12,15-Dichloro[3.0]orthometacyclophane: A Highly Strained Biphenylophane

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Abstract: The title compound, **3**, in which two methylene groups of the parent compound **4** have been replaced by an ortho-substituted benzene ring, has been synthesized. It exists exclusively in the endo-conformation, in contrast to **4** for which the exo-conformation is preferred. High-level density functional calculations are presented for both compounds. They show that the endo-conformation of **3** is favored over the exo-conformation by 3.3 kcal mol^{-1}. The incorporation of a benzene ring in the bridge leads to a substantial increase of the strain energy (ΔSE = SE (**3**) − SE (**4**) = 4.7 kcal mol^{-1}), making **3** the, thus far, smallest and most reactive, yet isolable, [*n*]metacyclophane.

Introduction

The remarkable chemical and physical properties of strained cyclophanes continue to fascinate many chemists.[1] In the [*n*]-metacyclophane series, the borderline for stability at room temperature has been found between [4]metacyclophane, which could only be intercepted as a Diels−Alder adduct,[2] and [5]-metacyclophane, which is an isolable compound.[3] In our quest for even more strained, yet isolable, [*n*]metacyclophanes, we are exploring the possibility of increasing the strain of a [5]-metacyclophane by shortening the bridge. This can be achieved by the introduction of sp^2-hybridized carbon atoms or by incorporation of heteroatoms such as nitrogen or oxygen. These strategies have successfully been applied in the synthesis of the mono Dewar benzene isomer of [1.1]metacyclophane[4] and of 3-aza[5]metacyclophane.[5]

In contrast to the [*n*]paracyclophane series,[6] only two small [*n*]metacyclophanes ($n = 6$) with a benzene ring incorporated in the bridge are known: a terphenylophane **1**, reported as early as 1969 by Vögtle,[7] and [2.2]orthometacyclophane (**2**), described by Hopf et al.[8] In this paper, we report the synthesis, unusual structure, and reactivity of the dichloro-substituted [3.0]orthometacyclophane **3**; as an analogue of 8,11-dichloro[5]metacyclophane (**4**), it is the first [5]metacyclophane benzoannelated at the bridge and also the, thus far, smallest representative of a new type of biphenylophanes (Figure 1).

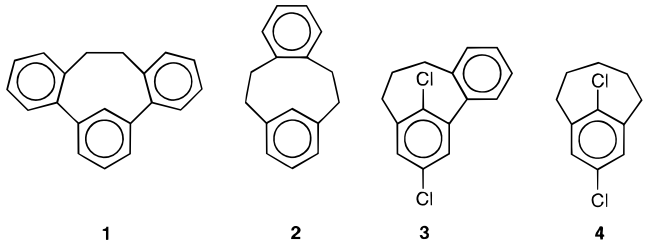

Figure 1.

Results and Discussion

The synthesis of the title compound is outlined in Scheme 1 and in general follows the strategy used in our preparation of other [5]metacyclophanes.[9] Benzosuberon (**5**) was converted to the air-sensitive and thermally unstable diene **6** by a four-step procedure involving successively a Mannich reaction, Wittig reaction, methylation, and Hoffmann degradation in an overall yield of 17%. Reaction of **6** with chloroform/*t*-BuOK in pentane afforded a 3:2 mixture of the dichlorocarbene adducts **7a** and **7b**. This mixture was subjected to flash vacuum thermolysis (FVT) to give **8** as the sole product. A second dichlorocarbene addition (Makosza conditions, $CHCl_3$/NaOH/PTC (phase transfer catalyst)) yielded the propellane **9**. Treatment of **9** with *t*-BuOK in DMSO resulted in the formation of the target compound **3**. After purification by column chromatography, **3** was obtained as a pale yellow oil in 87% yield, which crystallized on standing at 0 °C (mp ∼25 °C).

The ^1H NMR spectrum (400 MHz, $CDCl_3$, 298 K) indicated that **3** occurs as one conformer only. This is in sharp contrast to **4** and related compounds in which an equilibrium favoring the exo-conformer (the previously so-called A-conformer[9]) over the endo-conformer (the so-called B-conformer) was observed.[10] The eight-membered ring formed by the pentamethylene bridge and the three carbon atoms of the aromatic ring between the

(1) (a) Bodwell, G. J. *Angew. Chem.* **1996**, *108*, 2221; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2085. (b) Okuyama, M.; Tsuji, T. *Angew. Chem.* **1997**, *109*, 1157; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1085.

(2) Kostermans, G. B. M.; Van Dansik, P.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 7887.

(3) Van Straten, J. W.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667.

(4) Wijsman, G. W.; Van Es, D. S.; De Wolf, W. H.; Bickelhaupt, F. *Angew. Chem.* **1993**, *105*, 739. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 726. (5) Van Es, D. S.; Egberts, A.; Nkrumah, S.; De Nijs, H.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1997**, *119*, 615.

(6) Tobe, Y.; Kawaguchi, M.; Kakiuchi, K.; Naemura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1173.

(7) Vögtle, F. *Chem. Ber.* **1969**, *102*, 1449.

(8) Bodwell, G.; Ernst, L.; Haenel, M. W.; Hopf, H. *Angew. Chem.* **1989**, *101*, 509; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 455.

