Multibridged [3_n]Cyclophanes, 11[‡]

A Synthetic and Structural Study of 17,18-Dicyano[3_2](1,6)cyclooctatetraeno-(1,4)cyclophane Generated by Photolysis of [3_2](1,4)Barrelenophane

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[3_2]Cyclooctatetraenophane **(6)** has been generated by photolysis of [3_2](1,4)barrelenophane **(5)**, which, in turn, has been found to be most conveniently obtained by the uncatalyzed cycloaddition of dicyanoacetylene to [3_2](1,4)cyclophane **(4)** at 150 °C in a sealed ampoule. Under high-pressure conditions, the reaction furnished **5** in lower yield, along with trace amounts of the naphthalenophane **11** or the novel 1:2 adduct **12** depending on the pressure. Photoirradiation of **5** in CH_3CN led to the formation of **6**, while irradiation in toluene afforded the semibullvalenophane **13** as the major product along with some **6**. Interestingly, irradiation of **13** with a high-pressure Hg lamp in toluene led to the formation of an alternative semibullvalenophane **14**. The crystal structures of the new products **5**, **6**, **11**, **12**, and **13** are described.

Introduction

By taking advantage of the strong π-electron donating ability of [3_2](1,4)cyclophanes in [*m.n*](1,4)cyclophanes ($m = n = 2-4$) and the corresponding benzene derivatives,[2] the [3_n]cyclophanes serve as good π-ligands which form transition metal complexes with Fe^{II}, Ru^{II}, and Os^{II}.[3] All [3_n]cyclophanes ($n = 2-6$) are now available as a result of progress made in the relevant synthetic methods,[4,5] and their characteristic molecular structures have been elucidated by NMR spectroscopy and X-ray structural analyses.[6] The completely stacked benzene rings at transannular distances of ca. 3.0 Å are photoreactive and several novel polycyclic cage compounds have been obtained upon photoirradiation.[1,7]

As an extension of our studies on metal π-arene complexes,[8] we hoped to synthesize ([3_n]cyclophane)lanthanide complexes having cyclooctatetraene (COT) rings, because the dianion of COT is a good ligand for lanthanide metals.[9] In our previous study on the synthesis of COT-phane, we found that [3_4](1,2,4,5)cyclophane **(9)** reacts smoothly with dicyanoacetylene (DCA) to give barrelenophane **10**, which is transformed not to the desired COT-phane but to semibullvalenophane upon photoirradiation.[4]

We wish to describe here a synthetic study and the structural and electrochemical properties of [3_2](1,6)cyclooctatetraenyl(1,4)cyclophane **(6)** and its valence isomers, barrelenophane **5** and semibullvalenophanes **13** and **14**.

Results and Discussion

Synthesis

In general, benzene itself reacts very sluggishly in Diels−Alder reactions, even if the reaction is performed at high temperatures. Ciganek found that the addition of DCA to benzene gives a barrelene derivative, 2,3-dicyanobicyclo[2.2.2]octa-2,5,7-triene in low yield (14%), but that the use of a Lewis acid catalyst such as $AlCl_3$ allows a significant lowering of the reaction temperature and leads to an increase in the yield of the barrelene derivative (63%). Additionally, the Friedel−Crafts products, phenylmaleonitrile (4%) and phenylfumaronitrile (11%) were isolated as by-products.[10] Strain in the benzene ring also lowers the activation barrier, and Ciganek found that highly strained [2_2](1,4)cyclophane **(1)** reacts with DCA in benzene at 120 °C to give a mixture of the 1:1 (32%) and 1:2 (39%) adducts.[10] An X-ray structural analysis confirmed that these were the mono-barrelenophane and the bis-barrelenophane with a crossed double barrelene configuration, respectively.[11] Interestingly, however, Boekelheide et al. have reported that treatment of a CH_2Cl_2 solution of **1** with DCA in the presence of $AlCl_3$ at room temperature leads directly to dicyano[2_2](1,6)cyclooctatetraeno(1,4)cyclo-

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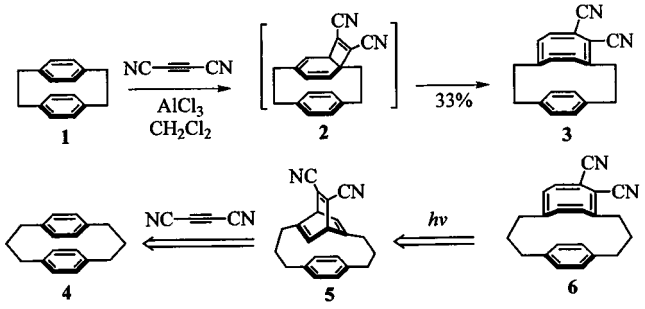
phane **(3)** (33%), presumably through ring-expansion of the intermediate **2** (Scheme 1).[12a]

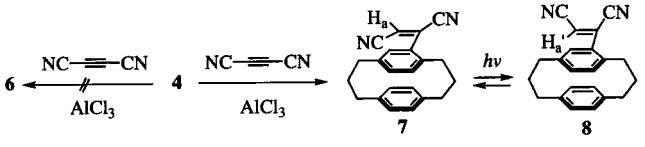


Scheme 1. Synthetic approaches to cyclooctatetraenophane **6**

We have examined two approaches to the synthesis of a COT-phane from [3_n]cyclophanes. One involves the direct formation of a COT-phane by means of Lewis acid-catalyzed addition of DCA to a benzene ring of the cyclophane, as reported by Boekelheide et al.[12a] An alternative approach involves the Diels–Alder reaction of DCA with a benzene ring of the cyclophane and subsequent photochemical conversion of the resultant barrelenophane to a COT-phane.[12b]

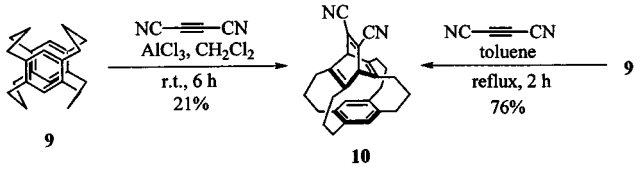
$AlCl_3$-Catalyzed Addition of DCA to [3_2](1,4)Cyclophane 4

[3_2](1,4)Cyclophane **(4)** and a slight excess of DCA were treated in CH_2Cl_2 in the presence of $AlCl_3$ at room temperature. Standard work-up did not furnish the desired COT-phane, but instead gave the Friedel–Crafts products as a mixture of *trans*- and *cis*-isomers **7** and **8** (ca. 40%) (Scheme 2). The ratio of *trans*-**7** to *cis*-**8** was estimated to be ca. 4:1 from the integrals of their olefinic proton signals at δ = 6.20 (H_a) for **7** and δ = 6.04 ($H_{a'}$) for **8**. The isomers **7** and **8** were separated by preparative silica gel TLC eluting with hexane/acetone (9:1) and were isolated as a yellow oil and as yellow crystals, respectively. They were characterized by their spectroscopic data and finally by an X-ray structural analysis of **8**. When a similar reaction was carried out in the dark at room temperature, a mixture of the 1,4-adduct, i.e. the barrelenophane **6**, and *trans*-**7** was obtained in a 3:2 ratio, along with trace amounts of *cis*-**8**. The photochemical isomerization between *trans*-**7** and *cis*-**8** was monitored by ^{1}H NMR spectroscopy in $CDCl_3$ and the ratio was found to be ca. 1:1 at the photostationary state.



