ = 12.5 Hz, H-3^a), 3.89−3.83 (m, 3 H, 3^b, H-1), 3.20−3.16 (m, 1 H, H-6^a), 2.75 (sept, 1 H, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.1 Hz, H-13), 2.56−2.51 (m, 1 H, H-6^b), 2.04−1.93 (m, 2 H, H-7^a, 10^a), 1.65−1.38 (m, 6 H, H-10^b, 8, 9, 7^b), 1.17, 1.16 (2 d, 6 H, H-14/15, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.0 Hz) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 140.1, 138.6 (C-3a/12b), 139.6 (C-12a), 136.7 (C-11), 134.4 (C-5a), 127.6 (C-4), 123.4 (C-5), 116.9 (C-12), 56.9 (C-3), 56.1 (C-1), 54.7 (C-13), 34.9 (C-6), 30.3 (C-10), 29.2, 27.6 (C-8/9), 26.6 (C-7), 21.9, 21.8 (C-14/15) ppm. HRMS (EI+): *m/z* calcd.

415.0156 [$C_{18}H_{23}{}^{81}Br_2N^+$], 413.0177 [$C_{18}H_{23}{}^{81}Br^{79}BrN^+$], 411.0197 [$C_{18}H_{23}{}^{79}Br_2N^+$]; found 415.0143, 413.0163, 411.0170.

5-Bromo-2-isopropyl-2,3,6,7,8,9,10,11-octahydrocyclonona-[*e*]isoindol-12(1*H*)-one (19c): According to the synthetic procedure for **18c**, compound **19c** (43 mg, 0.12 mmol, 10%) was isolated as a further product by column chromatography, eluting with petroleum ether/diethyl ether (5:1; R_f = 0.22), as a brown-green, oily liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.41 (s, 1 H, H-4), 3.90 (s, 2 H, H-3), 3.79 (s, 2 H, H-1), 2.49 (t, $^3J_{H\text{-}6,H\text{-}7}$ = 6.3 Hz, 2 H, H-6), 2.77 (m, 2 H, H-11), 2.72 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.3 Hz, 1 H, H-13), 1.89−1.84 (m, 2 H, H-10), 1.72−1.68 (m, 2 H, H-7), 1.55−1.49 (m, 2 H, H-9), 1.35−1.33 (m, 2 H, H-8), 1.15 (d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.3 Hz, 6 H, H-14/15) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 211.0 (C-12), 140.5, 140.3, 134.9, 134.5, 123.6 (C-3a/5/5a/12a/12b), 127.5 (C-4), 56.2 (C-3), 55.5 (C-1), 54.4 (C-13), 41.8 (C-11), 30.6 (C-6), 26.8 (C-7), 26.1 (C-9), 24.4 (C-10), 22.5 (C-8), 21.8 (C-14/15) ppm. HRMS (EI+): *m*/*z* calcd. 351.1020 [$C_{18}H_{24}{}^{81}BrNO^+$], 349.1014 [$C_{18}H_{24}{}^{79}BrNO^+$]; found 351.1018, 349.1036.

5-Chloro-2-isopropyl-1,2,3,6,7,8,9,10-octahydro-11,12-dehydrocyclonona[*e*]isoindole (20): Tetrayne **15b** (300 mg, 1.2 mmol) was heated in ethanol (10 mL) and concentrated hydrochloric acid (5 mL) to 80 °C with magnetic stirring for 5 h, and treated according to the synthesis of compound **16c**. Column chromatography (Alox III, petroleum ether/diethyl ether, 50:1) yielded **20** (196 mg, 0.68 mmol, 57%) as an oily, yellow liquid [R_f(petroleum ether/diethyl ether, 5:1) = 0.57]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08 (s, 2 H, H-4), 3.91 (s, 2 H, H-1), 3.89 (s, 2 H, H-3), 2.95 (t, $^3J_{H\text{-}6,H\text{-}7}$ = 6.7 Hz, 2 H, H-6), 2.72 (sept, $^3J_{H\text{-}13,H\text{-}14/15}$ = 6.3 Hz, 1 H, H-13), 2.52 (t, $^3J_{H\text{-}10,H\text{-}9}$ = 5.9 Hz, 2 H, H-10,), 1.92−1.90 (m, 2 H, H-9), 1.82−1.77 (m, 2 H, H-7), 1.73−1.69 (m, 2 H, H-8), 1.16 (d, $^3J_{H\text{-}14/15,H\text{-}13}$ = 6.3 Hz, 6 H, H-14/15) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0 (C-5a), 138.9 (C-12b), 137.6 (C-3a), 131.8 (C-5), 120.7 (C-12a), 108.8 (C-11), 84.9 (C-12), 57.0 (C-3), 56.4 (C-1), 54.6 (C-13), 30.7 (C-6), 28.2 (C-8), 27.1 (C-9), 26.7 (C-7), 21.7 (C-14/15), 20.6 (C-10) ppm. HRMS (EI+): *m*/*z* calcd. 287.1440 [$C_{18}H_{22}{}^{35}ClN^+$]; found 287.1426.

