Phenylethynyl- and Phenylethenylmetacyclophanes with π,π Interactions

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Two series of [8]metacyclophanes with *cis* or *trans* configurated double bonds or triple bonds in the bridges were prepared; the first series **6**, **8**, and **10** contains phenylethynyl, the second series **13**, **14**, and **15** phenylethenyl substituents so that ππ interactions between the π centres in the bridge and the π centres of the basic chromophores tolan and *trans*-stilbene, respectively, can be studied.

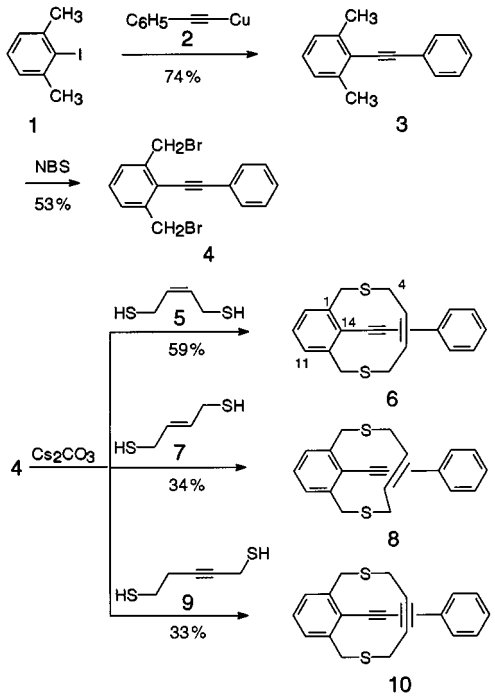
Among the variety of known cyclophanes[1−5] there are relatively few examples with ππ interactions caused by double or triple bonds in the bridges. Metacyclophanes with unsaturated segments in the bridge can normally adopt "*anti*" conformations in which ππ interactions between the double or triple bonds and the benzene ring are avoided.[6][7] This effect prompted us to study [8]metacyclophanes which contain additional π centres in phenylethynyl or phenylethenyl substituents in *ortho* position.[8]

The synthetic sequences for the dithiametacyclophanes **6**, **8**, and **10** (Scheme 1) were started with 2-iodo-1,3-dimethylbenzene (**1**) and copper phenylacetylide. The CC coupling reaction in pyridine yielded the alkyne **3** which was subsequently transformed by NBS to the dibromo derivative **4**. The dithiols **5**, **7**, and **9** were used for the generation of the metacyclophane bridges. The closure of the 11-membered rings could be achieved with reasonable yields for the cyclophanes **6**, **8** and **10** by applying the cesium effect.[9]

Scheme 2 contains the reaction sequence for the preparation of the dithiametacyclophanes **13**, **14**, and **15**. The reaction steps resemble the syntheses described above; bromination of the dimethylstilbene **11**[10] yielded compound **12**, in which the metacyclophane bridge was generated by the reaction with the dithiols **5**, **7**, and **9** in the presence of cesium carbonate.

Additionally to the formation of 11-membered rings, small amounts of 22-membered rings (2:2-products) could be detected in the raw materials (see also ref.[6]).

The intramolecular ππ interactions in the metacyclophanes **6**, **8**, **10**, **13**, **14**, **15** have to be discussed on the basis of the preferred conformations and the molecular dynamics. Force field calculations (MMX[11]) reveal that one has to face equilibria between energetically close minima. An illustration of the conformations is given in the previous paper[6]; see also ref.[8] Nevertheless, all NMR spectra indicate at room temperature a formal C_s symmetry. This can



Scheme 1

be easily rationalised for the compounds **6**, **10**, **13**, and **15**; for the systems **8** and **14** with (*E*)-configurated double bonds in the bridge this finding results from a fast rotation about the single bonds C4−C5 and C6−C7 which are adjacent to the double bond. Because the 11-membered rings cannot invert, the methylene groups of the CH_2-S-CH_2 segments of all cyclophanes discussed here contain diastereotopic geminal protons with characteristic ^2J coupling constants.

Some NMR signals, particularly of the compounds **8**, **13**, and **14** are already broadened at room temperature. The molecular dynamics start to become slow (in terms of the NMR time scale) in the bridge region C-4/C-5, whereas the rotations of the phenylethenyl and phenylethynyl groups are still fast.

