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Molecular Loops and Belts

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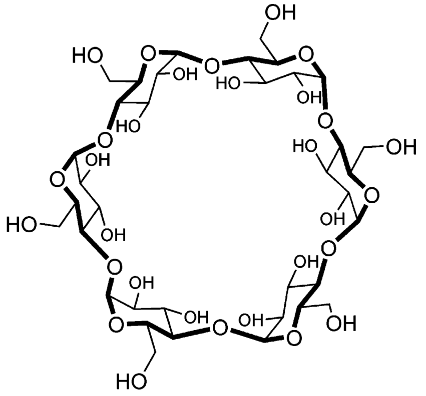
Contents

1. Introduction

Belt-like molecules have been attracting considerable interest of not only synthetic but also theoretical chemists for a number of reasons. First, belt-shaped molecules have been playing a central role in supramolecular chemistry. Because of the preorganized, defined space (cavity) inside the molecules, they form molecular complexes with a variety of guests that fit the volume, shape, and environment of the cavity. In this respect, many types of such molecules have been developed. These include, for example, cyclodextrins **1**, cucurbiturils **2** (cyclic oligomers of a bicyclic bisurea), cavitands **3**, and carcerands **4** (bridged calixresorcinarenes). The cavities of the above molecules are constructed by covalent linking of cyclic subunits—either saturated (glucose or a cyclic bisurea) or unsaturated (resorcinol)—with sp^3 carbon atoms, and therefore, the molecular frameworks are not fully conjugated. In contrast, belt-like molecules composed of conjugated π systems would exhibit unique supramolecular properties owing to not only the presence of weakly basic π bonds but also the characteristic geometry of the p orbitals. Namely, because of the deformation of the sp^2 (or sp) carbon atoms from planarity (or linearity), the p orbitals share partial s character.[1] This makes the π-electron densities along the outer and inner surfaces of the molecules different. The above polarization gives rise to unique supramolecular properties of belt-like molecules together with the shape and space recognition events.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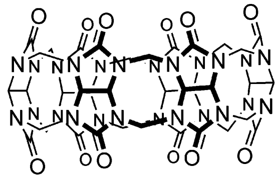
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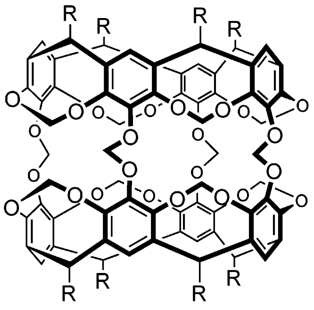
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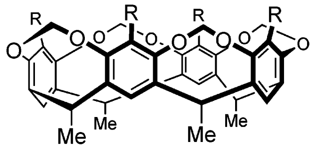
Cavitand **3**

In addition to the supramolecular aspects, the unusual geometry of the p orbitals of conjugated belt-like molecules makes them interesting targets of theoretical and synthetic studies for their own sake as novel aromatic compounds. Normally conjugated π systems consist of cyclic arrays of p orbitals that are oriented perpendicular to the molecular plane (Figure 1a). The aromatic/antiaromatic character of these cyclic arrays has been assessed based on the structural, energetic, and magnetic criteria. In contrast, belt-like molecules and the related loop-like molecules (Figure 1b), which correspond to the upper or lower rim of molecular belts, possess an unusual arrangement of p orbitals which align parallel to the molecular plane. Until recently, comprehensive aspects on their aromaticity have not been drawn, even though a number of theoretical works have been reported. On the other hand, synthetic chemists have been eager to synthesize conjugated molecular loops and belts not only because of their aesthetic attraction but also in order to assess the above-mentioned properties of unconventional π systems and develop potential applications to optoelectronic purposes.

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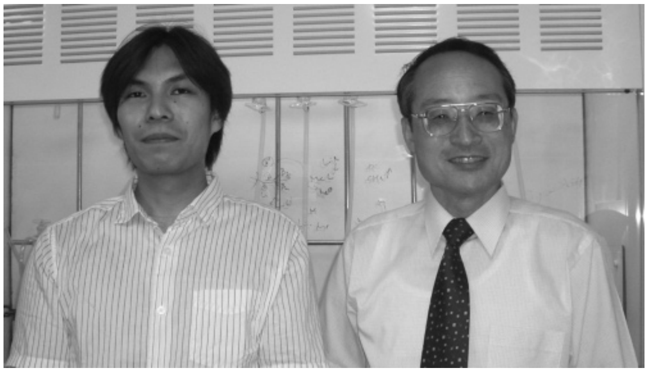


