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Transannular Ring Closure of a 1,8-Diazacyclotetradeca-3,5,10,12-tetrayne to a Tricyclic System with a Central Cyclooctatetraene Ring

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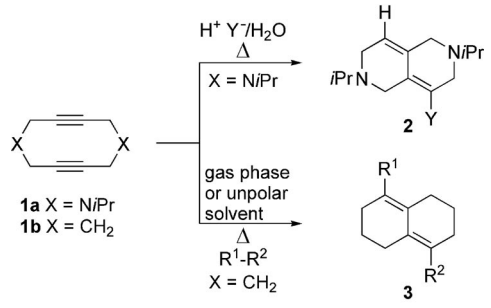
The addition of two equivalents of hydrochloric acid to *N*,*N*′-diisopropyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (**13**) afforded a tricyclic scaffold in which a central dichloro-substituted cyclooctatetraene ring is annelated by two *N*-isopropyl-2,5-dihydropyrrole rings (**14**). Three other minor products were congeners of **14** in which one (**15**, **16**) or both (**17**) of the 2,5-dihydropyrrole rings are oxidized. In **16** the chlorine atoms adopt different positions.The assignment of the structures of **14**–**17** is based on the result of an X-ray investigation on single crystals of **16** and NMR studies. The structural assignments of **14** and **15** were corroborated by labeling experiments with DCl. The regiochemistry in the addition of the second equivalent of hydrochloric acid to **13** was illuminated by DFT calculations.

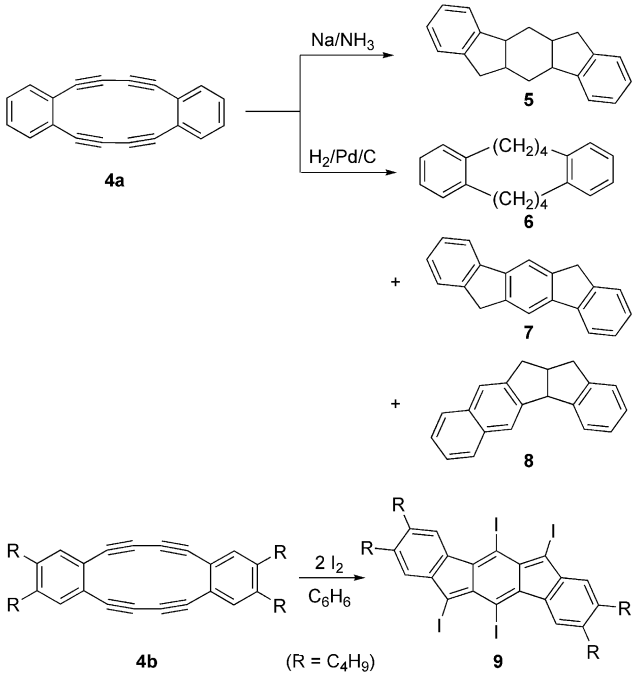
Introduction

Some time ago we demonstrated that two alkyne units oriented in close proximity in a 10-membered ring undergo a transannular reaction to yield a bicyclic system as schematically shown in Scheme 1 for a polar and radical addition.[1,2]



Scheme 1. Polar and radical additions to **1**.

These results stimulated us to look at systems where two 1,3-butadiyne units are oriented parallel to each other in a cyclic system. Earlier studies by various groups reported transannular reactions of the 1,2:7,8-dibenzocyclododeca-1,7-dien-3,5,7,11-tetrayne systems **4a** and **4b** which mainly led to 6-5-6-5-6-fused ring systems as shown in Scheme 2.[3–5] When the ring size of the cyclic tetrayne system was changed from 12 to 14,[6] 15 or 16,[7] other ring-closing modes were observed. In the case of *N*-isopropyl-1-azacyclotetradeca-3,5,10,12-tetrayne (**10**) we observed the tricyclic species **11** with a central cyclooctatetraene ring skeleton (Scheme 3).[6]



Scheme 2. Reduction-induced transannular ring closure of **4a** and reaction of **4b** with iodine.