The observed C_s symmetry can be due to C_s conformations of **6**, **10**, **13**, and **15** or to fast interconverting C_1 species in all cases including **8** and **14**. ^{1}H- and ^{13}C-NMR

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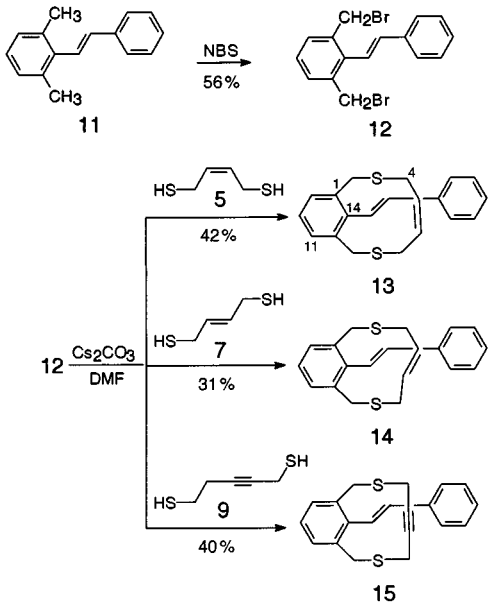
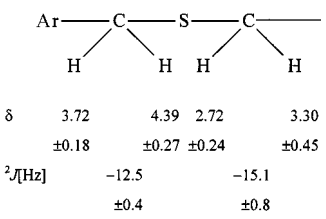
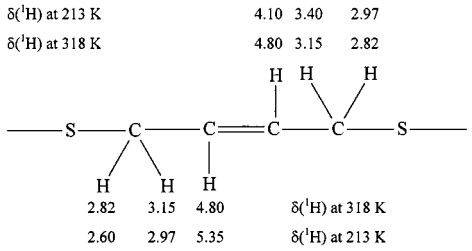


Scheme 2



measurements at 213 K showed that the signals of **6** did not change on cooling, whereas a doubling of *all* signals could be observed for **13**. The latter result is consistent with an equilibrium of two C_s species with a ratio close to 1:1. The rotation of the styryl group is − as one would expect − sterically more discriminating than the linear phenylethynyl substituent. The compounds with *trans* configurated double bonds in the bridges show a different behaviour. On cooling from 294 K to 223 K all NMR signals are doubled except those of nuclei which are in the original symmetry plane. Whereas for example the signals of the sp-C atoms (δ = 86.9 and 98.7) and the adjacent quaternary C atoms (δ = 123.4 and 127.2) of **8** remain constant, the broad resonance signal of C-1,10 at δ = 138.0 is split into two signals at δ = 134.2 and 141.6. An analogous result could be obtained for the ^{1}H NMR spectra. The AB spin pattern of the Ar−CH_2−S groups at δ = 3.76 and 4.49 is split into two AB systems at δ = 3.61, 4.55 and 3.95, 4.38. The AA′BB′MM′ spin system of the butenylene segment is transformed to a ABCDMN spin system:



These results prove that a C_1 conformation (and its enantiomer) is present at low temperatures. Contrary to the conformational equilibration between two C_s conformations of **13**, compound **8** shows an exchange mechanism between two enantiomeric C_1 conformations, which simulates a C_s symmetry.

The interaction of the π centres in the bridge with the π centres of the (*E*)-stilbene or tolan moiety can be studied in the ππ* transitions. Table 1 gives a comparison of the "basic" chromophores present in **3** and **11**, as model compounds and the cyclophanes. The long wavelength absorption maxima are increasingly red-shifted in the tolan series **6**, **8**, and **10** relative to those of **3**. In contrast, a hypsochromic effect could be observed in the stilbene series, especially for **15**. Obviously, the interaction of the basic chromophores with π centres of the bridges has the strongest effect when triple bonds are incorporated in the bridges.

The intensities of the absorptions of the cyclophanes are always lower than the intensities of the unbridged systems **3** and **11**. The strongest hypochromic effects are observed for the compounds **8** and **14**, which have *trans* configurated double bonds in the bridge. The shapes of the absorption bands within each of the two series of compounds are so similar[8] that the ε values, particularly those of **8** and **14**, represent a lower absorption intensity.