Scheme 2. Addition of dicyanoacetylene to [3_2](1,4)cyclophane **(4)** in the presence of $AlCl_3$

Thus, in sharp contrast to the reactivity of [2_2](1,4)cyclophane **(1)**,[12a] the predominant path followed upon $AlCl_3$-catalyzed addition of DCA to [3_2](1,4)cyclophane **(4)** is the Friedel–Crafts reaction. The reactivities of other [3_n]cyclophanes such as [3_2](1,2)-, [3_2](1,3)-, [3_3](1,3,5)-, and [3_4](1,2,4,5)cyclophanes have been tested under similar reaction conditions,[13] but a product was isolated only in the case of [3_4](1,2,4,5)cyclophane **(9)**. This was found to be the 1,4-adduct, [3_4](1,2,4,5)barrelenophanedicarbonitrile **(10)** (21%), when **9** and a slight excess of DCA were reacted in CH_2Cl_2 in the presence of $AlCl_3$ at room temperature for 6 h (Scheme 3).



Scheme 3. Addition of dicyanoacetylene to [3_4](1,2,4,5)cyclophane **(9)** in the presence and absence of $AlCl_3$

The structures of *trans*-**7** and *cis*-**8** have been established on the basis of their ^{1}H and ^{13}C NMR spectra. The olefinic proton H_a of *trans*-**7**, resonating at δ = 6.20 in $CDCl_3$, is slightly more deshielded than the corresponding proton H_a' of *cis*-**8**, resonating at δ = 6.04. Both signals show significant downfield shifts to δ = 7.15 (H_a) and 7.00 (H_a') in [D_6]DMSO, although the reason for this is not yet clear. The ^{13}C NMR spectra show two distinct cyano carbon signals at δ = 114.4 and 116.7 for *trans*-**7**, and at δ = 114.5 and 114.9 for *cis*-**8**. The IR spectra show CN stretching frequencies at 2195 and 2230 cm^{-1} for *trans*-**7** and at 2224 cm^{-1} for *cis*-**8**.

The *cis* geometry of **8** has been confirmed by an X-ray structural analysis (Figure 1). The torsion angle C3–C2–C19–C20 is 43.9(5)°; therefore, only weak π-conjugation is expected between the benzene ring and the dicyanoethylene moiety. The geometry of the substituted benzene ring in *cis*-**8** is slightly distorted from a planar to a boat-shaped form. The dihedral angles between the least-squares planes, the C3–C2–C6–C5 and C2–C1–C6 planes as well as the C3–C2–C6–C5 and C3–C4–C5 planes, are 6.7° and 6.1°, respectively, the magnitude of this angle being comparable to that in [3_2](1,4)cyclophane **(4)** (6.4°).[14]

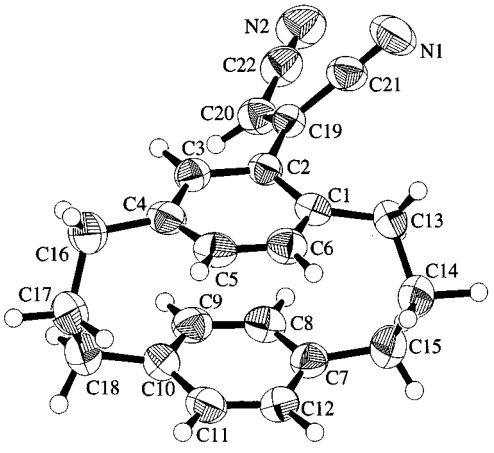


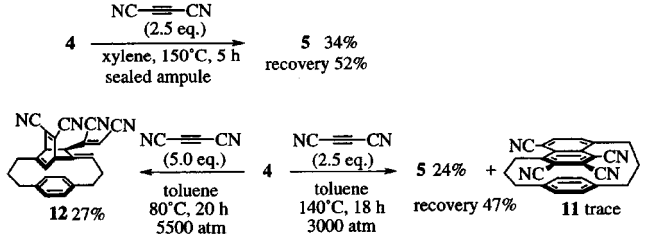
Figure 1. ORTEP drawing of *cis*-**8** with ellipsoids drawn at a 50% probability level; selected bond lengths [Å] and torsion angle [°]: C1–C2 1.404(5), C2–C19 1.474(5), C19–C21 1.441(5), C21–N1 1.165(5), C1–C7 3.171(5), C4–C10 3.108(6), C5–C11 3.321(6); C3–C2–C19–C20–43.9(5)

Uncatalyzed Diels–Alder Reaction of DCA and [3_n]Cyclophanes

In the $AlCl_3$-catalyzed Diels–Alder reaction of slightly strained [3_4](1,2,4,5)cyclophane **(9)** with DCA in CH_2Cl_2 at room temperature, barrelenophane **10** was obtained (21%), while the uncatalyzed reaction of **9** with DCA in refluxing toluene furnished **10** in much higher yield (76%), as reported previously (Scheme 3).[4] The uncatalyzed reaction conditions were applied to other [3_n]cyclophanes, but treatment of [3_2](1,2)-, [3_2](1,3)-, and [3_3](1,3,5)cyclophanes resulted in complete recovery of the starting materials. Only [3_2](1,4)cyclophane **(4)** reacted with DCA upon refluxing in xylene for a day to give barrelenophane **5**, albeit only in 5% yield along with 93% recovery of the starting **4**.

In order to increase the yield of **5**, we studied the effect of pressure on the cycloaddition.[11c,15,16] A xylene solution of **4** and DCA was heated at 150 °C for 5 h in a sealed ampoule to give **5** in 34% yield along with 52% recovery of **1** (Scheme 4). When the reaction was conducted at ca. 3000 atmospheres in an autoclave at 140 °C for 18 h, the yield of **5** was slightly decreased (24%) and the product was accompanied by trace amounts of naphthalenophane **11** with a [3_2](1,5)naphthaleno(1,4)cyclophane framework. The structure of the latter was subsequently confirmed by X-ray structural analysis (Figure 2). The formation of **11** may be ascribed to the initial formation of the 1:2 (**4**/DCA) adduct, followed by its thermal rearrangement to a dihydronaphthalene derivative and dehydrogenation, as suggested by Klärner et al.[15] A further increase in the pressure to ca. 5500 atmospheres and the use of a large excess of DCA at 80 °C resulted in formation of the 1:2 adduct **12** (27%), but no 1:1 adduct **5** was isolated.

Thus, the reaction was drastically affected by changes in the pressure and temperature. The second molecule of DCA does not attack at the benzene ring of the barrelenophane **5**, but instead reacts with an unsubstituted double bond of the barrelene moiety. This is in sharp contrast to the case of [2_2](1,4)cyclophane **(1)** which reacts with DCA at 170 °C in benzene to give the bis-adduct, bis(barrelenophane) (72%).[10,11a] The low reactivity of the benzene ring in **5** can be mainly attributed to the much lower strain of this ring than in the corresponding mono-barrelenophane derived from **1**. In fact, the benzene ring in **5** is not distorted, as shown by its X-ray structural analysis (Figure 3). The nonbonding distances between the decks in **5** are 3.96–4.01 Å for the bridgehead carbon atoms (C5–C11, C2–C8) and 3.22–3.33 Å for the other unsaturated carbon atoms



Scheme 4. Reaction of [3_2](1,4)cyclophane **(4)** with dicyanoacetylene at high pressures