The structure of **11** was underpinned by its oxidation product **12** whose structure was confirmed by an X-ray investigation on single crystals.[6] These results revealed that

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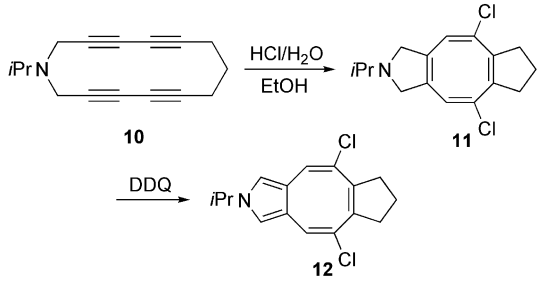


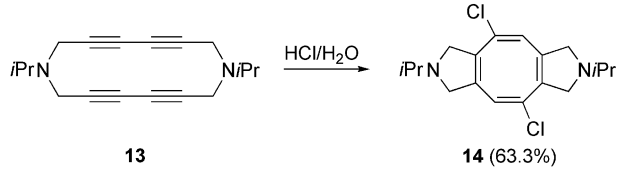
Scheme 3. Transannular reaction of **10** leading to **11** and **12**.

the longer tethers in **10** as compared to **4** allowed a ring closure at both termini of the 1,3-butadiyne units in **10**. This ring-closing mode was facilitated by the relative close proximity of the termini in **10** (3.1 Å) as compared to the distances of the inner sp-centers (3.4 Å). When the two tethers connecting the 1,3-butadiyne units are of different lengths only three of the four triple bonds are involved in the ring-closing process.[7]

In connection with our studies on the addition of hydrochloric acid to **1a**[2] and **10**[6] we also studied the behavior of *N*,*N*′-diisopropyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (**13**)[8] towards concentrated hydrochloric acid. This study was undertaken to find out more about the regioselectivity of the HCl addition.

Results

A solution of **13** in concd. hydrochloric acid was stirred under aerobic conditions at 50 °C for 48 h. After work-up four products were separated by column chromatography. The main product **14**, a yellow oil, was isolated in 63% yield. The yields for the other products, **15**–**17**, were low and in the order of 2% (**15**, **16**) to 0.6% (**17**). The mass spectrometric data revealed for **14** a molecular weight of 338, corresponding to a formula of $C_{18}H_{24}Cl_2N_2$. This shows that two equivalents of HCl were added to **13** (Scheme 4).



Scheme 4. Generation of **14** by HCl addition to **13**.

For **15** and **16** the masses recorded were *m*/*z* 336 corresponding to formulae of $C_{18}H_{22}Cl_2N_2$. For **17** the mass was 334 corresponding to $C_{18}H_{20}N_2Cl_2$. We assume that the side products **15**–**17** are due to an oxidation process of **14** under the aerobic condition that the reaction was carried out in (Figure 1).

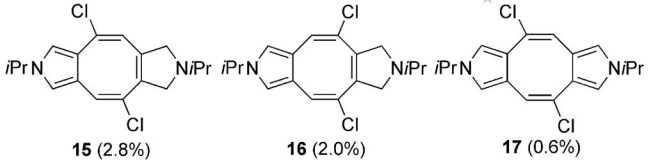


Figure 1. Structures of the side products obtained from the addition of HCl to **13**.

The NMR spectroscopic data of all four products revealed rather simple and very similar patterns indicating that the skeleton of all four molecules is very closely related. The ^{13}C NMR spectroscopic data reveal no signals for sp carbon atoms but signals for aliphatic and olefinic carbons. The ^{1}H NMR spectroscopic data in the olefinic region reveal for **14** only one singlet, for **16** two singlets, for **15** two singlets and two doublets, and for **17** one singlet and two doublets. We start with our structural assignments with **16** because we were able to grow single crystals of this species which allowed an X-ray diffraction study.[9] These investigations revealed a tricyclic ring system with a central eight-membered ring annelated to an *N*-isopropyl-2,5-dihydropyrrole and an *N*-isopropylpyrrole ring (Figure 2).