Table 1. UV absorption of the compounds **3**, **6**, **8**, and **10** (tolan series) and the compounds **11**, **13**, **14**, and **15** (*trans*-stilbene series) measured in dichloromethane

Compound	Absorption at long wavelengths	
	λ_{max}/nm[a]	$10^{-4}\varepsilon$/cm^2·mmol^{-1}
3	287.9	2.48
6	292.0	1.95
8	296.0	1.37
10	298.0	1.86
11	284.0	1.67
13	284.0	1.59.
14	283.0	1.03
15	273.9	1.56

[a] Limit of error: ±0.5 nm.

The opposite direction of the shift in the two series can be explained by the different mobility of the phenylethynyl and the phenylethenyl group; only the latter can partly evade the ππ interaction by torsion, but the *trans*-stilbene chromophore is then less planar than usual.[12] In order to sustain this assumption, we have made a crystal structure analysis of **15** (Figure 1). It indeed reveals a strong torsion about the C1−C13 single bond, whereas the olefinic double bond between C13 and C14 and the adjacent phenyl substituent are almost coplanar. Another interesting feature of the molecular geometry concerns the distances between the triple bond and the benzene ring and between the triple bond and the trans-configurated double bond. The *meta* bridge is arranged in such a position that the centre of the triple bond has a distance of 312.7 pm from C-1 and 368.9 pm from C-13; i.e. the bridge is far on the benzene side. Of course, in solution an equilibrium between different C_s (of C_1) conformations[6] can be assumed, but the *syn* arrange-

ment between the bridge with the triple bond and the benzene ring should be strongly preferred in **15**.

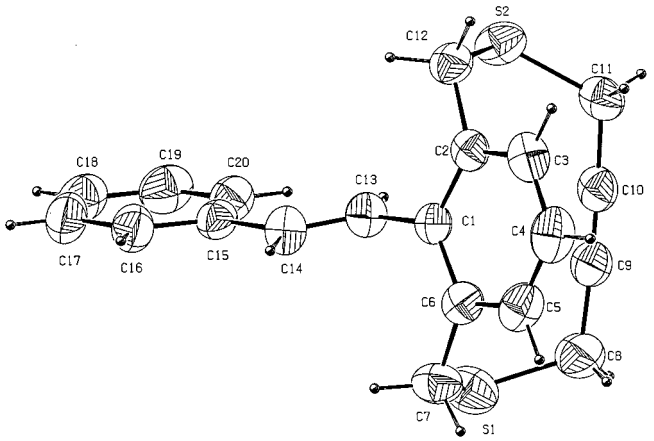


Figure 1. X-ray structural analysis of (*E*)-14-(2-phenylethenyl)-3,8-dithiabicyclo[8.3.1]tetradeca-1(14),10,12-trien-5-yne (**15**) (Thermal ellipsoids at non-hydrogen atoms are at 50% probability). Selected torsion angles: C(2)−C(1)−C(13)−C(14): −108.84(35)°, C(1)−C(13)−C(14)−C(15): 177.32(34)°, C(13)−C(14)−C(15)−C(16): −171.13(35)°. The distances of the middle of C-9 and C-10 and the atoms C-1, C-13, and C-4 amount to 312.7, 368.9, and 389.2 pm, respectively. All bond lengths and bond angles are in the expected range. (The numbering in the figure does not correspond to the nomenclature)

Experimental Section

General: Melting points (uncorrected): Büchi apparatus. − UV/Vis: Zeiss MCS 320/340. − IR: Beckman Acculab 4, KBr pellets. − NMR: Bruker AM 400, $CDCl_3$ with TMS as internal standard. − MS: Varian MAT CH 7A and Finnigan MAT 95.