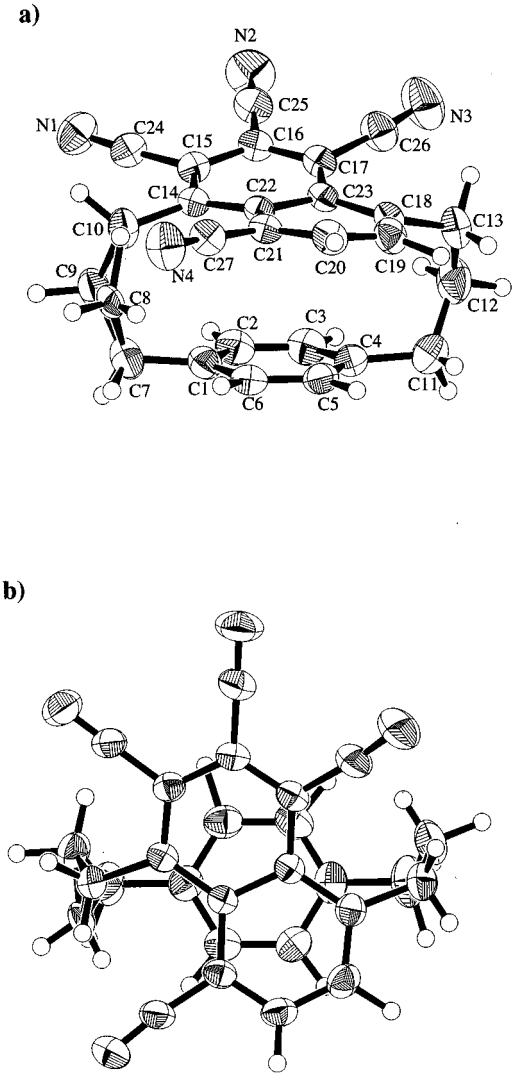


Figure 2. ORTEP drawings: (a) side view, (b) top view, of **11** with ellipsoids drawn at a 50% probability level; selected bond lengths [Å]: C14–C15 1.390(4), C14–C22 1.442(4), C15–C16 1.416(4), C16–C17 1.396(5), C17–C23 1.425(4), C18–C23 1.451(4), C18–C19 1.392(4), C19–C20 1.396(5), C20–C21 1.389(4), C21–C22 1.439(4), C22–C23 1.444(4), C15–C24 1.452(5), N1–C24 1.142(4)

(C1–C7, C3–C9, C4–C10, C6–C12). The bridgehead angles in the barrelene skeleton [107.3(2)° for C7–C8–C9 and 104.4(2)° for C7–C8–C13] are similar to the ideal angle for sp^3-hybridized carbons, suggesting low strain in **5**. The average nonbonding distance between the double bonds is 2.44 Å. The central carbon atom of the trimethylene bridge is disordered between C18 and C19 with a population ratio of 3:2.

The structures of **11** and **12** have been determined by X-ray crystal structural analyses (Figure 2 and Figure 4). In the ^1H NMR spectrum of **11**, the naphthalene ring proton signals appear at δ = 8.16 and 8.02. Substitution of four cyano groups and bridging at two positions distort the naphthalene ring from planarity. The C18–C19–C20–C21–C22–C23 ring of the naphthalene overlaps with the facing benzene ring in an almost parallel fashion (2.92°), whereas the other

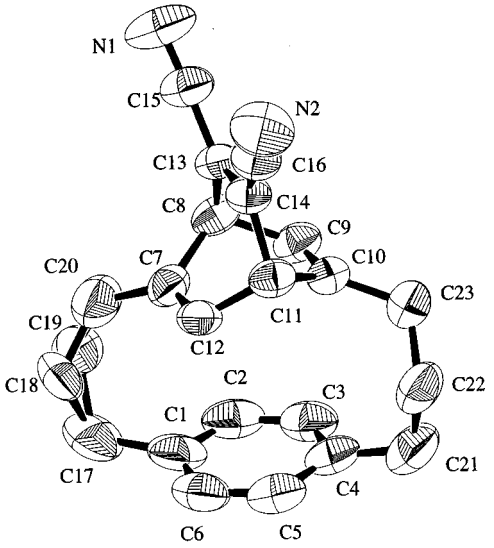


Figure 3. ORTEP drawing of **5** with ellipsoids drawn at a 50% probability level; all hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: C7−C12 1.316(3), C7−C8 1.540(3), C8−C9 1.533(3), C9−C10 1.311(3), C8−C13 1.528(3), C13−C14 1.334(3), C13−C15 1.434(3), C15−N1 1.137(3), C7−C9 2.466(2), C7−C13 2.424(3); C7−C8−C9 107.3(2), C7−C8−C13 104.4(2)

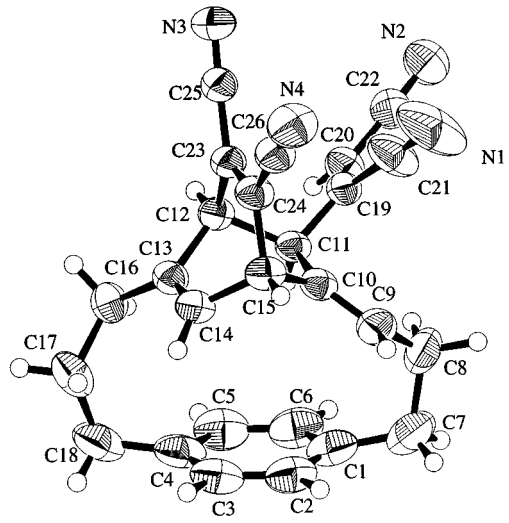


Figure 4. ORTEP drawing of **12** with ellipsoids drawn at a 50% probability level; selected bond lengths [Å] and torsion angles [°]: C9−C10 1.327(4), C10−C11 1.518(3), C11−C12 1.580(4), C11−C19 1.518(4), C12−C13 1.525(4), C12−C23 1.510(4), C13−C14 1.325(4), C19−C20 1.319(4), C19−C21 1.437(4), C23−C24 1.337(4), C21−N1 1.124(4); C8−C9−C10−C11 −5.5(5), C8−C9−C10−C15 168.2(3)

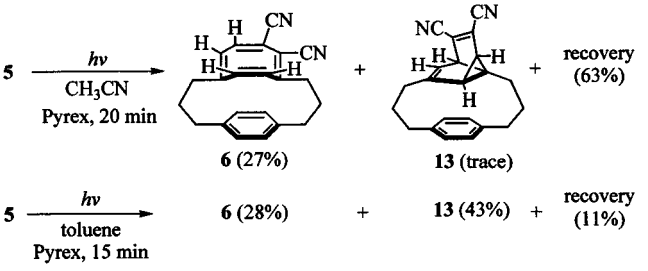
C14−C15−C16−C17−C23−C22 ring shows a slight deviation of 12° from the parallel arrangement (Figure 2a). The benzene and naphthalene rings are well overlapped (Figure 2b). The almost parallel stacking and complete overlap of the two rings makes them suitably disposed for charge transfer (CT) from the benzene ring to the naphthalene ring, and a characteristic broad CT band is observed at λ_{max} = 339 nm in the electronic spectrum recorded in CH_2Cl_2. The bond lengths of the central part of the naphthalene ring (C14−C22, C17−C23, C18−C23, C21−C22, C22−C23) are longer (1.439−1.451 Å) than the others (1.389−1.416 Å). The central carbon atom of the bridge shows disorder between C8 and C9 with the relative populations being 1:3.