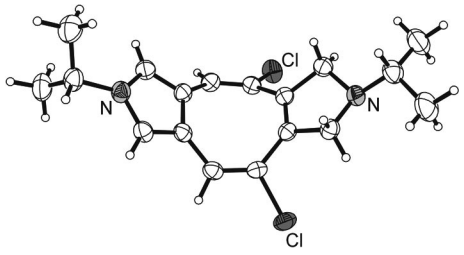


Figure 2. Molecular structure of **16**.

The molecular structure of **16** adopts a nearly C_s symmetry in the solid state and is reminiscent of **12**. As anticipated the pyrrole ring is almost planar whereas the dihydropyrrole ring adopts an envelope conformation with a bonding angle at the nitrogen center of 105.6°. For the central eight-membered ring a boat conformation was found. The folding angle of the eight-membered ring amounts to average 38.2° and 34.4° at the dihydropyrrole and the pyrrole side, respectively, being close to that reported for dibenzo[*a*,*e*]cyclooctatetraene (43.4°).[10] The knowledge of the molecular structure of **16** allowed us to interpret the NMR spectroscopic data of this molecule and the other three products. In the ^{1}H NMR spectrum of **16** the singlet at δ = 3.61 ppm corresponds to the equivalent CH_2 groups of the dihydropyrrole ring, and the singlet at δ = 6.34 ppm we assigned to the two equivalent protons of the pyrrole ring. The singlet at δ = 6.52 ppm is due to the equivalent CH groups of the eight-membered ring. These assignments are fully in line with ^{13}C NMR spectroscopic data and HMBC experiments.

The spectroscopic data of the ^{1}H NMR spectrum of **15** and the fact that the ^{13}C NMR spectroscopic data reveal sixteen signals, twice as many as found for **16**, indicate no

plane of symmetry or a C_2 axis perpendicular to the molecular plane for **15**. The same molecular weight of **15** as **16** suggests to assign to **15** the other possible regioisomer (Figure 1). With this assumption we were able to assign all of the NMR spectroscopic data of **15**. The signals of the isopropyl groups (δ = 4.06 and 2.54 ppm) in the ^{1}H NMR spectrum are very close to those recorded for **16**. The same holds for the ^{13}C NMR spectroscopic data of the isopropyl group. This supports one pyrrole and one 2,5-dihydropyrrole ring in **15**. The ^{1}H NMR signals of the CH_2 groups of the dihydropyrrole ring are found as multiplets at 3.57 to 3.60 ppm and at δ = 3.42 ppm. In the ^{13}C NMR spectrum of **15** the corresponding signals are found as triplets at δ = 62.3 and 61.0 ppm. The presence of the pyrrole ring is evidenced in the ^{1}H NMR spectrum of **15** by two doublets at δ = 6.67 and 6.28 ppm.The coupling constants of ^4J = 2.48 Hz and 2.42 Hz are in line with those reported in the literature.[2,11] The two singlets at δ = 6.51 and 5.94 ppm we assign to the non-equivalent hydrogen atoms at the COT ring.

The ^{1}H NMR spectrum recorded for the main product **14** is rather simple. We found only one singlet for the sp^2 CH groups, and the signals for the isopropyl groups (δ = 2.60 ppm) reveal their magnetic equivalence. Together with the measured molecular weight and the presence of only eight signals in the ^{13}C NMR spectrum, the assignment of the molecular structure of **14** is fully in line with the proposed C_2 symmetry.