(9) Bickelhaupt, F.; De Wolf, W. H. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Ltd: London, 1993; Vol. 3, p 185.

(10) The only other exception is the mono Dewar benzene isomer of [1.1]metacyclophane.[4]

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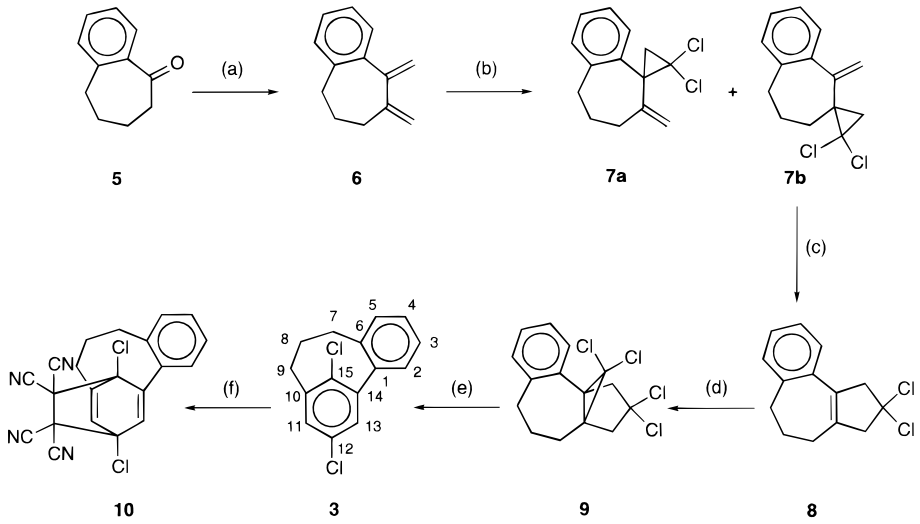
Scheme 1[a]



[a] Key: (a) 4 steps (see text); (b) $CHCl_3$, *t*-BuOK, pentane, 18 h, rt; (c) 2×10^{-3} mbar, 495 °C; (d) $CHCl_3$, 50% NaOH, PTC, 18 h, rt; (e) *t*-BuOK, DMSO, 3 h, rt; (f) tetracyanoethene, $CDCl_3$, 1 h, rt.

Table 1. Calculated Geometrical Parameters of **4**[a]

bond lengths (Å)			bond angles (deg)			distortion angles (deg)		
	exo	endo		exo	endo		exo	endo
C(1)−C(2)	1.576 [1.569][b]	1.591	C(10)−C(1)−C(2)	105.9 [104.7]	109.0	α	28.2 [26.8]	27.2
C(2)−C(3)	1.574 [1.566]	1.577	C(1)−C(2)−C(3)	121.3 [121.9]	120.4	*β*	47.4 [48.0]	45.9
C(1)−C(10)	1.511 [1.506]	1.510	C(2)−C(3)−C(4)	122.6 [122.2]	120.4	*γ*	12.2 [12.0]	11.0

[a] See ref 13. [b] X-ray values given in brackets.[14]

bridge possesses a chair−chair conformation in the exo-conformer, while this ring adopts a chair−boat conformation in the endo-conformer. A distinctive feature of the ^{1}H NMR spectrum of **3** is the high-field signal at 0.36 ppm which is assigned to H(7.1), one of the benzylic protons at the central C(7) (see Scheme 1); H(7.2), the other proton of this CH_2 group, appears at 2.18 ppm. This large upfield shift is caused by the location of H(7.1) in the shielding cone of the meta-bridged aromatic ring. This is corroborated by NOE experiments which indicate a strong interaction between H(7.1) and the aromatic protons H(11) and H(13). These results imply that **3** exists exclusively as the endo-conformer in which C(7) points toward the cyclophane benzene ring. The aromatic protons H(11) and H(13) of **3** appear as singlets around 6.9 ppm, indicating that the ring current is essentially intact, despite of the severe distortion of the aromatic ring.

Also of interest is the UV spectrum of **3** (λ_{max} (ϵ) = 332 nm (900), 276 nm (5200)), which, apart from a very minor red shift and the slightly increased extinction coefficients, is very similar to that of **4** (λ_{max} (ϵ) = 325 nm (200). One may conclude that there is little biphenyl-type conjugation between the two benzene rings.

Compared to **4**, **3** shows a strongly enhanced reactivity toward dienophiles. ^{1}H NMR experiments indicate that the Diels−Alder reaction of **3** with 1.1 equiv of a dienophile such as TCNE (tetracyanoethene) to form the adduct **10** proceeds roughly 20 times faster than the analogous reaction of **4**, making **3** one of the most reactive [5]metacyclophanes.[9]

To analyze the factors determining the stability of the two conformers of **3**, they were investigated by calculational techniques, ranging from molecular mechanics to density functional methods. In all cases, and in agreement with the experimental results, it was found that the endo-conformer is favored by 5.0 (MM2[11]), 4.0 (PM3[12]), and 3.3 kcal mol^{-1} (DF[13]), respectively. In the case of **4**, it is the exo-conformer, which is favored by 0.5 (MM2), 0.8 (PM3), and 1.8 kcal mol^{-1} (DF), respectively. The DF calculated structural parameters of **4-exo** are in very good agreement with the X-ray data (Table 1);[14] all calculated bond lengths deviate less than 0.01 Å from the experimental values (Figure 2). For the bond angles and distortion angles, the largest discrepancy is found for the distortion angle α (1.4°).