Recrystallization of **12** from CH_2Cl_2 led to the preferential formation of crystals of one stereoisomer, the structure of which was solved by carrying out an X-ray structural analysis (Figure 4). The geometry of the barrelene-like skeleton of **12** is similar to that of the barrelene moiety in **5**. The single- and double-bond characters of C10−C11 and C9−C10 are reflected in their bond lengths of 1.518(3) and 1.327(4) Å, respectively. The C9−C10 double bond is slightly distorted; the C8−C9−C10−C11 torsion angle is −5.5(5)°, whereas the C8−C9−C10−C15 angle is 168.2(3)°.

Photoirradiation of Barrelenophane 5

The photochemistry of barrelene is very interesting. It can be converted into various valence isomers such as semibullvalene or COT depending on the reaction conditions. Zimmerman et al. reported that acetone-sensitized photoirradiation of barrelene gives semibullvalene as a major product, whereas its direct irradiation leads to the formation of COT. Photolysis of semibullvalene gives COT but no barrelene.[17] Saito et al. found that direct irradiation of 2,3-dicyanobarrelene gives 1,2-dicyano-COT, while the acetone-sensitized reaction affords semibullvalene derivatives as the major products.[18] In the case of barrelenophanes, Boekelheide et al. reported that direct irradiation of [2_4](1,2,4,5)barrelenophane in THF using a low-pressure Hg lamp gave the corresponding COT-phane (41%),[12b] whereas [2_2](1,4)-[11b] and [3_4](1,2,4,5)barrelenophanes **5**[4] gave the corresponding semibullvalenophanes **15** and **16** on irradiation with a high-pressure Hg lamp.[19]

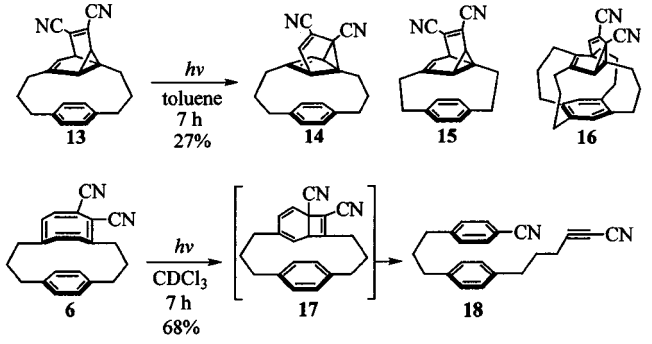
We have studied the photochemical reaction of [3_2](1,4)barrelenophane **5** (Scheme 5). A CH_3CN solution of **5** was irradiated with a high-pressure Hg lamp for 15 min through a Pyrex filter to give the desired COT-phane **6** (27%) along with trace amounts of semibullvalenophane **13**. When the reaction was carried out in toluene, a mixture of **6** (28%) and **13** (43%) was obtained. The COT-phane **6** may be formed via a [2+2] intermediate derived from a singlet excited state of **5**, whereas **13** is formed via a biradical intermediate generated from a triplet excited state of **5**.[17c,18]



Scheme 5. Photoirradiation of barrelenophane **5** with a high-pressure Hg lamp

Interestingly, irradiation of semibullvalenophane **13** with a high-pressure Hg lamp in toluene led to the formation

of an alternative semibullvalenophane **14** (27%), which was recovered along with unreacted **13** (Scheme 6). As far as we are aware, such a photochemical conversion of one semibullvalenophane into another has not previously been reported, making the conversion of **13** to **14** the first example. Similar irradiation of **14** resulted in polymerization. Photoirradiation of **6** gave the open-chain compound **18**, presumably via intermediate **17**. Thus, the COT-phane **6** is formed by direct irradiation of the barrelenophane **5**. The exclusive formation of the semibullvalenophanes **13** and **15**,[11b] in which the double bond is conjugated with two cyano groups, upon photolysis of the corresponding barrelenophanes may be attributed to the stabilization of these isomers by π-conjugation. In the case of [3$_4$]barrelenophane, however, the semibullvalenophane **16** was formed on photoirradiation and its semibullvalene framework is the same as that in **14**. The question as to why the cyano groups in **13** are attached to the double bond, while in **14** one is attached to the double bond and the other to the cyclopropane ring may be explained in terms of the PM3 calculation result; both **13** and **14** are more stable than the corresponding Cope-rearranged isomers by 4.8 and 4.4 kcal/mol, respectively.[20] The calculation also indicates that **13** is thermodynamically more stable than **14** by 3.0 kcal/mol.



Scheme 6. Photoirradiation of **13** and **6** with a high-pressure Hg lamp

The ^{1}H NMR spectra of **13** and **14** are similar. An olefinic proton signal is seen at δ = 4.94 (br. s) for **13**, whereas two signals are observed at δ = 6.16 (d, J = 2.63 Hz) and δ = 4.71 (br. s) for **14**. Two [δ = 2.43 and 2.70 (d, J = 6.60 Hz)] and one [δ = 3.20 (d, J = 2.97 Hz)] cyclopropyl proton signals are observed for **13** and **14**, respectively. Generally speaking, semibullvalene undergoes a Cope rearrangement on heating, but no Cope rearrangement is observed for **13** at up to 150 °C in [D$_6$]DMSO. The COT-phane **6** shows four distinct olefinic proton signals at δ = 5.38 and 5.42 (d, J = 12.5 Hz) and at δ = 5.57 and 6.53 (br. s). The benzene ring proton signals (δ = 6.95 and 6.99) are only slightly affected by the potential paramagnetic ring current effect of the facing COT ring because of its tub-shaped geometry (Figure 5).

The crystal structures of the COT-phane **6** and the semibullvalenophane **13** are consistent with their ^{1}H NMR spectroscopic data. The cyclopropyl ring of **13** is significantly distorted to a degree similar to that in [3$_4$]semibullvalenophane **(16)**. One of the bond lengths of the three-membered

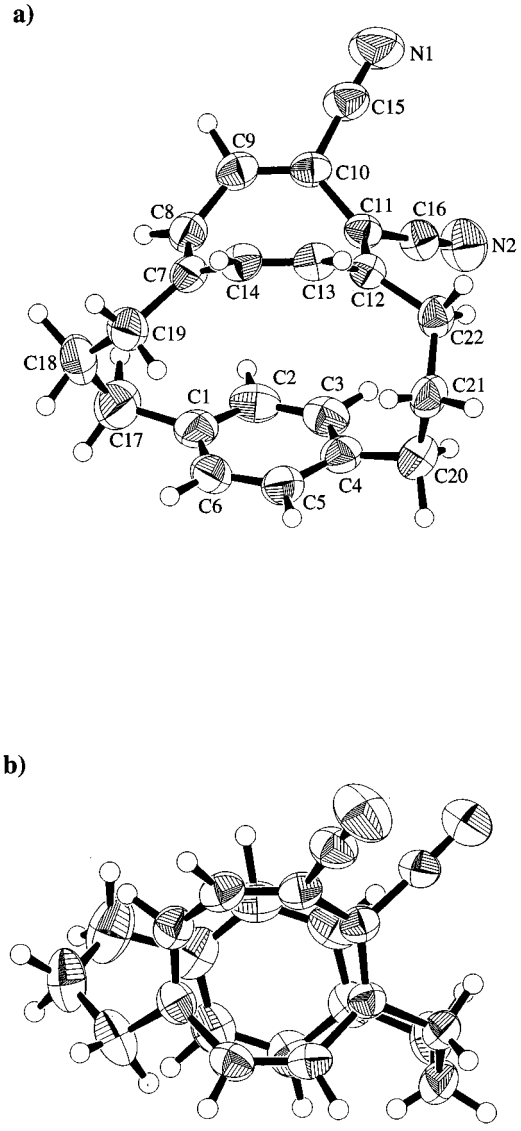


Figure 5. ORTEP drawings: (a) side view, (b) top view, of **6** with ellipsoids drawn at a 50% probability level; selected bond lengths [Å], angles [°], and torsion angle [°]: C7−C8 1.342(5), C8−C9 1.451(5), C9−C10 1.342(4), C10−C11 1.496(4), C11−C12 1.352(4), C12−C13 1.468(4), C13−C14 1.342(5), C7−C14 1.474(5), C1−C7 3.205(4), C2−C9 4.278(5), C4−C12 3.414(4), C13−C5 4.223(5); C8−C7−C14 123.7(3), C7−C8−C9 126.9(3), C14−C7−C8−C9 0.3(5)