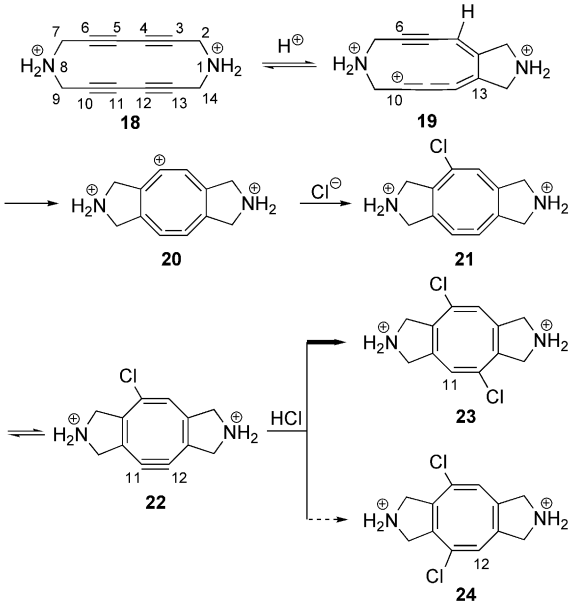
The assignment of the analytical data obtained for the most unsaturated product to **17** follows also from the spectroscopic data: only eight signals in the ^{13}C NMR spectrum, one singlet for the sp^2 CH protons (δ = 6.57 ppm) of the eight-membered ring, two doublets for the pyrrole protons (δ = 6.76 and 6.34 ppm) and the magnetic equivalence for the isopropyl protons (δ = 4.07 ppm) are fully in line with the proposed C_2-symmetrical structure in Figure 1.

The assignment of the ^{1}H NMR spectra of **14** and **15** was corroborated by the spectra of **14-d$_2$** and **15-d$_2$**, which were obtained by the addition of concd. DCl (in D_2O) to **13** (see Exp. Section).

Discussion

The discussion of the reaction mechanism of the HCl addition to **13** is based on recent model calculations[12] carried out on the diprotonated form of the tetrayne, **18**, using B3LYP/6-31G*. These calculations led us to postulate a stepwise mechanism for the ring closure of **18** to **24** (Scheme 5).

Adding a proton to one of the triple bonds in **18** (C4) causes a transannular ring closure affording the vinyl cation **19**. Further ring closure leads to the tricyclic cation **20** to which a Cl^- is added consecutively. The resulting highly strained cyclic 1,2,3-butatriene **21** can isomerize to **22** which is more stable but still suffers from a highly strained triple bond. Final HCl addition to the triple bond in **22** yields the product **23** corresponding to **14** (Scheme 4) in the experiment.



Scheme 5. Proposed reaction mechanism for the addition of HCl to **18**.

We further addressed the question why there was such a dominant regioselectivity to be observed in the HCl addition to **22**. In the reaction of **13** (Scheme 4) three of the four isolated products showed a 1,5-dichloro substitution pattern in the eight-membered ring with a total yield of 66.7%. **16** having a 1,4-dichloro-substituted eight-membered ring was found in only 2%. As **16** must have been formed by oxidation of a precursor corresponding to **24** and **15** and **17** are oxidation products of **14**, which corresponds to **23**, we traced the question back to the regioselectivity in the HCl addition to **22**. To illuminate this matter we compared the relative nucleophilicities of the sp-carbon centers C11 and C12 in **22**, as calculated from local softnesses.[12] The addition of HCl to a triple bond usually follows an Ad_E2 mechanism, starting with the protonation of one of the sp-carbon atoms. The carbon atom with the greater nucleophilicity should have a stronger attraction to the attacking proton. Our calculations showed that the relative nucleophilicity of C11 in **22** is larger than that of C12. This means that the majority of **22** is converted to **23** which confirms our experimental observation that **14** (Scheme 4) was predominantly formed. Interestingly, the regioselectivity in the reaction of the monoaza system **10** (Scheme 3) is the reverse. In the experiment only the regioisomer **11** could be isolated[6] which we were also able to confirm by relative nucleophilicity calculations.[12]

Conclusions

In contrast to the rather rigid 12-membered, cyclic tetraynes **4** (Scheme 2) which show ring-closing modes of the central bis-diyne units to 5-6-5 tricyclic systems, our more flexible 14-membered, cyclic tetrayne **13** yields a 5-8-5 patterned system. We were able to elucidate the structures of

four different isolated products by analytical methods. In contrast to the monoaza congener **10** (Scheme 3) the main cyclization product of **13**, **14**, reveals a 4,8-dichloro substitution of the central cyclooctatetraene ring. The corresponding 3,8-substituted product, **16**, is only found in low yields. This difference between the acid-induced reactions of **10** and **13** can be traced back to the relative nucleophilicity of the alkyne carbon atoms of the cycloocta-1,3,5-triene-7-yne intermediates (Scheme 5).