5-Chloro-2-isopropyl-2,3,7,8,9,10-hexahydro-1*H*-cycloocta[*e*]-isoindol-11(6*H*)-one (24c): A suspension of compound **15a** (200 mg, 0.84 mmol) in ethanol (3.6 mL) and concentrated hydrochloric acid (7.1 mL) was heated according to the synthetic procedure for **16c**. Purification by column chromatography (Alox III, petroleum ether/diethyl ether, 5:1; R_f = 0.22) yielded compound **24c** (49 mg, 0.17 mmol, 20%) as a yellow, viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.22 (s, 1 H, H-4), 3.96 (s, 2 H, H-3), 3.90 (s, 2 H, H-1), 2.85−2.65 (m, 5 H, H-6, 12, 10), 1.82−1.52 (m, 6 H, H-7, 9, 8), 1.14 (d, $^3J_{H\text{-}13/14,H\text{-}12}$ = 6.3 Hz, 6 H, H-13/14) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 210.8 (C-11), 140.3, 137.3, 134.9, 133.6, 132.7 (C-3a/5/5a/11a/11b), 124.2 (C-4), 56.6 (C-3), 55.5 (C-1), 54.5 (C-12), 46.9 (C-10), 29.7 (C-6), 27.7 (C-7), 26.3 (C-9), 23.2 (C-8), 21.8 (C-13/14) ppm. HRMS (EI+): *m*/*z* calcd. 293.1360 [$C_{17}H_{22}{}^{37}ClNO^+$], 291.1390 [$C_{17}H_{22}{}^{35}ClNO^+$]; found 293.1362, 291.1390.

X-ray Diffraction Analyses: All measurements were carried out with a Bruker SMART diffractometer with graphite-monochromated Mo-K_α radiation using a CCD detector. Frames corresponding to a sphere of data were collected using the ω-scan technique; in each

Table 1. Selected crystal data for **15a**, **15b** and **18c**

	15a	**15b**	**18c**
Empirical formula	$C_{17}H_{19}N$	$C_{18}H_{21}N$	$C_{18}H_{23}Br_2N$
M_r	237.33	251.36	413.19
Crystal size [mm]	0.20 × 0.20 × 0.12	0.48 × 0.34 × 0.07	0.25 × 0.25 × 0.23
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	5.1888(2)	5.1925(3)	20.2625(3)
b [Å]	10.4543(3)	11.3707(6)	9.1843(2)
c [Å]	25.5933(3)	12.7061(6)	9.7222(2)
α [°]	90	87.395(1)	90
β [°]	92.055(2)	88.173(1)	103.798(1)
γ [°]	90	89.454(1)	90
V [Å^3]	1387.42(7)	749.02(7)	1757.06(6)
$\rho_{calcd.}$ [g cm^{-3}]	1.14	1.12	1.56
θ range [°]	1.6−27.5	1.6−27.5	2.1−27.5
Z	4	2	4
F(000)	512	272	832
h_{min}/h_{max}	−6/6	−6/6	−26/26
k_{min}/k_{max}	−13/13	−14/14	−11/10
l_{min}/l_{max}	−19/33	−16/16	−12/12
μ [mm^{-1}]	0.06	0.06	4.61
T_{min}/T_{max}	0.99/0.99	0.99/0.95	0.42/0.39
Refl. collected	7129	7737	10631
Refl. unique	3161	3409	3982
Refl. observed	2344	2549	2934
Variables	165	174	192
$R(F^2)$	0.043	0.039	0.033
$R_w(F^2)$	0.099	0.095	0.064
S (Gof) on F^2	1.03	1.02	1.01
$[\Delta\rho]_{max}$ [e·Å^{-3}]	0.14	0.17	0.86
$[\Delta\rho]_{min}$ [e·Å^{-3}]	−0.18	−0.17	−0.76

case 20 s exposures of 0.3° in ω were taken. The reflections were integrated and equivalent reflections were merged. An absorption correction was applied to the structures using SADABS[11] and the data were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and expanded using Fourier techniques (SHELXTL 5.10).[11] The structural parameters of the non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions. The final cycle of full-matrix least-squares refinement converged. The function minimised was $\Sigma w[(F_o)^2 - (F_c)^2]^2$. All calculations were performed using the SHELXTL crystallographic software package of Bruker.[11] Table 2 contains the crystallographic data and details of the refinement procedure for compounds **15a**, **15b** and **18c**. The X-ray studies were performed at 200(2) K. CCDC-229998 (**15a**), -229999 (**15b**) and -230000 (**18c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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