Unfortunately, we did not succeed in obtaining crystals of **3**, which were suitable for an X-ray structure determination. However, the high accuracy of the DF calculations in the case of **4** suggests that this also applies for other [*n*]metacyclophanes.

From the DF-optimized geometry of **3-endo** (Table 2), we immediately notice that the bond C(1)−C(6) (1.434 Å) in the ortho-bridged benzene ring is considerably elongated (Figure 3). Surprisingly, this does not effect the other C−C bond lengths in this ring; they have normal values (1.395−1.402 Å). The bonds C(7)−C(8) (1.581 Å) and C(8)−C(9) (1.583 Å) are rather long, too. Despite the fact that the bridge length in **3-endo** (Σ *d*(C−C) = 9.157 Å) is considerably shortened compared to **4-exo** (9.322 Å; exptl 9.282 Å), the total bending of the meta-bridged benzene ring (α + *γ*) is nearly equal: 41.2° for **3-endo**

(11) MM2 calculations were performed using CSC Chem3D Plus 3.1.1, Serial Number 460045, licensed to the Vrije Universiteit.

(12) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. The calculations were performed using MOPAC 93 (QCPE no. 445).

(13) (a) The density functional calculations were performed using the Amsterdam Density Functional (ADF) program, version 2.3.3, developed by Baerends et al. (b) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (c) Te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84. (d) Fonseca Guerra, C.; Visser, O.; Snijders, J. G.; Te Velde, G.; Baerends E. J. In *Methods and Techniques for Computational Chemistry*; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, Italy, 1995; p 305.

(14) Jenneskens, L. W.; Klamer, J. C.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F.; Stam, C. H. *Angew. Chem.* **1984**, *96*, 236; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 238.

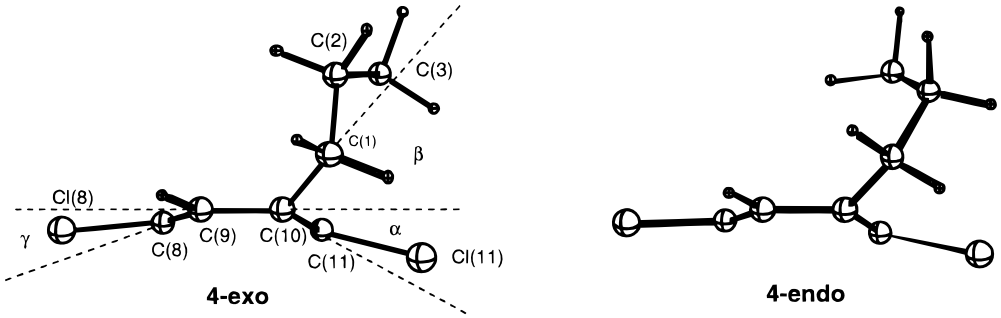


Figure 2. Density functional optimized geometries of **4**.

Table 2. Calculated Geometrical Parameters of **3**[a]

bond lengths (Å)			bond angles (deg)			dihedral angles (deg)		
	exo	endo		exo	endo		exo	endo
C(1)−C(14)	1.482	1.492	C(6)−C(1)−C(14)	117.6	113.6	α[b,c]	30.0	28.6
C(1)−C(6)	1.436	1.434	C(1)−C(6)−C(7)	129.6	124.4	β	47.9	45.4
C(6)−C(7)	1.557	1.550	C(6)−C(7)−C(8)	127.6	121.2	γ	12.6	12.6
C(7)−C(8)	1.577	1.581	C(7)−C(8)−C(9)	120.1	118.1	C(2)−C(1)−C(14)−C(13)	56.4	82.9
C(8)−C(9)	1.575	1.583	C(8)−C(9)−C(10)	104.8	109.2	C(2)−C(1)−C(14)−C(15)	32.8	55.9
C(9)−C(10)	1.514	1.517				C(6)−C(1)−C(14)−C(13)	65.8	98.6
						C(6)−C(1)−C(14)−C(15)	42.2	54.4

[a] See ref 13. [b] For the definition of the distortion angles α, β, and γ, see Table 1. [c] The distortion angles of **3** are the averages of two dihedral angles, since **3** is sligthly distorted from C_s symmetry.

Table 3. Density Functional Calculated HOMO−LUMO Energies of **3** and **4**[a,b]

	3−exo	3−endo	4−exo	4−endo
HOMO	−5.655	−5.736	−5.610	−5.704
LUMO	−2.529	−2.506	−2.244	−2.232
Δ (LUMO−HOMO)	3.126	3.230	3.366	3.472

[a] Reference 13. [b] Energies are in eV.

and 40.4° (exptl 38.8°) for **4-exo**. A comparison between the DF-optimized geometries of **3** (Table 2) shows that the most striking differences occur at some of the bond angles in the bridge. In **3-endo**, these angles deviate less from their ideal values than in **3-exo**, which suggests that angle strain is the origin of the lower energy of the former. Indeed, a detailed MM2 analysis confirms that the difference in bond angle strain (4.1 kcal mol^{-1}) comprises the major part of the total energy difference of 5.0 kcal mol^{-1}. The large dihedral angle between the two benzene rings in **3-endo** (which has four values because of the distortion of the meta-bridged ring of 54.4°, 55.9°, 82.9°, and 98.6°, respectively), offers an explanation for the low degree of conjugation which was evident from the UV spectrum. In **3-exo**, these values are much smaller (32.8−65.8°); obviously, the stabilization to be gained from conjugation between the two benzene rings in the exo-conformation is smaller than the increased strain energy.