Experimental Section

Preparation of 14–17: The reaction was carried out in a Schlenk flask. A solution of 400 mg (1.5 mmol) of *N*,*N*′-diisopropyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (**13**) in 30 mL of concd. HCl (36%) was heated to 50 °C for 48 h. After cooling the brown-colored solution to room temperature, 100 mL of chloroform were added, followed by 400 mL of 2 N NaOH, saturated with NaCl at 0 °C. The alkaline phase was extracted with chloroform (3 × 50 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and in a rotary evaporator to get a brown-colored solid as crude product. The crude product was absorbed on neutral alumina and subjected to column chromatography on silica gel with chloroform/methanol (30:1, v/v) as eluent obtaining pure **17** (3 mg, 0.008 mmol, 0.6%) and a mixture of **14**–**16**. Further separation of the mixture **14**–**16** was achieved on silica gel with cyclohexane/ethyl acetate (10:1, v/v) as eluent obtaining pure **14** (322 mg, 0.95 mmol, 63.3%), **15** (14 mg, 0.04 mmol, 2.8%), and **16** (10 mg, 0.03 mmol, 2%).

4,9-Dichloro-2,7-diisopropyl-1,2,3,6,7,8-hexahydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (14): Yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.90 (s, 2 H, C*H*, cyclooctatetraene), 3.67–3.61 (m, 2 H, CH_2, dihydropyrrole), 3.48–3.43 (m, 4 H, CH_2, dihydropyrrole), 3.39–3.35 (m, 2 H, CH_2, dihydropyrrole), 2.60 (hept, ^3J = 6.3 Hz, 2 H, NC*H*, isopropyl), 1.06 (d, ^3J = 6.3 Hz, 12 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.3, 136.1, 131.0, 125.9, 61.2, 59.8, 54.2, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 2973, 2767, 1621, 1530 cm^{-1}. MS (EI): *m*/*z* (%) = 342 (3) [M$^+$Cl^{37}Cl^{37}], 340 (18) [M$^+$Cl^{37}Cl^{35}], 338 (28) [M$^+$Cl^{35}Cl^{35}], 327 (11), 325 (65), 323 (100), 305 (93), 303 (24), 301 (39), 282 (21), 281 (18), 280 (15), 263 (2), 261 (14), 259 (24). HRMS (EI): *m*/*z*: Calcd. for $C_{18}H_{24}{}^{35}Cl_2N_2$: 338.1317; found 338.1286.

4,9-Dichloro-2,7-diisopropyl-1,2,3,7-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (15): Yellow wax-like solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.67 (d, ^4J = 2.48 Hz, 1 H, C*H*, pyrrole), 6.51 (s, 1 H, C*H*, cyclooctatetraene), 6.28 (d, ^4J = 2.42 Hz, 1 H, C*H*, pyrrole), 5.94 (s, 1 H, C*H*, cyclooctatetraene), 4.08 [hept, ^3J = 6.7 Hz, 1 H, NC*H*, isopropyl(pyrrole)], 3.60–3.57 (m, 2 H, CH_2, dihydropyrrole), 3.42 (m, 2 H, CH_2, dihydropyrrole), 2.57 [hept, ^3J = 6.3 Hz, 1 H, NC*H*, isopropyl(dihydropyrrole)], 1.41 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.08 (d, ^3J = 6.3 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.8, 134.3, 131.3, 128.0, 125.4, 122.2, 121.8, 120.2, 119.3, 118.7, 62.3, 61.0, 54.7, 51.7, 24.0, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 2972, 2768, 1633, 1527, 1460 cm^{-1}. MS (EI): *m*/*z* (%) = 340 (2) [M$^+$Cl^{37}Cl^{37}], 338 (16) [M$^+$Cl^{37}Cl^{35}], 336 (29) [M$^+$Cl^{35}Cl^{35}], 325 (4), 323 (21), 321 (34), 303 (34), 301 (100), 261 (5), 259 (29), 257 (42), 219 (4), 217 (17), 215 (27). HRMS (EI): *m*/*z*: Calcd. for $C_{18}H_{22}N_2{}^{35}Cl_2$: 336.1160; found 336.1143.