1,3-Dimethyl-2-phenylethinylbenzene (3): Copper phenylacetylide (**2**) (7.13 g, 43.0 mmol) was added under nitrogen to a solution of 2-iodo-1,3-dimethylbenzene (**1**) (10.0 g, 43.0 mmol) in 150 mL of dry pyridine. The mixture was heated at reflux for 20 h, during which time the solution turned brown. After cooling, the reaction mixture was diluted with 300 mL of water, and extracted repeatedly with ether. The combined extracts were washed with 5% HCl, 5% $NaHCO_3$, and water, and dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was chromatographed on a silica gel column (3× 50 cm) with petroleum ether (40−70°C) as eluant to obtain 6.61 g (74%) of **3** as a colourless liquid. IR (film): $\tilde{\nu}$ = 3030 cm^{-1}, 2900, 2200, 1588, 1482. − UV (CH_2Cl_2): λ_{max} = 287.9 nm, ε = 2.48·10^4 cm^2/mmol. − ^{1}H-NMR ($CDCl_3$): δ = 7.62−7.10 (m, 8 H, Ar-H), 2.61 (s, 6 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 140.4 (C-1,3), 131.5, (o-C, Phenyl), 128.5 (m-C, Phenyl), 128.4, 128.2 (C-12; p-C, Phenyl), 127.9 (C-11, 13), 125.2, 123.6 (C-14; i-C, Phenyl), 98.1, 86.3 (sp-C), 21.3 (CH_3). − MS (70 eV): *m*/*z* (%) = 206 (100) [$M^{+\cdot}$], 191 (80), 165 (15), 128 (17), 105 (15). − $C_{16}H_{14}$ (206.3): calcd. C 93.16, H 6.84; found C 93.36, H 6.82.

1,3-Bis(bromomethyl)-2-phenylethinylbenzene (**4**): *N*-bromosuccinimide (8.55 g, 48.0 mmol) was added portionwise within 24 h to a boiling solution of **3** (4.95 g, 24.0 mmol) in 80 mL of dry CCl_4. Each addition was completed by adding small amounts of AIBN. After 44 h total reaction time at reflux, the mixture was cooled and the succinimide was removed by filtration. The solvent was evaporated and the residue chromoatographed on silica gel (60 × 2.5 cm) with toluene/petroleum ether (1:9) as eluant to give 4.33 g (53%) of **4**; m.p. 139−141°C. − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2980, 2224, 1594, 1490, 1212. − ^{1}H NMR ($CDCl_3$): δ = 7.70−7.20 (m, 8 H, Ar-H), 4.73 (s, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 140.0 (C-1,3), 131.6 (o-C, Phenyl), 129.8 (C-4,6), 129.0, 128.7 (C-5, p-C, Phenyl), 128.5 (m-C, Phenyl), 123.3, 122.8 (C-2, i-C, Phenyl), 101.3, 83.6 (sp-C). − MS (70 eV): *m*/*z* (%): 364 (10), [$M^{+\cdot}$], Br_2 pattern, 283 (20), 204 (100), 202 (48). − $C_{16}H_{12}Br_2$ (364.1): calcd. C 52.78, H 3.32; found: C 52.80, H 3.28.

(*Z*)-14-Phenylethynyl-3,8-dithiabicyclo[8.3.1]tetradeca1(14),5,10,12-tetraene (**6**):[12][13] A solution of **4** (0.61 g, 1.9 mmol) in 100 mL of dry DMF and a solution of (*Z*)-but-2-ene-1,4-dithiol **5** (0.22 g, 1.9 mmol) in 100 mL of DMF were added slowly and simultaneously dropwise to a well-stirred suspension of Cs_2CO_3 (1.0 g, 3.0 mmol) in 300 mL of DMF at room temperature. The total time for the addition under nitrogen amounted to 24 h. Subsequently the mixture was stirred for another day. The solvent was removed under vacuum, and the residue was extracted with 300 mL CH_2Cl_2, washed with water, and dried with $MgSO_4$. The solvent was evaporated and the residue chromatographed on silica gel (40 × cm) with dichloromethane/petroleum ether (40−70°C) (4:6) as eluant. The crude product was recrystallized from dichloromethane/pentane to afford 0.32 g (59%) of **6** as colorless crystals; m.p. 143−145°C. − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2940, 2200, 1585, 1480. UV (CH_2Cl_2): λ_{max} = 292.0 nm, ε = 1.95·10^4 cm^2/mmol. − ^{1}H NMR ($CDCl_3$): δ = 7.58 (m, 2 H, *o*-H, Phenyl), 7.39 (m, 3 H, *m*-H, *p*-H, Phenyl), 7.27 (d, 2 H, 11-H, 13-H), 7.17 (t, 1 H, 12-H), 4.63 (m, 2 H, 5-H, 6-H), 4.66, 3.54 (AB, ^2J = −12.3 Hz, 4 H, 2-H, 9-H), 3.75, 2.73 (AB[15], ^2J = −15.5 Hz, 4 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 141.9 (C-1,10), 131.4, 129.0, 128.7, 128.6, 128.6 (aromat. CH), 128.5 (olefin. CH), 122.9, 123.7 (C-14; i-C, Phenyl), 99.6, 87.5 (sp-C), 33.5 (C-2,9), 27.7 (C-4,7). − MS (FD): *m*/*z* (%): 322 (72) [$M^{+\cdot}$], 268 (100). − $C_{20}H_{18}S_2$ (322.5): calcd. C 74.49, H 5.63; found: C 74.44, H 5.68.