Kazukuni Tahara (left) received his B.S. degree from the School of Science and Technology, Meiji University, in 2000 and then studied at the School of Science, The University of Tokyo, obtaining his Ph.D. degree in 2005 under the direction of Professor Eiichi Nakamura. After postdoctoral work (JSPS research fellow) with Professor Yoshito Tobe at the Graduate School of Engineering Science, Osaka University, he became an assistant professor at the same institute in 2006. His current interests include synthesis of novel conjugated π-electron systems and application in supramolecular chemistry.

Yoshito Tobe (right) received his bachelor's and doctoral degrees with Professor Yoshinobu Odaira from the Faculty of Engineering, Osaka University in 1974 and 1979, respectively. After receiving his doctoral degree, he was appointed as an assistant professor at the same institute. From 1987 to 1988 he was a visiting professor with Professor Philip E. Eaton at the University of Chicago. In 1992 he moved to the Faculty of Engineering Science of Osaka University as an associate professor and was promoted to a professor in 1998. His current research interests include synthesis of strained organic molecules and novel conjugated π-electronic systems and molecular recognition and self-assembly of shape-persistent molecules. He was a recipient of the Chemical Society of Japan Award for Young Chemists in 1986.

Another motivation of this activity is how to construct the unusual conjugated architecture from flat precursors, which need to overcome enormous strain.

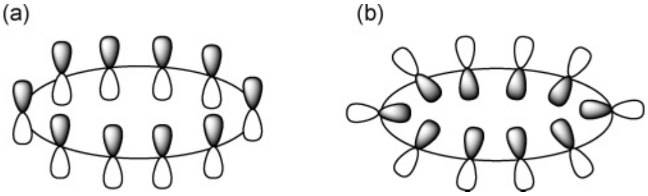
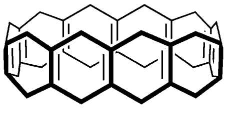


Figure 1. (a) Out-of-plane alignment of p orbitals in *normal* π-conjugated systems. (b) Unusual in-plane alignment of p orbitals in molecular loops.

From the above points of view, this review focuses on recent advances in the chemistry of conjugated loop- and belt-like molecules. Since there are several reviews that have already been published,[2] the topics included in the previous reviews will be only briefly mentioned here to avoid duplication.

Here we define molecular loops as conjugated π systems whose p orbitals align parallel to the molecular plane as shown in Figure 1b. On the other hand, there seems to be no consensus for the definition of molecular belts. They can be either fully conjugated or not. They may be wide like a champion's belt or be constricted like a kind of fashionable belt. Recently, Scott proposed a definition of true "molecular belts" as distinguished by the presence of upper and lower edges that are conjugated but never coincide, i.e., they share no atoms in common.[3] Because single-stranded "loops" are also discussed in this review, we classify molecular loops and belts on the basis of structural features (either single or double stranded) and hybridization of carbon atoms (either sp^2, sp, or both). We restrict ourselves to completely conjugated loops and belts (and their potential precursors); structurally resembling, nonconjugated, and homoconjugated cyclic π systems are not included. These are, for example, beltene (**5**),[4] oligo-1,4-bis(cyclohexylidene)s such as **6**,[5] homoconjugated alkenes such as **7**,[6] triquinacene (**8**),[7] tri-1,3-bis(cyclobutylidene) (**9**),[8] homoconjugated cyclic oligoacetylenes such as **10**,[9] and trishomocyclopropenium ion **11**,[10] all having p orbitals aligned parallel to the molecular plane. Also, concave molecules[10] such as molecular tweezers **12** and clip **13**, which share some common features with that of belt-like molecules, are not included.