4,10-Dichloro-2,7-diisopropyl-1,2,3,7-tetrahydro-cycloocta[1,2-*c*:5,6-*c*′]dipyrrole (16): Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.52 (s, 2 H, C*H*, cyclooctatetraene), 6.34 (s, 2 H, C*H*, pyrrole), 4.06 [hept, ^3J = 6.7 Hz, 1 H, NC*H*, isopropyl(pyrrole)], 3.61 (s, 4 H, CH_2, dihydropyrrole), 2.59 [hept, ^3J = 6.3 Hz, 1 H, NC*H*, isopropyl(dihydropyrrole)], 1.39 (d, ^3J = 6.7 Hz, 6 H, CH_3), 1.08 (d, ^3J = 6.3 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.3, 126.7, 126.6, 120.6, 118.3, 61.7, 55.2, 51.8, 24.3, 22.4 ppm. IR (KBr): $\tilde{\nu}$ = 2972, 2766, 1623, 1530 cm^{-1}. MS (EI): *m*/*z* (%) = 340 (3) [M$^+$Cl^{37}Cl^{37}], 338 (20) [M$^+$Cl^{37}Cl^{35}], 336 (34) [M$^+$Cl^{35}Cl^{35}], 325 (6), 323 (38), 301 (100), 259 (24), 257 (41), 219 (2), 217 (12), 215 (20). HRMS (EI): *m*/*z*: Calcd. for $C_{18}H_{22}{}^{35}Cl_2N_2$: 336.1160; found 336.1173.

Analytical Data for 4,9-Dichloro-2,7-diisopropyl-2,7-dihydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (17): Brown wax-like solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.76 (d, ^4J = 2.6 Hz, 2 H, C*H*, pyrrole), 6.57 (s, 2 H, C*H*, cyclooctatetraene), 6.34 (d, ^4J = 2.6 Hz, 2 H, C*H*, pyrrole), 4.07 (hept, ^3J = 6.7 Hz, 2 H, NC*H*, isopropyl), 1.39 (d, ^3J = 6.7 Hz, 12 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 127.6, 122.1, 120.9, 120.0, 119.3, 118.6, 51.5, 23.9 ppm. IR (KBr): $\tilde{\nu}$ = 2963, 2930, 1635, 1602, 1517 cm^{-1}. MS (EI): *m*/*z* (%) = 338 (12) [M$^+$Cl^{37}Cl^{37}], 336 (63) [M$^+$Cl^{37}Cl^{35}], 334 (100) [M$^+$Cl^{35}Cl^{35}], 301 (9), 299 (24). HRMS (EI): *m*/*z*: Calcd. for $C_{18}H_{20}N_2{}^{35}Cl_2$: 334.1004; found 334.0984.

DCl-Addition to 13: The addition of DCl to **13** was carried out analogously to the HCl addition. After chromatography of the crude product on silica gel with chloroform/methanol (30:1, v/v) as eluent a mixture of **14-d$_2$** and **15-d$_2$** (298 mg, 0.88 mmol, 58.4%) was obtained. Further chromatography of the mixture was achieved on silica gel with cyclohexane/ethyl acetate (3:1, v/v) as eluent obtaining pure **14-d$_2$** (136 mg, 0.40 mmol, 26.7%) and **15-d$_2$** (62 mg, 0.18 mmol, 12.2%).