For the strain energy (SE) of **3-endo**, a value of 48.0 kcal mol^{-1} was derived.[15,16] Although it is larger than that for **4-exo** (43.3 kcal mol^{-1}), the difference between these values (ΔSE = 4.7 kcal mol^{-1}) is less than we had anticipated considering the substantial decrease of the bridge length (9.157 Å versus 9.322 Å, vide supra). Obviously, an *increase* of the strain due to the shorter bond lengths is in part compensated by a *decrease* due to the larger angles at the sp^2-hybridized carbon atoms of the benzene ring in the bridge and to the reduction of torsial interactions. In this context, it is of interest to point out that 3-aza[5]metacyclophane[5] was found to be less strained than **4**, although the bridge length (9.093 Å) is even shorter than in **3**. In this case, too, the reduced strain energy was ascribed to a reduction of the angular as well as the torsial strain. To determine the distribution of the extra strain energy (4.7 kcal mol^{-1}) in **3** between bridge and bent benzene ring, a single-point DF calculation was performed on the benzene ring which had been frozen in the conformation calculated for **3**. The hydrogen atoms at the bridgehead carbon atoms were placed at a distance of 1.09 Å. As anticipated, the benzene rings in **4-endo** and **3-exo** were found to be almost equally strained (ΔE is less than 1 kcal mol^{-1}). Thus, we may conclude that the extra strain energy in **3** relative to **4** is exclusively residing in the bridge.

Besides strain, electronic effects need to be considered as causing factors for the increased reactivity of **3**. According to the frontier molecular orbitals (FMO) theory, the Diels−Alder reaction of a [5]metacyclophane is mainly determined by the interaction of the HOMO of the cyclophane and the LUMO of the dienophile; when the HOMO of the cyclophane is raised, the HOMO−LUMO gap becomes smaller resulting in a lower activation barrier. As the HOMO energy of **3-endo** (−5.704 eV) is even lower than that of **4-exo** (−5.655 eV), electronic effects may be ruled out. We must conclude that the increased reactivity of **3** compared to **4** originates from the increased strain energy of **3**.

Experimental Section

General Procedures. ^{1}H NMR Spectra were recorded at 400.132 MHz (Bruker MSL 400). ^{13}C NMR Spectra were recorded at 100.32 MHz (Bruker MSL 400). All NMR samples were measured in $CDCl_3$ with $CHCl_3$ as a reference (δ = 7.27 ppm). The assignment of NMR signals is based on HH-COSY, CH correlation, and NOE experiments. HRMS spectra were recorded on a Finnigan MAT-90 mass spectrometer operating at an ionization potential of 70 eV. GC-MS spectra were recorded on a Hewlett-Packard 5971 series mass selective detector. Sample separation for GC-MS was performed on a Hewlett-Packard 5890 series II gas chromatograph fitted with an HP-1 column (50 m,

(15) The total strain energy (SE(total)) was calculated using the equation: SE(total) = $\Delta H°_f$ (PM3) − $\Delta H°_f$ (Benson's group increments[16]).

(16) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

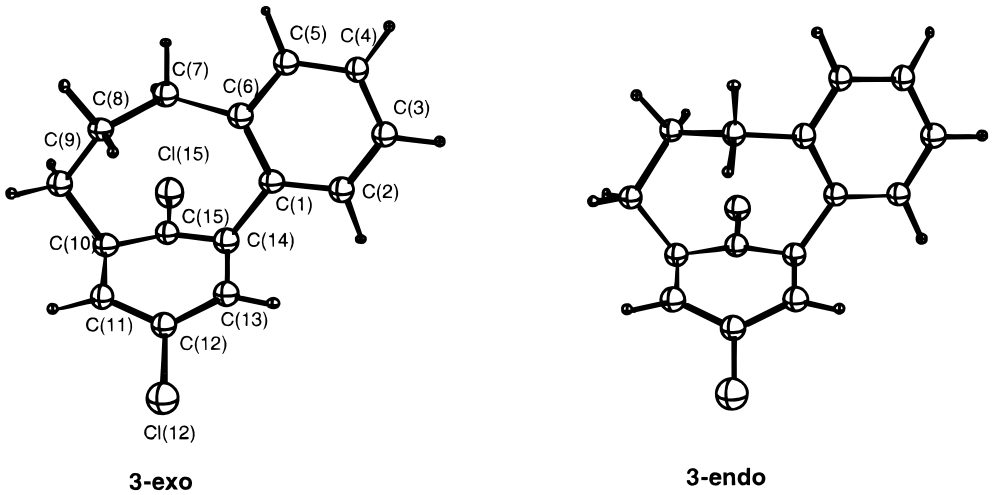


Figure 3. Density functional optimized geometries of **3**.