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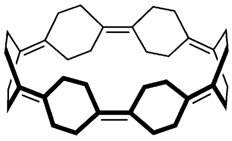

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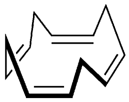

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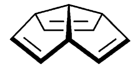

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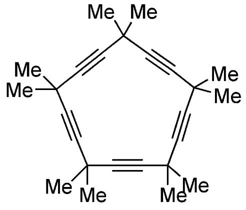

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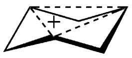

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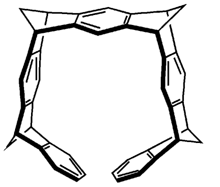

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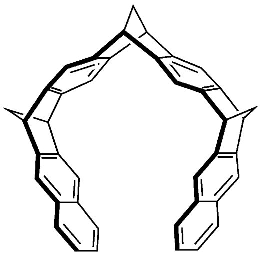

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For molecular loops, we consider (i) [*n*]trannulenes, annulenes consist of all-trans double bonds, (ii) all-*cis*-[*n*]-annulenes and their benzoannelated analogues and bridged analogues (i.e., cyclic paraphenylenes), and (iii) cyclo[*n*]-carbons, having both in-plane and out-of-plane p orbitals. For molecular belts, (i) [*n*]cyclacenes, which are regarded as double-stranded [*n*]trannulenes, (ii) cyclo[*n*]phenacenes, which correspond to double-stranded all-*cis*-[*n*]annulenes, and (iii) cyclic paraphenylene−ethynylenes, which are viewed as hybrids of cyclic paraphenylenes and cyclo[*n*]-carbons, are discussed. The representative molecules that will appear in this review are illustrated in Figure 2.

2. Single-Stranded π Systems: Molecular Loops

2.1. [*n*]Trannulenes

In large annulenes of Hückel geometry, i.e., those having π orbitals oriented perpendicular to the molecular plane, the

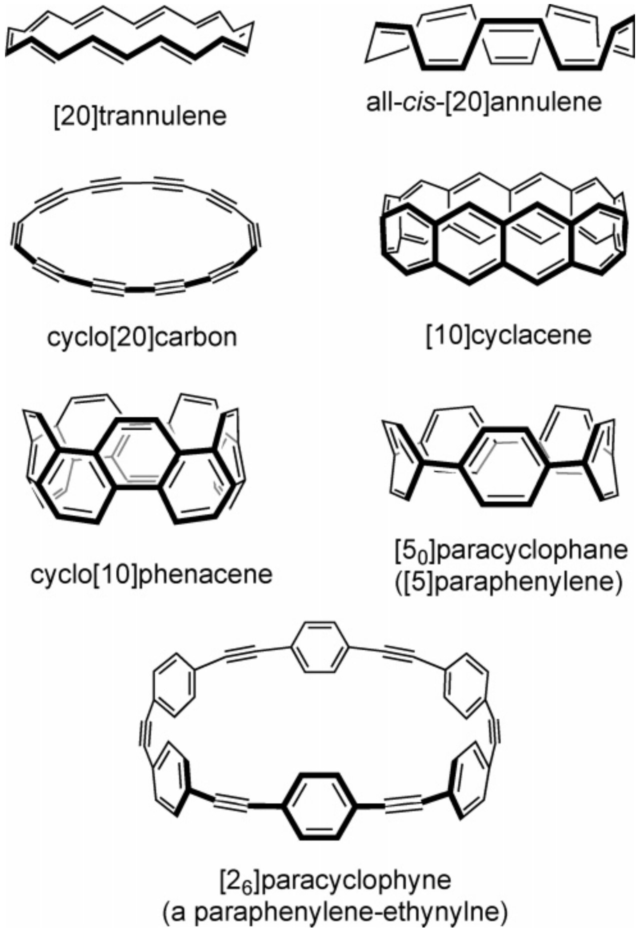


Figure 2. Representative molecular loops and molecular belts.

double bonds adopt a cis,trans configuration in order to maximize the overlap of p orbitals while minimizing the strain cost. In contrast, [*n*]trannulenes (annulenes in which the C−C double bonds in the ring are exclusively of trans configuration) have a completely different p orbital orientation: they lie parallel to the ring plane. Schleyer et al. elegantly predicted that a supporting molecular framework such as dodecahedrapentaene (**14**) would provide a suitable three-dimensional setting for such “in-plane” aromaticity of trannulenes, which are otherwise higher energy isomers of the corresponding annulenes (Figure 3).[12] All [*n*]trannulenes (where *n* refers to the number of carbon atoms) follow the Hückel rule exactly as shown in Table 1. Thus, for the $n = 4k + 2$ (k = integer) series, trannulenes adopt a D_{nd}-symmetric structure with minimal carbon−carbon bond alternation (from 1.397 Å for $n = 30$ to 1.412 Å for $n = 10$). Regarding the magnetic criteria, [$4k + 2$]trannulenes exhibit negative NICS values at the center of ring (NICS = −17.9 − −4.0) and the signals of the vinyl protons shift upfield because they are located in the diatropically shielded region owing to their perpendicular orientation over the ring faces. These results indicate that they are regarded as aromatic. In contrast, singlet [*n*]trannulenes of $n = 4k$ have a D_n-symmetric structure with strong carbon−carbon bond length alternation (1.363 vs 1.468 Å for $n = 12$, Table 1), resulting in their NICS values being significantly highly positive (NICS = 13.4−35.7). At the triplet state on the other hand, [*n*]trannulenes ($n = 4k$) have unified bond lengths, large negative NICS values (NICS = −17.7 − −15.3), and downfield shifts of the proton signals, indicating that the 4*k* electron trannulenes are aromatic at the triplet state. The small singlet−triplet energy gaps reflect the considerable aromatic stabilization of the triplet state as well as the destabilization of the singlet state.