ring in **13** is abnormally long [C17−C18, 1.630(5) Å] compared with the other two [1.525(5) and 1.535(5) Å] as well as the longest bond length (1.601 Å) in the cyclopropyl ring of **16**.[4] In accordance with the unusually long bond length, the C17−C16−C18 angle is widened from the regular 60° to 64.4(2)°. The C14−C15−C19 angle measures 98.5(3)° (Figure 6). The nonbonding distances between C14−C19 and C13−C20 are 2.322(5) and 3.066(5) Å, respectively.

The COT deck of **6** has a tub-shaped geometry with alternating single and double bond character, and the cyano groups are twisted out of conjugation.[12a] The dihedral angles between the least-square planes, i.e. the C9−C10−C13−C14 and C14−C7−C8−C9 planes as well as the C9−C10−C13−C14 and C10−C11−C12−C13 planes, are 38.7° and 38.2°, respectively. Bond shifts in COT

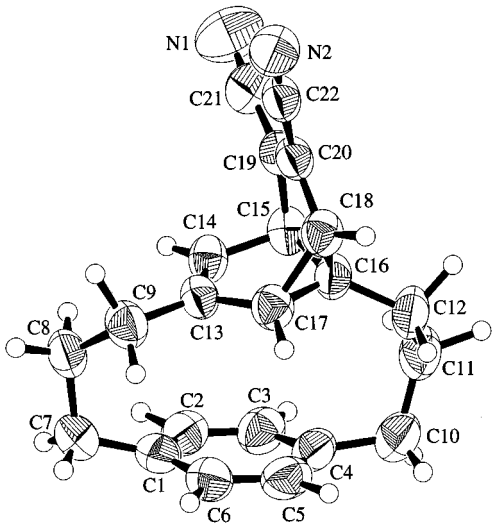


Figure 6. ORTEP drawing of **13** with ellipsoids drawn at a 50% probability level; selected bond lengths [Å] and angles [°]: C13−C14 1.319(5), C13−C17 1.473(5), C14−C15 1.519(5), C15−C16 1.536(5), C15−C19 1.546(5), C16−C17 1.525(5), C16−C18 1.535(5), C17−C18 1.630(5), C18−C20 1.462(5), C19−C20 1.355(4), C13−C20 3.066(5), C14−C19 2.322(5); C17−C16−C18 64.4(2), C14−C15−C19 98.5(3)

derivatives are generally observed,[21] but such isomers are not observed in the case of **6**, neither in the crystal nor in solution, presumably because of a high energy barrier in these ring-constrained COT derivatives.[12,21] The transannular distances between the least-square planes, C1−C6−C4−C3 and C7−C8−C11−C12 as well as C1−C6−C4−C3 and C9−C10−C13−C14, amount to 3.22 and 3.98 Å (Figure 5, a). The benzene and COT rings are completely overlapped, forming an electron-rich cavity of sufficient volume to accommodate metal species (Figure 5, b).

COT itself is reduced to its dianion through a two-electron transfer, with a reduction potential ($E_{1/2}$) of −1.61 V,[22] whereas [2_2](1,6)cyclooctatetraenyl(1,4)cyclophane has been reported to show two irreversible one-electron reduction waves at −2.36 and −2.69 V.[12a] The COT dianion is known to be planar; therefore the ease of reduction of COT is associated with the energy required to form the planar ring of the dianion. Cyclic voltammetry of **6** in CH_3CN using nBu$_4$NClO$_4$ as the supporting electrolyte shows a reversible one-step two-electron transfer with a half reduction potential $E_{1/2}$ of −0.99 V. Although direct comparison of the reduction potentials of the COT rings of the two cyclophanes is impossible, the COT ring in **6** is much more readily reduced to its dianion than that in [2_2](1,6)cyclooctatetraenyl(1,4)cyclophane or COT itself, mainly due to the presence of the two electron-withdrawing cyano groups.

Conclusions

Dicyano[3_2]cyclooctatetraenophane **(6)** has been obtained from the barrelenophane **5** by direct high-pressure Hg lamp irradiation or by photosensitized irradiation in modest yields. The former method affords **6** almost exclusively, while the latter gives a mixture of **6** and semibullvalenophane **13**. We have found that the barrelenophane **5** is most effectively prepared by Diels−Alder reaction of [3_2](1,4)cyclophane **4** with DCA in refluxing xylene in a sealed ampoule. Application of high-pressure conditions resulted in a lower yield of **5**, along with the formation of trace amounts of the naphthalenophane **11** or exclusive formation of the novel 1:2 adduct **12**. Interestingly, photolysis of **13** afforded an alternative semibullvalenophane **14**. The COT deck of **6** has a normal tub-shaped geometry. Cyclic voltammetry of **6** in CH_3CN shows a reversible one-step two-electron transfer with a half reduction potential $E_{1/2}$ of −0.99 V, and the COT ring is more readily reduced to its dianion than that in [2_2](1,6)cyclooctatetraenyl(1,4)cyclophane or COT itself because of the presence of the two electron-withdrawing cyano groups. The COT deck of **6** may react with lanthanide metal ions, and the preparation of lanthanide-COT-phane complexes is currently in progress.

Most new cyclophanes such as the barrelenophane **5**, the semibullvalenophane **13**, the COT-phane **6**, and the naphthalenophane **11** are obtained as racemic mixtures, and the optical properties of their enantiomers are of special interest. In preliminary studies, we found that racemic **5** was completely resolved into enantiomers by HPLC on a chiral stationary phase (Daicel Chemical Industries, Ltd, CHIRALCEL OD) eluting with hexane/2-propanol (10:90).[23] Work aimed at resolving other compounds is in progress and the results will be reported elsewhere.

Experimental Section

General: Melting points: Yanaco micro melting point apparatus MP-S3. − NMR: JEOL JNM-EX 270 (270 MHz and 68 MHz for ^{1}H and ^{13}C, respectively) or Bruker DRX600 (151 MHz for ^{13}C). For ^{1}H and ^{13}C NMR, $CDCl_3$ as solvent unless otherwise noted, TMS as internal standard. − FAB-MS: JEOL JMS110A (m-nitrobenzyl alcohol). − UV/vis: Hitachi U-3500. − IR: Hitachi Nicolet I-5040 FT-IR. − Elemental analyses were provided by the Service Center for the Elemental Analysis of Organic Compounds affiliated to the Faculty of Science, Kyushu University. − High-pressure equipment: HIKARI KOUATU KIKI high-pressure pump 5-B. − Analytical thin-layer chromatography (TLC) and column chromatography were performed on silica gel 60 F_{254} (Merck) and silica gel 60 (Merck, 40−63 μm) or activated alumina 300 (Nacalai Tesque, 300 mesh), respectively. − DMF was dried with 4 Å molecular sieves. Xylene and toluene were dried with CaH_2. CH_3CN was dried with P_2O_5. Dicyanoacetylene **2** was prepared according to literature procedures.[24] − Cyclic voltammetry was performed using a BAS100B/W (CV-50 W) system with a three-electrode cell. The working electrode was glassy carbon (GC) with a diameter of 3.0 mm. Before each experiment, the electrode was polished using 0.05 μ alumina. The scan rate was 100 mV s^{-1} on saturated 1.0 mM solutions of **6** with 0.1 M nBu$_4$NClO$_4$ in CH_3CN as the supporting electrolyte. Potentials were scanned from 0.0 to −1.8 V with respect to the quasi-reference electrode in a single-compartment cell fitted with Ag/Ag$^+$ electrodes. The counterelectrode was a platinum tab.