0.2 mm i.d., 0.33 mm film thickness). UV spectra were recorded on a Cary 1 Bio UV−vis spectrophotometer. Aluminum oxide used: Merck, aluminum oxide 90, standardized (activity II−III), 0.063−0.200 mm. Silica gel used: Riedel-de Haën, silica gel S, 0.2−0.5 mm. All chemicals used were commercially available from either Acros or Aldrich Chemicals.

6-(Dimethylamino)methyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (I). The preparation of **I** from benzosuberon (**5**) was achieved by procedures analogous to those reported for similar compounds.[9] For **I**: yield 42.15 g (0.194 mol, 65%) as a slightly yellow oil; ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.62 (dd, J = 7.7 Hz, 1.5 Hz, 1H), 7.34 (dt, J = 7.5 Hz, 1.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 3.03 (m, 1H), 2.96 (m, 2H), 2.61 (AB-system, δ_A = 2.82 (dd, J_{AB} = −12.4 Hz, 6.7 Hz, 1H), δ_B = 2.40 (dd, J_{AB} = −12.4 Hz, 6.6 Hz, 1H)), 2.17 (s, 6H), 2.06 (m, 2H), 1.66 (m, 1H), 1.55 (m, 1H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 208.4 (s), 141.8 (m), 140.0 (m), 131.0 (m), 129.8 (m), 128.3 (m), 126.3 (m), 60.0 (t, J = 135 Hz), 48.3 (m), 45.8 (m, J = 133 Hz, 4.9 Hz, 2C), 33.8 (t, J = 127 Hz), 28.9 (t, J = 131 Hz), 25.2 (t, J = 128 Hz); MS (70 eV) m/z 217 (M^+ ($C_{14}H_{19}NO$), 2.5), 128 (2.4), 115 (3.3), 91 (3.9), 77 (2.1), 58 (100); HRMS calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1466 ± 0.0005. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.37; H, 8.82; N, 6.44. Found: C, 77.30; H, 8.72; N, 5.91.

Dimethyl(5-methylene-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-6-ylmethyl)amine (II). To a mechanically stirred suspension of methyltriphenylphosphonium iodide (84.4 g, 209 mmol) in dry THF (400 mL) under nitrogen at 0 °C were added *t*-BuOK (23.4 g, 209 mmol) and 18-crown-6 (50 mg). The resulting bright yellow suspension was stirred for 1 h at 0 °C. Compound **I** (41.2 g, 190 mmol) was then added dropwise during 2 h at 0 °C. The mixture was warmed to room temperature and stirred for an additional 64 h. Water was then added, and the precipitated triphenylphosphine oxide was removed by suction filtration. The filtrate was concentrated in vacuo, and the remaining brown oil was dissolved in diethyl ether and poured into a solution of 2 M HCl. The layers were separated, and the organic layer was extracted with a 2 M HCl solution. The combined aqueous layers were washed with ether (3×). Aqueous NaOH (10%) was then added to obtain pH ≈ 12, and the water layer was extracted with ether (3×). The combined ether layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure, yielding **II** (16.3 g, 76 mmol, 40%) as a yellow oil: ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.15 (m, 3H), 7.08 (m, 1H), 5.15 (dd, J = 1.95 Hz, 0.8 Hz, 1H), 4.99 (d, J = 1.95 Hz, 1H), 2.74 (m, 2H), 2.62 (m, 1H), 2.15 (s, 6H), 2.15 (m, 2H), 1.92 (m, 1H), 1.75 (m, 3H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 154.8 (s), 143.2 (m), 139.8 (m), 128.9 (d), 128.6 (d), 127.0 (d), 125.9 (d), 113.1 (dt, J = 156 Hz, 5.3 Hz), 62.9 (t, J = 131 Hz), 45.8 (q, J = 133 Hz), 42.5 (d, J = 124 Hz), 36.1 (t, J = 126 Hz), 34.8 (t, J = 128 Hz), 24.2 (t, J = 126 Hz); MS (70 eV) m/z 215 (M^+ ($C_{15}H_{21}N$), 0.9), 141 (2.3), 128 (3.4), 115 (3.0), 58 (100); HRMS calcd for $C_{15}H_{21}N$ 215.1674, found 215.1677 ± 0.0007.

Trimethyl(5-methylene-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-6-ylmethyl)ammonium iodide (III). To a stirred solution of **II** (10.0 g, 46.5 mmol) in dry diethyl ether (75 mL) under nitrogen at 0 °C was added dropwise methyl iodide (19.5 g, 140 mmol) during 2 h. After 18 h of allowing the solution to stand at room temperature, the white precipitate was filtered off, washed with diethyl ether, and dried in vacuo over P_2O_5, yielding **III** (13.8 g, 38.8 mmol, 84%) as a white powder: ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.14 (m, 3H), 7.00 (m, 1H), 5.51 (s, 1H), 5.15 (s, 1H), 3.82 (m, 1H), 3.81 (s, 9H), 3.57 (AB-system, δ_A = 3.81 (d, J_{AB} = −11.8 Hz, 1H), δ_B = 3.32 (d, J_{AB} = −11.8 Hz, 1H)), 2.73 (t, J = 4.6 Hz, 2H), 1.85 (m, 4H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 151.6 (s), 139.7 (s, 2C), 129.9 (d), 129.2 (d), 128.2 (d), 126.7 (d), 117.0 (t), 69.1 (t), 54.1 (q, 3C), 39.9 (d), 37.9 (t), 35.9 (t), 22.9 (t).