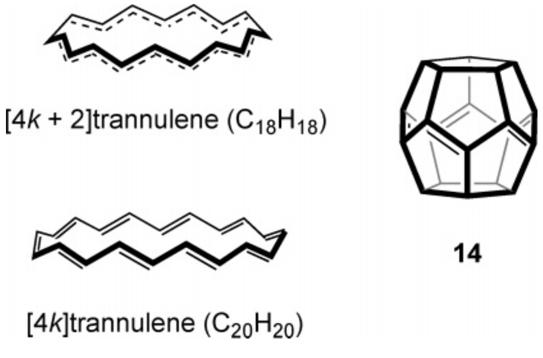


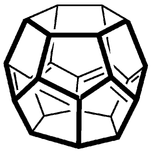
Figure 3. [*n*]Trannulenes and dodecahedratenpaene (**14**).

Table 1. B3LYP/6-31G*-Computed Geometries and Magnetic Properties of [*n*]Trannulenes[a]

formula	point group	C−C (Å)	NICS[b]	δ ^{1}H[c]	$\Delta E_{\mathrm{S-T}}$ (kcal/mol)[d]
$C_{10}H_{10}$	D_{5d}	1.412	−14.0	2.0	
$C_{14}H_{14}$	D_{7d}	1.404	−17.2	1.8	
$C_{18}H_{18}$	D_{9d}	1.401	−17.9	1.0	
$C_{22}H_{22}$	D_{11d}	1.399	−17.9	0.4	
$C_{26}H_{26}$	D_{13d}	1.398	−17.8	−0.1	
$C_{30}H_{30}$	D_{15d}	1.397	−17.8	−0.5	
$C_{12}H_{12}$	D_6	1.363, 1.468	35.7	10.6	
$C_{16}H_{16}$	D_8	1.364, 1.451	27.8	10.7	
$C_{20}H_{20}$	D_{10}	1.365, 1.442	21.6	10.3	
$C_{24}H_{24}$	D_{12}	1.366, 1.437	17.0	9.8	
$C_{28}H_{28}$	D_{14}	1.367, 1.434	13.4	9.1	
$C_{12}H_{12}$(triplet)	D_{6d}	1.412	−15.3	2.7	5.1
$C_{16}H_{16}$(triplet)	D_{8d}	1.405	−17.2	1.5	5.9
$C_{20}H_{20}$(triplet)	D_{10d}	1.401	−17.6	0.6	6.4
$C_{24}H_{24}$(triplet)	D_{12d}	1.400	−17.7	0.2	6.7
$C_{28}H_{28}$(triplet)	D_{14d}	1.399	−17.7	−0.1	7.3

[a] Reference 12b. [b] NICS (ppm) at the geometric midpoint. [c] Relative to tetramethylsilane (δ ^{1}H = 31.0 ppm). [d] Singlet−triplet energy difference.

The ab initio current density maps of [10]trannulene derivative **14** and [12]trannulene derivative **15** incorporated into the respective cage structure were calculated by Fowler et al.[13] Compounds **14** and **15** exhibit four-electron diatropicity and two-electron paratropicity, respectively, indicating that [*n*]trannulenes obey the conventional Hückel rule. Although the existence of dodecahedrapentaene $C_{20}H_{10}$ (**14**) was invoked, it awaits verification.[14]