X-ray Crystallographic Study: All measurements were made on a Rigaku RAXIS-IV imaging plate diffractometer using graphite-monochromated Mo-K_α radiation and a rotating anode generator.

The crystal structure was solved by direct methods [SIR-88[25] (**5**), SIR-92[26] (**6**, **8**, **13**), SHELX-86[27] (**11**), SHELX-97[28] (**12**), Table 1] and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotopically. All computations were performed using the teXsan package.[29] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137456 (**12**), -137457 (**5**), -137458 (**8**), -137459 (**13**), -137460 (**11**), and -137461 (**6**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Summary of crystallographic data and refinement details

Compound	**5**	**6**	**8**	**11**	**12**	**13**
Empirical formula	$C_{22}H_{20}N_2$	$C_{22}H_{20}N_2$	$C_{22}H_{20}N_2$	$C_{26}H_{18}N_4$	$C_{26}H_{20}N_4$	$C_{22}H_{20}N_2$
Formula weight	312.41	312.41	312.41	386.45	388.47	312.41
Crystal color, habit	colorless, prismatic	yellow, prismatic	yellow, prismatic	yellow, plate	colorless, prismatic	colorless, prismatic
Crystal size [mm]	0.35 × 0.35 × 0.25	0.50 × 0.50 × 0.40	0.50 × 0.50 × 0.40	0.50 × 0.40 × 0.20	0.35 × 0.35 × 0.20	0.50 × 0.50 × 0.40
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)
Temperature [°C]	29 ± 1	15 ± 1	15 ± 1	15 ± 1	23 ± 1	15 ± 1
a [Å]	11.4843(2)	12.757(3)	17.733(5)	10.504(8)	8.1777(4)	12.47(1)
b [Å]	11.6831(3)	9.272(2)	20.902(4)	15.748(4)	15.4790(6)	9.684(4)
c [Å]	13.7244(2)	15.616(3)	9.413(4)	13.123(4)	8.7929(5)	14.83(1)
α [°]	90	90	90	90	90	90
β [°]	108.095(2)	109.05(3)	90	110.83(1)	110.629(2)	101.93(9)
γ [°]	90	90	90	90	90	90
V [Å^3]	1750.36(7)	1745.8500	3488.9700	2028(1)	1041.66(9)	1751.7200
Z	4	4	8	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.185	1.188	1.189	1.265	1.238	1.185
$F(000)$	664.00	664.00	1328.00	808.00	408.00	664.00
μ (Mo-K_α)[cm^{-1}]	0.70	0.70	0.70	0.77	0.75	0.69
$2\theta_{max}$ [°]	55.0	55.2	55.1	55.0	55.0	54.9
No. of reflections:						
measured	3979	3520	3274	3746	2493	3410
independent	3979	3520	3274	3746	2493	3410
No. of observations [$I > 3.00\sigma(I)$]	1707	2986	2086	2770	1591	2497
No. of parameters	315	298	298	300	353	298
Reflection/parameter ratio	5.419	10.020	7.000	9.233	4.51	8.38
R	0.0399	0.0655	0.0622	0.0681	0.0314	0.0689
R_w	0.0317	0.0712	0.0623	0.0666	0.0363	0.0622
GoF	1.989	2.789	1.421	4.115	1.117	2.714
Max. Δ/σ	0.1753	0.0520	0.0698	0.0050	0.0634	0.0368
Max. Δρ [e^- nm^{-3}]	0.15	0.20	0.23	0.25	0.13	0.13

[3$_2$](1,4)Cyclophane (4):[30] To a mixture of NaH (60%, 2.08 g, 52 mmol) and DMF (800 mL),[31] a solution of 1,4-bis(bromomethyl)benzene (4.57 g, 17.3 mmol) and 1,4-bis(2-isocyano-2-tosylethyl)benzene (8.50 g, 17.3 mmol) in DMF (1000 mL) was added dropwise over a period of 10 h at room temperature. After the addition, the mixture was stirred overnight. The DMF was then removed by distillation in vacuo and the residue was diluted with MeOH. The insoluble solid was collected by filtration, washed with MeOH, and dried in vacuo at room temperature to give the cyclic TosMIC adduct[30] as a pale-brown powder (7.01 g, 68%).

To a solution of the cyclic TosMIC adduct (2.06 g, 3.46 mmol) in CH_2Cl_2 (1000 mL) was added conc. HCl (100 mL) and the mixture was stirred at room temperature for 30 min. It was then washed successively with water and brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated to dryness in vacuo, the residue was diluted with MeOH, and the solid was collected by filtration to give [3$_2$](1,4)cyclophane-2,11-dione[30a] as a pale-brown powder (0.78 g, 85%).

To a stirred mixture of KOH (13.8 g) and diethylene glycol (40 mL) at 80 °C, the diketone (4.65 g, 17.6 mmol) and 98% hydrazine hydrate (24.4 mL, 502 mmol) were added, and the resulting mixture was heated at 130 °C for 3 h and thereafter at 200 °C for 1.5 h. After cooling, the mixture was poured into water, acidified with conc. HCl, and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and the filtrate was concentrated in vacuo. Purification of the crude product by silica gel column chromatography eluting with hexane afforded **4** (2.97 g, 71%) as a white powder.

***trans*- and *cis*-5-(1,2-Dicyanovinyl)[3$_2$](1,4)cyclophanes (7) and (8):** To a solution of **4** (473 mg, 2.00 mmol) in CH_2Cl_2 (50 mL) was added dicyanoacetylene (168 mg, 2.20 mmol, 1.2 molar equiv.) and $AlCl_3$ (1.12 g, 8.40 mmol). After stirring for one day at room temperature, the mixture was poured into aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated in vacuo, and the residue was passed through a short silica gel column (hexane/acetone, 9:1) to give a mixture of **7** and **8** (237 mg, 38%), which was separated by preparative silica gel TLC (hexane/acetone, 9:1) to give **7** (82.4 mg, R_f = 0.25) and **8** (130 mg, R_f = 0.17). **7:** yellow oil. − IR (KBr): $\tilde{\nu}$ = 2195 and 2230 cm^{-1} (−CN). − ^{1}H NMR: δ = 2.11 (br., 4 H, $-CH_2CH_2CH_2-$), 2.75−2.90 (m, 8 H, $-CH_2CH_2CH_2-$), 6.20 (s, 1 H, −CH=C−), 6.67−6.85 (m, 6 H, ArH), 6.96 (s, 1 H, ArH). − [D$_6$]DMSO: δ = 2.08 (br., 4 H, $-CH_2CH_2CH_2-$), 2.69 (br., 7 H, $-CH_2CH_2CH_2-$), 2.81 (br., 1 H, $-CH_2CH_2CH_2-$),

6.69−6.85 (m, 6 H, ArH), 6.95 (s, 1 H, ArH), 7.15 (s, 1 H, −CH=C−). − ^{13}C NMR: δ = 29.1, 29.3, 35.5, 35.7, 35.9, 111.5, 114.4 (−CN), 116.7 (−CN), 128.1, 128.6, 128.9, 129.0, 129.2, 130.9, 132.6, 133.6, 134.0, 137.6, 138.3, 138.7, 139.7. − UV (CH_2Cl_2): λ_{max} (ε) = 316 nm (6690). − FAB HRMS: *m/z*: calcd. for $C_{22}H_{20}N_2$ 312.1626 [M$^+$]; found 312.1633.