5,6-Dimethylene-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (6). A solution of **III** (13.5 g, 37.9 mmol) in demiwater (200 mL) was eluted over an ion-exchange column conditioned with a 2 M NaOH solution. The eluate was carefully (T < 40 °C) concentrated at reduced pressure. The syrupy residue was transferred to a pyrolysis flask and gradually heated to 80 °C under vacuum (8 mm). Pentane was added to the pyrolysate, and the layers were separated. The organic layer was washed sequentially with 1 M HCl (2×), water (2×), and brine (1×), dried ($MgSO_4$), and concentrated under reduced pressure to yield **6** (4.19 g, 24.6 mmol, 65%) as a colorless oil: ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.39 (m, 1H), 7.25 (m, 2H), 7.10 (m, 1H), 5.67 (dt, J = 1.33 Hz, ≤0.5 Hz, 1H), 5.50 (dt, J = 1.68 Hz, ≤0.5 Hz, 1H), 5.18 (dt, J = 1.33 Hz, ≤0.5 Hz, 1H), 4.89 (dt, J = 1.68 Hz, ≤0.5 Hz, 1H), 2.75 (t, J = 6.7 Hz, 2H), 2.21 (t, J = 6.7 Hz, 2H), 1.84 (tt, J = 6.6 Hz, 6.6 Hz, 2H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 149.8 (m), 146.7 (m), 140.1 (m), 138.8 (m), 128.6 (m), 128.2 (m), 128.1 (m), 126.7 (m), 112.0 (t, J = 158 Hz), 109.7 (tt, J = 157 Hz, 6.0 Hz), 32.3 (t, J = 132 Hz), 31.4 (t, J = 128 Hz), 28.7 (t, J = 129 Hz); MS (70 eV) m/z 170 (M^+ ($C_{13}H_{14}$), 86.2), 155 (46.7), 141 (100), 128 (48.4), 115 (54.7); HRMS calcd for $C_{13}H_{14}$ 170.1095, found 170.1096 ± 0.0005.

6,7,8,9-Tetrahydro-6-methylenespiro-2′,2′-dichlorospiro[5*H*-benzocycloheptene-5,1′-cyclopropane] (7a) and 5,7,8,9-Tetrahydro-5-methylenespiro-2′,2′-dichlorospiro[6*H*-benzocyclohepten-6,1′-cyclopropane] (7b). To a solution of **6** (1.36 g, 8.0 mmol) and $CHCl_3$ (4.30 g, 36.0 mmol) in dry pentane (40 mL) was added under nitrogen at 0 °C *t*-BuOK (3.58 g, 32.0 mmol) during a period of 1.5 h. After 1 h of stirring at room temperature, $CHCl_3$ (2.15 g, 18.0 mmol) was added, and the reaction mixture was cooled again to 0 °C. *t*-BuOK (1.79 g, 16.0 mmol) was then added during a period of 1.5 h. After 18 h of stirring at room temperature, the resulting brown reaction mixture was poured into ice water. The water layer was extracted with pentane (3×), and the combined organic layers were washed with water (3×), brine (1×), dried ($MgSO_4$), and concentrated at reduced pressure. A yellow oil remained, which after column chromatography (silica gel, pentane) afforded a 3:2 mixture of **7a** and **7b** (1.60 g, 6.4 mmol, 80%)

as a colorless oil. For **7a**: ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.18 (m, 4H), 5.02 (m, 1H), 4.96 (m, 1H), 3.04 (AB-system, δ_A = 3.25 (ddd, J_{AB} = −13.1 Hz, 13.3 Hz, 1.8 Hz, 1H), δ_B = 2.84 (m, J_{AB} = −13.1 Hz, 6.2 Hz, 1H)), 2.84 (AB-system, δ_A = 3.10 (m, J_{AB} = −14 Hz, 1H), δ_B = 2.58 (dt, J_{AB} = −14 Hz, 7.3 Hz, 1H)), 2.15 (AB-system, δ_A = 2.26 (d, J_{AB} = 7.3 Hz, 1H), δ_B = 2.04 (d, J_{AB} = 7.3 Hz, 1H)), 1.83 (AB-system, δ_A = 2.14 (m, 1H), δ_B = 1.52 (m, 1H)); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 147.2 (s), 143.8 (s), 141.2 (s), 129.0 (d), 127.8 (d), 127.0 (d), 126.4 (d), 115.6 (t), 64.0 (s), 45.6 (s), 37.6 (t), 34.7 (t), 31.9 (t), 28.2 (t); MS (70 eV) *m*/*z* 252 (M^+ ($C_{14}H_{14}{}^{35}Cl_2$), 32.8), 217 (12.8), 181 (100), 165 (34.0), 152 (15.7), 141 (21.1); HRMS calcd for $C_{14}H_{14}{}^{35}Cl_2$ 252.0473, found 252.0474 ± 0.0006.