15

Recently, Schleyer’s prediction was proved experimentally by destructing the spherical π conjugation of [60]fullerene. Taylor et al. reported the unexpected formation of $C_{60}F_{15}$-$[CBr(CO_2Et)_2]_3$ (**16**) having a 18π-electron trannulene substructure in the reaction of $C_{60}F_{18}$ with diethyl bromomalonate and 1,8-diazabicyclo[5.4.0]undec-7-ene.[15] Formation of **16** is explained in terms of the remote substitution of fluorine atoms with C−C bond formation. The unexpected

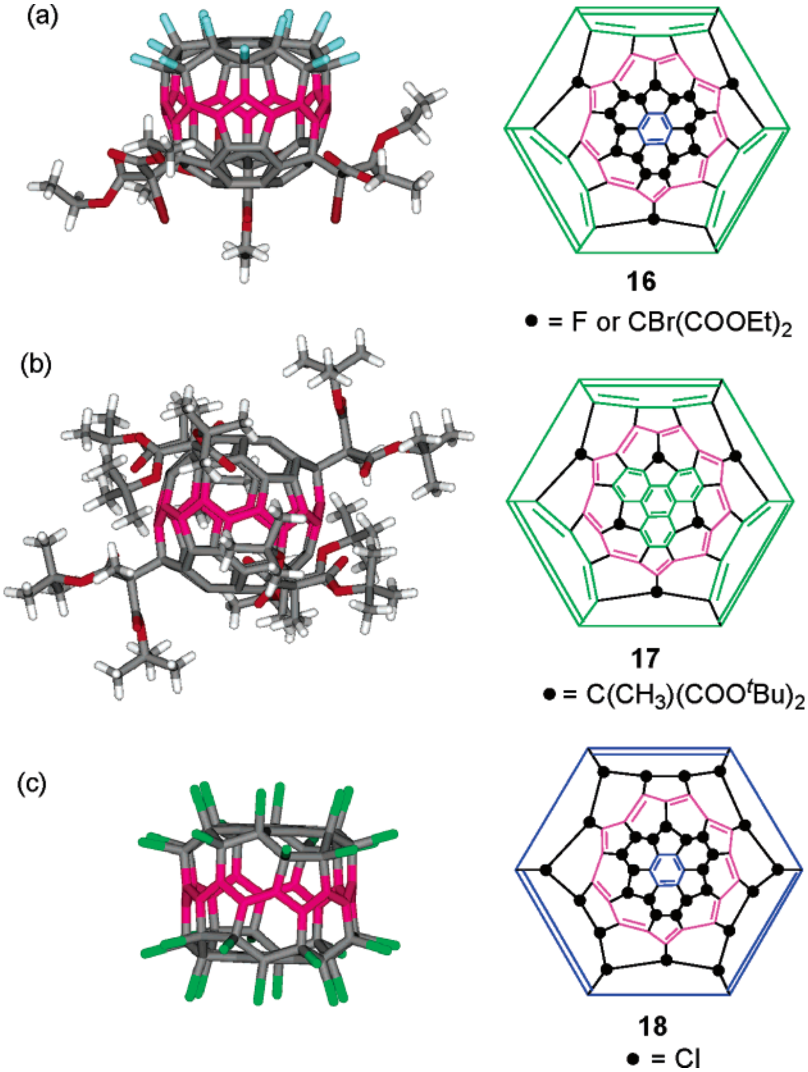


Figure 4. X-ray crystallographic structures and Schlegel diagrams of [18]trannulene derivatives (a) **16**,[15] (b) **17**,[19] and (c) **18**.[20] X-ray structures reproduced from the respective data files available from the Cambridge Crystallographic Data Centre for **16** and **18** or the American Chemical Society as Supporting Information for **17**. The red part of the structures indicates the [18]trannulene circuit.