(*E*)-14-Phenylethynyl-3.8-dithiabicyclo[8.3.1]tetradeca1(14),5,10,12-tetraene (**8**): The same procedure was followed as for **6** starting from (*E*)-but-2-ene-1,4-dithiol (**7**) (0.18 g, 1.49 mmol), **4** (0.54 g, 1.49 mmol) and Cs_2CO_3 (0.70 g, 2.14 mmol) except that the total addition time was 36 h. The residue was chromatographed on silica gel (40 × 2 cm) with toluene as eluant to obtain 0.16 g (34%) of **8** as colourless crystals: m.p. 78−80°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2910, 2210, 1590, 1485. − UV (CH_2Cl_2): λ_{max} = 296.0 nm, ε = 1.37·10^4 cm^2/mmol. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.63 (m, 2 H, *o*-H, Phenyl), 7.38 (m, 3 H, *m*-H, *p*-H, Phenyl), 7.24 (m, 3 H, 11-H, 12-H, 13-H), 4.80 (br.m, 2 H, 5-H, 6-H), 4.49, 3.76 (AB, ^2J = −12.4 Hz, 4 H, 2-H, 9-H), 3.15, 2.82 (br. m, 4 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$, 293 K): δ = 138.0 (br., C-1,10), 131.4, 129.3, 129.3, 128.5, 128.5 (aromat. CH), 127.9 (br., olefin. CH), 127.2, 123.4 (C-14; *i*-C, Phenyl), 98.7, 86.9 (sp-C), 34.0 (C-2,9), 33.6 (br., C-4,7). − MS (FD): *m*/*z* (%): 322 (94) [$M^{+\cdot}$], 268 (100). − ^{13}C NMR ($CDCl_3$, 223 K): δ = 141.6, 134.2 (C-1, C-10), 131.3, 129.3, 129.2, 129.0, 128.5, 128.4, 127.9, 125.8 (aromat. and olefin. CH), 126.7, 122.8 (C-14; i-C, Phenyl), 98.0, 86.3 (sp-C), 34.8, 34.2, 33.0, 32.0 (C-2, 4, 7, 9). − $C_{20}H_{18}S_2$ (322.5): calcd. C 74.49, H 5.63; found: C 74.09, H 5.38.

14-Phenylethynyl-3,8-dithiabicyclo[8.3.1]tetradeca-1(14),10,12-trien-5-yne (**10**): The same procedure was followed as for **6** starting from but-2-yne-1,4-dithiol (**9**) (0.24 g, 2.0 mmol), **4** (0.73 g, 2.0 mmol) and Cs_2CO_3 (0.94 g, 2.87 mmol) except that the total addition time was 40 h. The residue was chromatographed on silica gel (50 × 2 cm) with toluene as eluant to afford 0.21 g (33%) of **10** as colourless crystals: m.p. 135−137°C. − IR (KBr): $\tilde{\nu}$ = 2942 cm^{-1}, 2910, 2220, 1592, 1565, 1486. − UV (CH_2Cl_2): λ_{max} = 298.0 nm, ε = 1.86·10^4 cm^2/mmol. − ^{1}H NMR ($CDCl_3$): δ = 7.61 (m, 2