Analytical Data for 4,9-Dichloro-5,10-dideuterio-2,7-diisopropyl-1,2,3,6,7,8-hexahydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (14-d$_2$): Yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.68–3.64 (m, 2 H, CH_2, dihydropyrrole), 3.50–3.45 (m, 4 H, CH_2, dihydropyrrole), 3.40–3.37 (m, 2 H, CH_2, dihydropyrrole), 2.62 (hept, ^3J = 6.3 Hz, 2 H, NC*H*, isopropyl), 1.07 (d, ^3J = 6.3 Hz, 12 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.9, 136.8, 131.6, 61.8, 60.4, 54.9, 22.3 ppm. MS (EI): *m*/*z* (%) = 342 (40) [M$^+$Cl^{37}Cl^{37}], 341 (19), 340 (52) [M$^+$Cl^{37}Cl^{35}], 339 (11), 338 (10) [M$^+$Cl^{35}Cl^{35}], 327 (62), 325 (100), 323 (10), 305 (49), 303 (45).

Analytical Data for 4,9-Dichloro-5,10-dideuterio-2,7-diisopropyl-1,2,3,7-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (15-d$_2$): Yellow wax-like solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.67 (d, ^4J = 2.45 Hz, 1 H, C*H*pyrrole), 6.28 (d, ^4J = 2.45 Hz, 1 H, C*H*, pyrrole), 4.08 [hept, ^3J = 6.7 Hz, 1 H, NC*H*, isopropyl(pyrrole)], 3.59 (t, ^4J = 3.8 Hz, 2 H, CH_2, dihydropyrrole), 3.42 (t, ^4J = 3.8 Hz, 2 H, CH_2, dihydropyrrole), 2.57 [hept, ^3J = 6.3 Hz, 1 H, NC*H*, isopropyl(dihydropyrrole)], 1.41 (d, ^3J = 6.7 Hz, 6 H, CH_3), 1.06 (d, ^3J = 6.3 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 138.0, 134.5, 131.5, 128.2, 122.5, 120.5, 119.6, 118.9, 62.6, 61.3, 55.0, 52.0, 24.4, 22.4 ppm. MS (EI): *m*/*z* (%) = 342 (40) [M$^+$Cl^{37}Cl^{37}], 341 (19), 340 (52) [M$^+$Cl^{37}Cl^{35}], 339 (11), 338 (10) [M$^+$Cl^{35}Cl^{35}], 327 (62), 325 (100), 323 (10), 305 (49), 303 (45).

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[9] Colourless crystals, dimensions $0.7 \times 0.5 \times 0.2\ mm^3$, crystal system monoclinic, space group $P2_1/c$, $Z = 4$, $a = 12.536(6)$ Å, $b = 9.009(4)$ Å, $c = 16.044(8)$ Å, $\alpha = 90°$, $\beta = 102.29(3)°$, $\gamma = 90°$, $V = 1770.4(15)$ Å^3, $\rho = 1.265\ g/cm^3$, $T = 203(2)$ K, $\Theta_{max} = 25.01°$, radiation Mo-K_α, $\lambda = 0.71073$ Å, 0.3° ω-scans with scintillation area detector, 3123 reflections measured, 3123 unique, 2397 observed [$I > 2\sigma(I)$], intensities were corrected for Lorentz and polarization effects, an absorption correction was applied using psi-scans, $\mu = 0.365\ mm^{-1}$, $T_{min} = 0.885$ $T_{max} = 0.999$, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (6.12) software package,[13] 244 parameters refined, methyl hydrogen atoms were treated using appropriate riding models, the rest was refined isotropically, goodness of fit 1.027 for observed reflections, final residual values $R_1(F) = 0.042$, $wR(F^2) = 0.105$ for observed reflections, residual electron density –0.230 to 0.313 e Å^{-3}. CCDC-719401 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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