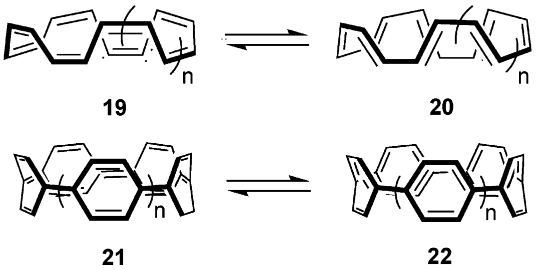
substitution at the δ position was attributed to the steric effect of the nucleophile on the basis of the results obtained using a variety of malonate esters.[16] X-ray structure analysis of **16** (Figure 4a) revealed that the all-trans 18π-electron trannulene unit is embedded in the fullerene framework and separated by sp^3 carbon atoms from the upper benzene ring surrounded by fluorine atoms and the nonplanar triphenylene unit in the bottom. The bond lengths of the [18]trannulene unit (1.392, 1.397, and 1.410 Å) exhibit little alternation, in accord with the theoretical calculations for the model compound without bromomalonate substituents (1.387−1.400 Å).[15] The calculated ring current with a maximum value of 0.151 au (cf. 0.079 au for benzene) for the 18π system of a model compound indicates a large diamagnetic circulation.[17] Owing to the highly delocalized 18π-electron system, this molecule exhibits a long wavelength absorption band (λ_{max} = 658 nm), resulting in a emerald green solution. The first reduction potential of **16** ($E_{1/2} = -0.09$ V vs Ag/AgCl) is significantly more positive than [60]fullerene due to the electron-withdrawing effects of fluorine atoms.[16] Taking advantage of the low reduction potential and kinetic stability of **16**, a number of its derivatives possessing electron-donor subunits were prepared aiming at construction of long-lived charge separation systems.[18]

Chiang et al. synthesized $C_{60}[C(CH_3)(CO_2\text{-}t\text{-}Bu)_2]_6$ (**17**) by quenching [60]fullerene hexaanion (C_{60}^{6-}) with di-*tert*-butyl bromomethylmalonate, which also contains 18π electron trannulene conjugation (Figure 4b) and exhibits intense near-infrared optical absorption (λ_{max} = 760 and 850 nm).[19] The first reduction potential of **17** ($E_{1/2} = -0.49$ V vs SEC) is similar to that of [60]fullerene. Chlorination of [60]fullerene with SbCl$_5$ was reported by Troyanov et al. to afford D_{3d}-symmetrical $C_{60}Cl_{30}$ (**18**), the third known [18]trannulene derivative.[20] Single-crystal X-ray analysis of $C_{60}Cl_{30}$ (**18**) proved that it has perfect 18π all-trans annulene conjugation which is separated from the top and bottom benzene rings by the 15-membered ring composed of sp^3 carbons (Figure 4c). Equalization of two types of trannulene bond lengths was observed by X-ray crystallography (1.381 and 1.391 Å), agreeing perfectly with the theoretical prediction.

2.2. All-*cis*-[*n*]annulenes

All-*cis*-[*n*]annulenes **19** ($n = 4k$), in which all double bonds possess s-cis conformation, may adopt a crown-like shape. Hence, these systems can be regarded as conjugated cyclic π arrays with in-plane p orbitals, even though the π orbitals are not perfectly perpendicular to the mean molecular plane and considerably tilted depending on the ring size.

Unlike [*n*]trannulenes of which bond-shifted resonance forms are identical with the original forms, the bond-shifted forms **20**, in which all double bonds adopt trans configuration with s-cis conformation, cannot maintain the crown-like morphology in order to maximize the overlap of p orbitals. Accordingly, all-*cis*-[*n*]annulenes **19** would be thermodynamically unfavorable and therefore may not exist as stable isomers unless steric or electronic constraints such as bridging or benzoannelation are exerted. Indeed, with an exception of cyclooctatetraene having all-cis-double bonds, the [*n*]annulenes ($n = 4k$) synthesized to date such as [12]- and [16]-annulenes are known to possess both cis and trans configurations.[21] In contrast, benzoannelation to all-*cis*-[*n*]annulenes **19** would fix them in the s-cis conformation, thereby maintaining their crown-like shape. On the other hand, bridging **19** with ethenylene linkages would result in oligobis(1,4-cyclohexadienylidene)s **21**, which are also regarded as their bond-shift forms, $[0_n]$paracyclophanes or cyclic oligoparaphenylenes **22**. The relative stability of **21** and **22** would depend on the ring size. In view of the structural similarity of benzoannelated or bridged all-*cis*-[*n*]annulenes with the double-stranded molecular belts, i.e., cyclophenacenes, and their possible transformation into the belt-like structures, this section deals with the benzoannelated and bridged all-*cis*-[*n*]annulenes.