H, *o*-H, Phenyl), 7.35 (m, 3 H, *m*-H, *p*-H, Phenyl), 7.26 (t, 1 H, 12-H), 7.20 (d, 2 H, 11-H, 13-H), 4.51, 3.90 (AB, ^2J = −12.6 Hz, 4 H, 2-H, 9-H), 3.22, 2.95 (AB[16], ^2J = −15.8 Hz, 4 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 138.6 (C-1,10), 131.4, 129.2, 128.4, 128.4, 128.1 (aromat. CH), 126.4, 123.6 (C-14; *i*-C, Phenyl), 99.4, 86.5 (sp-C, Phenylethynyl), 78.8 (C-5,6), 36.0 (C-2,9), 19.9 (C-4,7). − MS (FD): *m/z* (%): 320 (3) [$M^{+\cdot}$], 268 (100). − MS (EI, 70 eV): *m/z* (%): 320 (0.1) [$M^{+\cdot}$], 270 (10), 269 (20), 268 (100), 267 (25), 234 (14). − $C_{20}H_{16}S_2$ (320.5): calcd: C 74.96, H 5.03; found: C 74.02, H 5.10.

(*Z*)-1,3-Bis(bromomethyl)-2(2-phenylethenyl)benzene (**12**): *N*-bromosuccinimide (4.86 g, 27.3 mmol) was added portionwise within 16 h to a solution of 2,6-dimethylstilbene (2.58 g, 12.4 mmol) in 60 mL of dry CCl_4. Each addition was completed by adding small amounts of AIBN. After 24 h refluxing, the mixture was cooled and the succinimide was filtered off. The solvent was evaporated and the residue chromatographed on silica gel (40 × 2 cm) with petroleum ether/toluene (9:1) to give 2.55 g (56%) of **12**: m.p. 89.0−90.5°C. − IR (KBr): $\tilde{\nu}$ = 3018 cm^{-1}, 1630, 1488, 1450, 1204. − ^{1}H NMR ($CDCl_3$): δ = 7.58 (m, 2 H, Ar-H), 7.42 (m, 4 H, Ar-H), 7.33 (d, ^3J = 16.7 Hz, 1 H), 7.02 (d, ^3J = 16.7 Hz, 1 H) (AB, olefin. H), 7.27 (m, 2 H, Ar-H), 4.57 (s, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 138.3 (C-2), 136.7 (i-C, Phenyl), 136.6 (C-1,3), 135.9, 128.3 (olefin.C), 131.0 (C-4,6), 128.8 (*m*-C, Phenyl), 127.9 (*p*-C, Phenyl), 126.8 (*o*-C, Phenyl), 123.0 (C-5), 32.6 (CH_2). − MS (70 eV): *m/z* (%): 364 (8) [$M^{+\cdot}$], 285 (22), 206 (27), 205 (100), 191 (17). − $C_{16}H_{14}Br_2$ (362.1): calcd. C 52.49, H 3.85; found: C 52.14, H 3.69.