For **7b** ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.18 (m, 4H), 5.34 (d, J = 1.3 Hz, 1H), 5.32 (d, J = 1.3 Hz, 1H), 2.90 (m, 2H), 2.08 (AB-system, δ_A = 2.16 (m, 1H), δ_B = 2.0 (m, 1H)), 1.95 (m, 2H), 1.60 (AB-system, δ_A = 1.73 (d, J_{AB} = 7.0 Hz, 1H), δ_B = 1.47 (d, J_{AB} = 7.0 Hz, 1H)); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 150.5 (s), 139.7 (s), 138.3 (s), 130.1 (d), 128.9 (d), 127.3 (d), 125.8 (d), 118.5 (t), 66.3 (s), 39.6 (s), 39.8 (t), 35.6 (t), 33.3 (t), 25.7 (t); MS (70 eV) *m*/*z* 252 (M^+ ($C_{14}H_{14}{}^{35}Cl_2$), 6.3), 217 (10.6), 181 (100), 165 (26.6), 153 (17.7), 141 (38.4), 128 (30.0), 115 (23.2); HRMS calcd for $C_{14}H_{14}{}^{35}Cl_2$ 252.0473, found 252.0474 ± 0.0006.

2,2-Dichloro-1,2,3,4,5,6-hexahydrobenzo[*e*]azulene (8). The mixture of **7a** and **7b** was subjected to flash vacuum thermolysis (495 °C, 2 × 10^{-3} mbar, preheating zone at 100 °C). The pyrolysate was collected on a cold trap (acetone/dry ice) and purified by column chromatography (silica gel, pentane) to yield **8** (1.26 g, 4.98 mmol, 87%) as a colorless oil: ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.15 (m, 4H), 3.76 (t, J = 2.6 Hz, 2H), 3.44 (bs, 2H), 2.84 (m, 2H), 2.38 (m, 2H), 1.93 (m, 2H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 142.3 (s), 138.0 (s), 133.9 (s), 130.9 (s), 129.0 (d), 127.0 (d), 126.9 (d), 125.9 (d), 87.7 (s), 61.4 (t), 59.4 (t), 35.6 (t), 32.6 (t), 26.1 (t); MS (70 eV) *m*/*z* 252 (M^+ ($C_{14}H_{14}{}^{35}Cl_2$), 44.0), 217 (21.7), 181 (100), 165 (26.8), 141 (24.9); HRMS calcd for $C_{14}H_{14}{}^{35}Cl_2$ 252.0473, found 252.0474 ± 0.0005.

3,3,15,15-Tetrachloro[11,5.01,5][8]orthocyclophane (9).[17] To a solution of **8** (1.15 g, 4.55 mmol), 0.01 g of *N*,*N*,*N*,*N*-cetyltrimethylammonium bromide and 2 drops of ethanol in $CHCl_3$ (9.8 g, 82 mmol) was added under cooling (0 °C) 50% aqueous NaOH (2.74 g, 68.3 mmol) over 15 min. This brown two-phase system was vigorously stirred during 18 h at room temperature and 2 h at 45 °C. After cooling to room temperature, the reaction mixture was poured into ice water and CH_2Cl_2 was added. The layers were separated, and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed with water (2×), brine (1×), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, pentane), followed by crystallization from ethanol to yield **9** (1.01 g, 2.41 mmol, 53%) as colorless crystals (mp 88.6−89.2 °C): ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.22 (m, 3H), 7.10 (dd, J = 6.7 Hz, 2.2 Hz, 1H), 3.48 (AB-system, δ_A = 3.54 (d, J_{AB} = −16.0 Hz, 1H), δ_B = 3.41 (dd, J_{AB} = −16.0 Hz, 1.4 Hz, 1H)), 3.45 (m, 1H), 3.31 (AB-system, δ_A = 3.32 (d, J_{AB} = −16.0 Hz, 1H), δ_B = 3.30 (dd, J_{AB} = −16.0 Hz, 1.4 Hz, 1H)), 2.64 (m, 1H), 2.08 (m, 1H), 2.04 (m, 1H), 1.93 (m, 1H), 1.79 (m, 1H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 140.6 (s), 135.3 (s), 130.9 (dd, J = 156.8 Hz, 6.2 Hz), 129.9 (d, J = 157.2 Hz), 128.0 (dd, J = 159.9 Hz, 7.3 Hz), 126.4 (dd, J = 161.1 Hz, 7.9 Hz), 91.7 (s), 76.2 (s), 60.7 (t, J = 137.6 Hz), 59.1 (t, J = 136.0 Hz), 47.3 (s), 44.2 (s), 31.7 (t, J = 126.7 Hz), 28.2 (t, J = 131.0 Hz), 23.2 (t, J = 127.8 Hz); MS (70 eV) *m*/*z* 334 (M^+ ($C_{15}H_{14}{}^{35}Cl_4$), 28.4), 299 (24.8), 263 (49.0), 215 (88.8), 191 (37.7), 179 (100), 165 (64.8); HRMS calcd for $C_{15}H_{14}{}^{35}Cl_4$ 333.9850, found 333.9853 ± 0.0006. Anal. Calcd for $C_{15}H_{14}Cl_4$: C, 53.61; H, 4.20; Cl, 42.19. Found: C, 53.32; H, 4.20; Cl, 42.20.

(17) Concerning the nomenclature, see: Vögtle, F.; Neumann, P. *Tetrahedron* **1970**, *26*, 5847.