8: Yellow crystals, m.p. 160.5−161.5 °C. − IR (KBr): $\tilde{\nu}$ = 2224 cm^{-1} (−CN). − ^{1}H NMR: δ = 2.09 (br., 4 H, −$CH_2CH_2CH_2$−), 2.73, 3.11 (br., 8 H, −$CH_2CH_2CH_2$−), 6.04 (s, 1 H, −CH=C−), 6.64−6.83 (m, 7 H, ArH). [D$_6$]DMSO: δ = 2.04 (br., 4 H, −$CH_2CH_2CH_2$−), 2.69 (br., 7 H, −$CH_2CH_2CH_2$−), 3.07 (br., 1 H, −$CH_2CH_2CH_2$−), 6.68−6.84 (m, 6 H, ArH), 6.88 (s, 1 H, ArH), 7.00 (s, 1 H, −CH=C−). − ^{13}C NMR (68 MHz): δ = 28.6, 29.5, 33.1, 35.4, 35.8, 111.7, 114.5 (−CN), 114.9 (−CN), 127.7, 129.4, 129.6, 129.8, 133.0, 133.6, 134.5, 137.1, 138.4, 138.7, 140.1. − UV (CH_2Cl_2): λ_{max} (ε) = 329 nm (3160). − FAB-MS; *m/z* (%) = 312 [M + H]$^+$. − $C_{22}H_{20}N_2$ (312.4): calcd. C 84.58, H 6.45, N 8.97; found C 84.74, H 6.44, N 9.02. Yellow crystals suitable for X-ray crystallography were grown by slow evaporation of the solvent from a $CHCl_3$ solution.

[3$_2$](1,4)Barrelenophanedicarbonitrile (5): A mixture of **4** (286 mg, 1.21 mmol), dicyanoacetylene (231 mg, 3.03 mmol), and dry xylene (10 mL) was heated at 150 °C for 5 h in a sealed ampoule. After cooling, the solution was concentrated in vacuo, and the concentrate was chromatographed on silica gel eluting with hexane/diethyl ether (9:1) to give recovered **4** (150 mg, 52%) and barrelenophane **5** (130 mg, 34%). **5:** colorless crystals (toluene), m. p. 198.5−200.0 °C. − IR (KBr): $\tilde{\nu}$ = 2215 cm^{-1} (−CN). − ^{1}H NMR: δ = 1.71−1.86 (m, 4 H, −$CH_2CH_2CH_2$−), 2.11−2.34, 2.29−2.39 (m, 4 H, −$CH_2CH_2CH_2$−), 2.54−2.65 (m, 4 H, −$CH_2CH_2CH_2$−), 4.21 (d, *J* = 5.94 Hz, 2 H, −CH−), 5.57−5.59 (m, 2 H, −CH=C−), 6.81, 6.91 (dd, *J* = 7.68, 1.73 Hz, 4 H, ArH). − ^{13}C NMR (68 MHz): δ = 27.5, 32.8, 36.5, 54.3 (−CH=), 114.4 (−CN), 127.8, 128.4, 129.9, 137.9, 139.2, 150.7. − UV (CH_2Cl_2): λ_{max} (ε) = 272 (1215), 279 (sh), 360 nm (541). − FAB-MS; *m/z* (%) = 312 [M$^+$]. − $C_{22}H_{20}N_2$ (312.4): calcd. C 84.58, H 6.45, N 8.97; found C 84.50, H 6.41, N 8.92. Colorless crystals suitable for X-ray crystallography were grown by slow evaporation of the solvent from a toluene solution.

Preparation of 5 Under High-Pressure Conditions: A solution of **4** (0.50 g, 2.12 mmol) and dicyanoacetylene (0.29 g, 3.81 mmol) in toluene (4 mL) was heated at 140 °C for 18 h at ca. 3000 atmospheres in a sealed 4 mL Teflon tube. After cooling, the solution was concentrated in vacuo and the residue was chromatographed on silica gel eluting with hexane/ethyl acetate (4:1) to give barrelenophane **5** (24%) and naphthalenophane **11** (trace). **11:** yellow crystals (toluene/acetone), m.p. >300 °C. − IR (KBr): $\tilde{\nu}$ = 2220 cm^{-1} (−CN). − ^{1}H NMR ([D$_6$]acetone): δ = 2.30−2.85, 3.23−3.34, 3.62−3.73, 4.15−4.24, 4.39−4.49 (m, 12 H, −CH_2−), 6.12, 6.28 (d, *J* = 7.92 Hz, 2 H, ArH), 6.45, 6.59 (d, *J* = 5.94 Hz, 2 H, ArH), 8.02, 8.16 (d, *J* = 7.59 Hz, 2 H, ArH). − ^{13}C NMR (150 MHz): δ = 31.2, 31.6, 34.6, 35.0, 35.1, 36.4, 109.1 (−CN), 114.7 (−CN), 114.8 (−CN), 115.0 (−CN), 115.6, 116.4, 119.3, 112.0, 128.0, 128.1, 128.3, 129.8, 131.9, 133.3, 134.9, 137.7, 138.3, 140.3, 148.5, 153.8. − UV (CH_2Cl_2): λ_{max} (ε) = 261 (23300), 281 (2770), 339 nm (5180). − FAB HRMS: *m/z*: calcd. for $C_{26}H_{18}N_4$ [M$^+$] 386.1531; found 386.1526. Yellow crystals suitable for X-ray crystallography were grown by slow evaporation of the solvents from a toluene/acetone (1:1) solution.

The same reaction was conducted under ca. 5500 atmospheres. The sealed 4 mL Teflon tube was heated at 80 °C for 20 h at this pressure. After cooling, the solution was concentrated in vacuo and the residue was chromatographed on alumina eluting with CH_2Cl_2 to give **12** (27%) as pale-brown crystals (CH_2Cl_2); m.p. 177.0−178.0 °C. − IR (KBr): $\tilde{\nu}$ = 2226 cm^{-1} (−CN). − ^{1}H NMR: δ = 1.55−3.04 (m, 11 H, −CH− and −CH_2−), 3.63 (br. s, 1 H, −CH−), 4.06 (d, *J* = 6.27 Hz, 1 H, −CH−), 5.39 (m, 1 H, −CH=C−), 5.64 (d, *J* = 1.65 Hz, 1 H, −CH=C−), 5.77 (m, 1 H, −CH=C−), 6.66 (d, *J* = 6.60 Hz, 1 H, ArH), 7.00−7.09 (m, 3 H, ArH). − ^{13}C NMR (151 MHz): δ = 32.3, 33.9, 34.2, 36.5, 44.3 (−CH−), 50.2 (−CH−), 51.4 (−CH−), 112.9, 113.05 (−CN), 113.14 (−CN), 113.7 (−CN), 113.8 (−CN), 126.0, 127.7, 128.1, 128.3, 129.4, 130.4, 131.6, 131.7, 132.5, 134.3, 139.1, 139.2, 144.1. − UV (CH_2Cl_2): λ_{max} (ε) = 251 (7426), 271 nm (sh). − FAB-MS: *m/z*: 389 [M + H]$^+$. − $C_{26}H_{20}N_4$·0.25H_2O (393.0): calcd. C 79.47, H 5.26, N 14.42; found C 79.29, H 5.23, N 14.09. Brown crystals suitable for X-ray crystallography were grown by slow evaporation of the solvent from a CH_2Cl_2 solution.