(*E*,*Z*)-14-(2-Phenylethenyl)-3,8-dithiabicyclo[8.3.1]tetradeca-1(14),5,10,12-tetraene (**13**): The same procedure was followed as for **6**. Starting with (*Z*)-but-2-ene-1,4-dithiol (**5**) (0.24 g, 2.0 mmol) and **12** (0.73 g, 2.0 mmol) the total reaction time was 3 d. The residue was chromatographed on silica gel (40 × 2 cm) with CH_2Cl_2/petroleum ether (40−70°C) (1:1) as eluant. The product was recrystallized from CH_2Cl_2/pentane to afford 0.3 g (46%) of **13** as colourless crystals: m.p. 148−149°C. − IR (KBr): $\tilde{\nu}$ = 3006 cm^{-1}, 2864, 1585, 1480, 1450, 1395. − UV (CH_2Cl_2): λ_{max} = 284.0 nm, ε = 1.59·10^4 cm^2/mmol. − ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.50 (m, 2 H, *o*-H, Phenyl), 7.43, 6.38 (AB, ^3J = 16.4 Hz, 2 H, olefin. H)[15], 7.40 (m, 2 H, *m*-H, Phenyl), 7.30 (m, 3 H, 11-H, 13-H; *p*-H; Phenyl), 7.20 (t, 1 H, 12-H), 5.01 (br. m, 2 H, 5-H, 6-H), 4.34, 3.62 (AB, ^2J = −12.1 Hz, 4 H, 2-H, 9-H), 2.85, 2.48 (br. AB[16], ^2J = −14.3 Hz, 4 H, 4-H, 7-H). − ^{1}H NMR ($CDCl_3$, 213 K): δ = 7.55−7.05 (m, 16 aromat. and 2 olefin. H), 6.40 (d, 1 H, olefin. H), 6.33 (d, 1 H, olefin. H), 5.38 (m, 2 H, 5-H, 6-H), 4.60 (m, 2 H, 5-H, 6 H), 4.45, 3.56 (AB, 4 H, 2-H, 9-H), 4.25, 3.72 (AB, 4 H, 2-H, 9-H), 3.20, m / 2.80, d (4 H, 4-H, 7-H), 2.53, d / 2.20, m (4 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 139.5, 136.9 (C-14; *i*-C, Phenyl), 136.0 (C-1,3), 136.0 (C-5,6), 129.5, 128.7, 126.5 (C-11,13; *o*-C, Phenyl; *m*-C, Phenyl), 129.3, 128.0, 127.5, 126.4 (C-12; olefin. CH; *p*-C, Phenyl), 31.6 (C-2,9), 26.2 (C-4,7). − ^{13}C NMR ($CDCl_3$, 213 K): δ = 139.9, 138.6, 137.6, 136.8, 136.3, 134.1 (aromat. C_q), 137.8, 134.7 (C-5,6), 130.6, 129.7, 129.5, 129.0, 128.5, 128.0, 127.9, 126.5, 125.2 (aromat. and olefin. CH, partly superimposed), 31.8, 31.4 (C-2,4), 27.5, 25.2 (C-4,7). − MS (70 eV): *m/z* (%): 324 (5) [$M^{+\cdot}$], 205 (10), 148 (100). − $C_{20}H_{20}S_2$ (324.5): calcd. C 74.03, H 6.21; found: 74.13, H 6.29.

(*E*,*E*)-14-(2-Phenylethenyl)-3,8-dithiabicyclo[8.3.1]tetradeca-1(14),5,10,12-tetraene (**14**): The same procedure was followed as for **6**. Starting with (*E*)-but-2-ene-1,4-dithiol (**7**) (0.13 g, 1.1 mmol), **12** (0.40 g, 1.1 mmol) and Cs_2CO_3 (0.49 g, 1.5 mmol) the time for the addition amounted to 40 h. The residue was chromatographed on silica gel (40 × 2 cm) with CH_2Cl_2/petroleum ether (40−70°C) (1:1) as eluant. The crude product was recrystallized from CH_2Cl_2/pentane to afford 0.11 g (31%) of **14** as colourless crystals: m.p. 86−88°C. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3000, 2936, 2900, 1580, 1482, 1448, 1395. − UV (CH_2Cl_2): λ_{max} = 258.1 nm, ε = 1.08·10^4 cm^2/mmol, λ_{max} = 283.0 nm, ε = 1.03·10^4 cm^2/mmol. − ^{1}H NMR ($CDCl_3$): δ = 7.79, 6.50 (AB, ^3J = 16.5 Hz, 2 H, olefin. H)[17], 7.58 (m, 2 H, *o*-H, Phenyl), 7.41 (m, 2 H, *m*-H, Phenyl), 7.32 (m, 1 H, *p*-H, Phenyl), 7.23 (d, 2 H, 11-H, 13-H), 7.18 (t, 1 H, 12-H), 4.71 (br. m, 2 H, 5-H, 6-H), 4.13, 3.78 (AB, ^2J = −12.9 Hz, 4 H, 2-H, 9-H), 3.07, 2.82 (br. AB[15], ^2J = −14.8 Hz, 4 H, 4-H, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 141.2, 137.5 (C-14; *i*-C, Phenyl), 135.2 (C-5,6), 134.8 (C-1,3), 129.8, 128.6, 126.5 (C-11,13; *o*-C, Phenyl, *m*-C, Phenyl), 127.7, 127.5, 127.5, 126.4 (C-12; olefin. CH; *p*-C, Phenyl), 34.3 (C-2,9), 32.9 (C-4,7). − MS (70 eV): *m/z* (%): 324 (3) [$M^{+\cdot}$], 204 (10), 190 (8), 148 (100). − $C_{20}H_{20}S_2$ (324.5): calcd. C 74.03, H 6.21; found: C 73.64, H 6.29.