12,15-Dichloro[3.0]orthometacyclophane (3)[17]. To a stirred solution of **9** (250 mg, 0.74 mmol) in dry DMSO (35 mL) under nitrogen was added *t*-BuOK (208 mg, 1.86 mmol) over 1.5 h at room temperature. After another 1.5 h of stirring, the dark brown reaction mixture was poured into ice water and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (3×), brine (1×), dried ($MgSO_4$), and concentrated under reduced pressure. The resulting brown oil was purified by column chromatography (alumina, pentane), yielding **3** (170 mg, 0.65 mmol, 87%) as a slightly yellow oil, which crystallized on standing at 0 °C (mp ∼25 °C) ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.46 (dd, J = 7.2 Hz, 1.7 Hz, 1H), 7.26 (dt, J = 7.2 Hz, 1.5 Hz, 1H), 7.22 (dt, J = 7.5 Hz, 1.7 Hz, 1H), 7.05 (dd, J = 7.4 Hz, 1.5 Hz, 1H), 6.945 (s, 1H), 6.943 (s, 1H), 3.42 (dd, J = −13.1 Hz, 9.2 Hz, 1H), 2.83 (m, 1H), 2.20 (m, 1H), 2.18 (m, 1H), 2.12 (m, 1H), 0.36 (dd, J = −14.6 Hz, 9.5 Hz 1H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 149.4 (m), 147.7 (s), 147.4 (m), 146.9 (bs), 143.4 (bs), 132.7 (d, J = 158 Hz), 131.2 (dd, J = 3.6 Hz, 3.6 Hz), 128.5 (dd, J = 160.8 Hz, 7.9 Hz), 126.6 (d, J = 168.5 Hz), 126.1 (dd, J = 162.4 Hz, 7.7 Hz), 124.4 (dd, J = 170.7 Hz, 6.5 Hz), 124.0 (dd, J = 162.6 Hz, 7.9 Hz), 31.6 (t, J = 134.8 Hz), 31.5 (t, J = 126.8 Hz), 28.5 (t, J = 131.9 Hz); MS (70 eV) *m*/*z* 262 (M^+ ($C_{15}H_{12}{}^{35}Cl_2$), 36.2), 227 (82.6), 212 (35.9), 192 (100), 165 (20.2); HRMS calcd for $C_{15}H_{12}{}^{35}Cl_2$ 262.0316, found 262.0316 ± 0.0005; UV (cyclohexane) λ_{max} (ϵ) = 332 nm (900), 276 nm (5200), 252 nm (12 000), 217 nm (17 000) Anal. Calcd for $C_{15}H_{12}Cl_2$: C, 68.46; H, 4.60; Cl, 26.94. Found: C, 68.60; H, 4.71; Cl, 26.3.

Diels−Alder Reactions. The reactions were performed in a NMR tube containing approximately 0.1 mmol of **3** dissolved in 0.5 mL of $CDCl_3$. To this solution was added 1.1 mol equiv of the dienophile. The reactions were monitored by ^{1}H NMR spectroscopy. Evaporation of the solvent provided the pure adduct as a white solid. The yield was quantitative, according to ^{1}H NMR and analytical GLC.

TCNE Adduct (10): mp = 185 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K) δ 7.36 (ddd, J = 7.8 Hz, 7.5 Hz, 1.3 Hz, 1H), 7.31 (ddd, J = 7.6 Hz, 7.5 Hz, 1.2 Hz, 1H), 7.26 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.22 (dd, J = 7.6 Hz, 1.3 Hz, 1H), 2.88 (dd, J = −13.6 Hz, 8.4 Hz, 1H), 2.79 (dd, J = −14.1 Hz, 11.0 Hz, 1H), 2.53 (ddd, J = −13.6 Hz, 9.5 Hz, 9.2 Hz, 1H), 2.31 (ddd, J = −14.2 Hz, 11.0 Hz, 9.2 Hz, 1H), 2.11 (dddd, J = −14.2 Hz, 9.5 Hz, 8.4 Hz, 8.4 Hz, 1H), 2.08 (dd, J = −14.1 Hz, 8.4 Hz, 1H); ^{13}C NMR (100.64 MHz, $CDCl_3$, 298 K) δ 154.6 (s), 153.1 (s), 141.5 (s), 135.3 (d), 135.2 (d), 133.7 (s), 131.3 (d, J = 158 Hz), 129.9 (d, J = 161 Hz), 126.7 (d, J = 163 Hz), 125.8 (d, J = 162 Hz), 110.27 (s), 110.23 (s), 110.16 (s), 109.82 (s), 77.5 (s), 66.8 (s), 55.2 (s), 53.4 (s), 30.8 (t), 29.7 (t), 24.4 (t, J = 131 Hz); MS (70 eV) *m*/*z* 390 (M^+ ($C_{21}H_{12}N_4{}^{35}Cl_2$), 1.7), 355 (2.5), 262 (32.4), 227 (81.9), 192 (100), 165 (29.6), 128 (74.1); HRMS calcd for $C_{21}H_{12}N_4{}^{35}Cl_2$ 390.0439, found 390.0437 ± 0.0007. Anal. Calcd for $C_{21}H_{12}N_4Cl_2$: C, 64.46; H, 3.09; N, 14.32; Cl, 18.12. Found: C, 64.03; H, 3.06; N, 13.8.

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Supporting Information Available: Calculational details (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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