17,18-Dicyano[3$_2$](1,6)cyclooctatetraenyl(1,4)cyclophane (6) and [3$_2$](1,4)Semibullvalenocyclophanedicarbonitrile (13): A solution of **5** (110 mg, 0.35 mmol) in toluene (250 mL) was irradiated with a high-pressure Hg lamp (400 W) through a Pyrex filter under nitrogen for 15 min at room temperature. The solution was then concentrated in vacuo and the residue was purified by preparative silica gel TLC eluting with toluene to afford **13** (R_f = 0.3, 46.8 mg, 43%) as white crystals and **6** (R_f = 0.2, 30.9 mg, 28%) as yellow crystals. **6:** yellow crystals (toluene), m.p. 200.8−202.0 °C. − IR (KBr): $\tilde{\nu}$ = 2209 (−CN) cm^{-1}. − ^{1}H NMR: δ = 1.57−3.02 (m, 12 H, −CH_2−), 5.38, 5.42 (d, *J* = 12.5 Hz, 2 H, −CH=C−), 5.57 (br. s, 1 H, −CH=C−), 6.53 (br. s, 1 H, −CH=C−), 6.95, 6.99 (d, *J* = 7.62 Hz, 2 H, ArH), 7.07, 7.25 (d, *J* = 7.59 Hz, 2 H, ArH). − ^{13}C NMR (151 MHz): δ = 23.3, 28.5, 32.6, 33.3, 36.5, 39.1, 106.0, 110.3, 116.3 (−CN), 116.9 (−CN), 123.7, 128.1, 128.5, 129.3, 130.3, 130.9, 137.0, 137.9, 139.2, 148.6, 150.3, 165.2. − UV (CH_2Cl_2): λ_{max} (ε) = 246 nm (11900). − FAB-MS: *m/z* (%) = 313 [M + H]$^+$. − $C_{22}H_{20}N_2$ (312.4): calcd. C 84.58, H 6.45, N 8.97; found C 84.52, H 6.43, N 8.99. Yellow crystals suitable for X-ray crystallography were grown by slow evaporation of the solvent from a toluene solution.

13: Colorless crystals (toluene), m.p. >300 °C. − IR (KBr): $\tilde{\nu}$ = 2212 cm^{-1} (−CN). − ^{1}H NMR: δ = 1.20−2.64, 2.82−2.97 (m, 12 H, −CH_2−), 2.43, 2.70 (d, *J* = 6.60 Hz, 2 H, −CH−), 3.09 (d, *J* = 2.31 Hz, 1 H, −CH−), 4.94 (br. s, 1 H, −CH=C−), 6.96, 7.10 (d, *J* = 7.93 Hz, 2 H, ArH), 7.01, 7.14 (d, *J* = 7.59 Hz, 2 H, ArH). − ^{13}C NMR (68 MHz): δ = 26.0, 29.2, 29.8, 30.5, 36.0, 36.5, 52.8, 56.3, 59.3, 62.9, 113.2 (−CN), 113.7 (−CN), 114.0, 117.0, 119.3, 128.0, 129.0, 130.1, 131.8, 139.4, 139.7, 141.9. − UV (CH_2Cl_2): λ_{max} (ε) = 279 (4690), 337 nm (4040). − FAB-MS: *m/z* (%) = 313 [M + H]$^+$. − $C_{22}H_{20}N_2$ (312.4): calcd. C 84.58, H 6.45, N 8.97; found C 84.45, H 6.45, N 8.86. Colorless crystals suitable for X-ray crystallography were grown by slow evaporation of the solvent from a toluene solution.

4-{3-[4-(5-Cyanopent-4-ynyl)phenyl]propyl}benzonitrile (18): A solution of **6** (7.5 mg, 0.35 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube was irradiated with a high-pressure Hg lamp (400 W) through a Pyrex filter for 7 h at room temperature. The solution was then concentrated and the residue was separated by preparative silica gel TLC eluting with toluene to give **18** (R_f = 0.3, 5.1 mg, 68%) as a colorless oil. − IR (neat): $\tilde{\nu}$ = 2224, 2260, 2312, and 2355 cm^{-1} (−CN and −C≡C−). − ^{1}H NMR: δ = 1.85−1.99 (m, 4 H, −$CH_2CH_2CH_2$−), 2.34 (t, *J* = 6.93 Hz, 2 H), 2.61 (t, *J* = 7.76 Hz, 2 H, −CH_2−), 2.69 (t, *J* = 7.42 Hz, 4 H, −CH_2−), 7.10 (s, 4 H, ArH), 7.28, 7.57 (d, *J* = 8.25 Hz, 4 H, ArH). − ^{13}C NMR (151 MHz): δ = 18.2, 28.6, 32.4, 34.1, 34.9, 35.5, 55.7, 86.9, 105.2

(−CN), 109.7 (−CN), 119.1, 128.5, 128.6, 129.2, 132.2, 137.8, 139.7, 147.9. − UV (CH_2Cl_2): λ_{max} (ε) = 265 (1125), 338 nm (119). − FAB HRMS: *m/z* calcd. for $C_{22}H_{21}N_2$ 313.1705 $[M + H]^+$; found 313.1702.

Semibullvalenophane (14): A solution of the semibullvalenophane **13** (15.4 mg, 0.49 mmol) in toluene (5 mL) was irradiated with a high-pressure Hg lamp (400 W) through a Pyrex filter for 7 h at room temperature. The solution was then concentrated in vacuo and the residue was purified by silica gel preparative TLC eluting with toluene to give recovered **13** (R_f = 0.3, 3.3 mg, 21%) and an alternative semibullvalenophane **14** (R_f = 0.2, 4.1 mg, 27%) as a brown oil. **14:** − IR (KBr): $\tilde{\nu}$ = 2223 cm^{-1} (−CN). − ^1H NMR: δ = 1.36−2.01, 2.29−2.47, 2.91−2.93 (m, 12 H, $-CH_2-$), 2.75 (d, *J* = 2.63 Hz, 1 H, −CH−), 3.20 (d, *J* = 2.97 Hz, 1 H, −CH−), 4.71 (br. s, 1 H, −CH=C−), 6.16 (d, *J* = 2.63 Hz, 1 H, −CH=C−), 6.93−7.11 (m, 4 H, ArH). − ^{13}C NMR (151 MHz): δ = 27.1, 27.2, 27.6, 29.3, 35.8, 36.0, 44.3, 54.8, 66.0, 66.8, 101.9, 114.1 (−CN), 116.7 (−CN), 117.5, 128.6, 129.0, 129.2, 131.4, 138.5, 139.2, 148.8, 151.4. − UV (CH_2Cl_2): λ_{max} (ε) = 344 (1140), 396 nm (sh). − FAB HRMS: *m/z:* calcd. for $C_{22}H_{21}N_2$ 313.1705 $[M + H]^+$; found 313.1708.

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