(*E*)-14-(2-Phenylethenyl)-3,8-dithiabicyclo[8.3.1]tetradeca1(14),10,12-trien-5-yne (**15**): The same procedure was followed as for **6**. Starting from but-2-yne-1,4-dithiol (**9**) (0.24 g, 2.0 mmol), **12** (0.73 g, 2.0 mmol) the total time for the addition amounted to 3 d. The residue was chromatographed on silica gel (40 × 2 cm) with toluene as eluant. The crude product was recrystallized from CH_2Cl_2/pentane to obtain 0.26 g (40%) of **15** as colourless crystals: m.p. 151−152°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2930, 1650, 1600, 1495, 1464, 1400. − UV (CH_2Cl_2): λ_{max} = 273.9 nm, ε = 1.56·10^4 cm^2/mmol. − ^{1}H NMR ($CDCl_3$): δ = 8.00, 6.58 (AB, ^3J = 16.6 Hz, 2 H, olefin. H)[17], 7.58 (m, 2 H, *o*-H, Phenyl), 7.39 (m, 2 H, *m*-H, Phenyl), 7.29 (m, 1 H, *p*-H, Phenyl), 7.19 (t, 1 H, 12-H), 7.13 (d, 2 H, 11-H, 13-H), 4.19, 3.82 (AB, ^2J = −12.8 Hz, 4 H, 2-H, 9-H), 3.05, 2.94 (AB, ^2J = −15.7 Hz, 4 H, 4-H, 7-H)[16]. − ^{13}C NMR ($CDCl_3$): δ = 142.1, 137.5 (C-14; *i*-C, Phenyl), 134.9 (C-1,3), 132.7, 127.6, 127.1, 127.0 (C-12; olefin. CH; *p*-C, Phenyl), 129.8, 128.7, 126.6 (C-11,13; *o*-C, Phenyl; *m*-C, Phenyl), 77.8 (C-5,6), 35.9 (C-2,9), 19.4 (C-4,7). − MS (70 eV): *m/z* (%): 322 (1) [$M^{+\cdot}$], 276 (11), 218 (40), 148 (100). − $C_{20}H_{18}S_2$ (324.5): calcd. C 74.49, H 5.63; found: C 74.47, H 5.59.

X-ray Structural Analysis of 15:[18] $C_{20}H_{18}S_2$, 322.46 g·mol^{-1}; a colourless laminar crystal of the size 0.45 × 0.51 × 1.02 mm was grown by recrystallization of **15** from dichloromethane: monoclinic, *C*2/c (NO. 15), *a* = 30.240(5), *b* = 6.9856(9), *c* = 15.922(2) Å, β = 90.58(1)°; *V* = 3363.2(8) Å^3; *Z* = 8; $D_{calc.}$ = 1.274 g·cm^{-3}; μ = 0.31 mm^{-1}; $F_{(000)}$ = 1360. CAD4 (Enraf-Nonius) diffractometer; Mo-K_α radiation (λ = 0.7107 Å); 298 K; ω/2Θ scan, 1.0° ≤ Θ ≤ 30°, 0 ≤ *h* ≤ 42, 0 ≤ *k* ≤ 9, −22 ≤ *l* ≤ 22; number of unique reflections 4884, criterion for unobserved reflections $F_0 < 4\,\sigma(F_0)$; programs used for structure solution and refinement: SIR-92, SHELX-93; hydrogen atoms were placed at calculated positions and refined isotropically; all other atoms were refined anisotropically. The final refinement with 213 parameters converged with *R*1 = 0.0740. wR_2 = 0.2512, *S* = 1.071.

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[13] The nomenclature of the cyclophanes described here corresponds to the nomenclature of bicycles and not to the special phane nomenclature.[14]
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[15] Additional couplings to the olefinic protons.
[16] An additional long-range coupling takes place across the triple bond.
[17] INDOR and NOE measurements reveal that the signal at higher field belongs to the proton in α-position to the phenyl substituent.
[18] Crystallographic data for **15** can be obtained on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quotation of the deposition number CSD-410325, the authors' names, and the full journal citation.

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