19 **20**

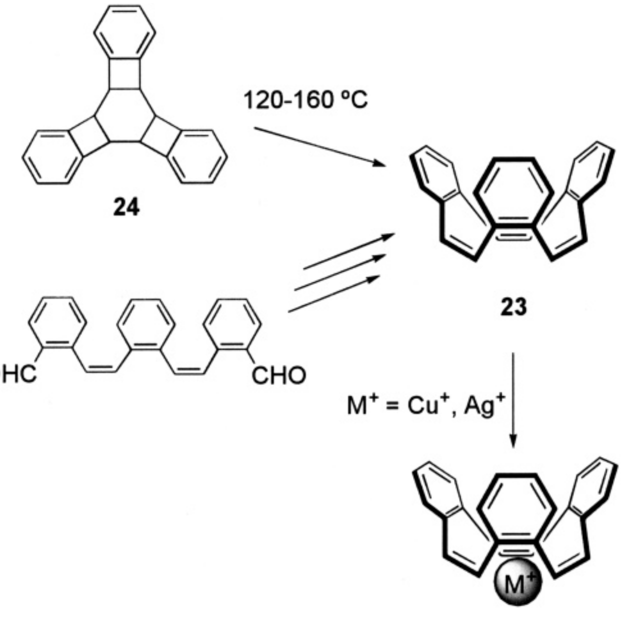
21 **22**

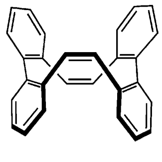
2.2.1. Benzoannelated All-cis-[n]annulenes

The structure and conformational behavior of cyclooctatetraene (COT) and its benzoannelated derivatives have been extensively studied;[21,22] COT adopts a shallow tub-shaped conformation and flips through both ring inversion and bond-shifting mechanisms with relatively low activation energies, which increase with increasing number of benzoannelation. The all-*cis*-tribenzo[12]annulene (**23**) was synthesized independently by Vollhardt et al.[23] and Iyoda et al.[24] by [2 + 2 + 2] cycloreversion of tris(benzocyclobuteno-)cyclohexane (**24**), which was obtained by either hydrogenation of tris(benzocyclobutadieno)benzene or reductive cyclotrimerization of dibromobenzocyclobutene with low-valent nickel complexes (Scheme 1). An improved synthesis of **23** was reported by Iyoda and Kuwatani et al. utilizing a pinacol coupling followed by a modified Corey−Winter dehydroxylation protocol.[24b,25] Even though an X-ray crystallographic structural analysis of **23** was not reported, in view of the absence of temperature dependence in the NMR spectra, it should have a rigid structure. Compound **23** forms complexes with Ag(I) and Cu(I) salts, of which crystal structures were determined by X-ray analyses.[24b,26] Both Ag(I) and Cu(I) ions coordinate to the double bonds of **23**, forming a basket-like framework of the all-*cis*-tribenzo[12]annulene unit.

cis,*cis*-Tetrabenzo[12]annulene (**25**) and its *trans*,*trans*-isomer **26** were first synthesized by Wittig et al.[27,28] Their structures were finally established by X-ray crystallographic analyses. X-ray analysis of **25** revealed that it adopts an approximate C_{2h}-symmetric conformation and the 12-membered ring has a crown-like shape similar to the hexabenzo derivative, hexaphenylene **28**, described later.[29] The double bonds are parallel with a transannular distance of 3.396 Å, and the dihedral angle between the twisted benzene rings is 68.7°. Its diastereomer, *trans*,*trans*-tetrabenzo-[12]annulene (**26**), was shown to possess a C_2-symmetric structure, which is only slightly deviated from a D_2 structure, with a dihedral angle of 49° between the double bond and the benzene ring.[30]

Scheme 1





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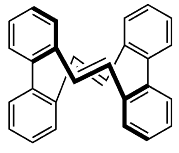

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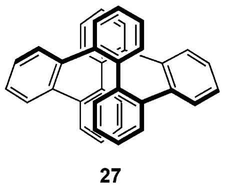

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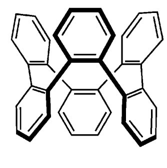

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Two atropic isomers of hexabenzo[12]annulene, one chiral **27** and the other achiral **28**, were also synthesized first by Wittig et al. from the reaction of 2,2′-dilithiobiphenyl with a variety of metal salts.[31] The chiral isomer **27** was resolved by spontaneous recrystallization or chiral chromatography on a modified silica gel even though the absolute configuration was not determined.[31b] The X-ray crystal structure of achiral isomer **28** revealed that it has a crown-like conformation with torsional angles of the inner 12-membered ring ranging from 102.5° to 110.8°, indicating little overlap of the p orbitals between the neighboring benzene rings.[32] Thermolysis of either **27** or **28** at 450−480 °C gave small amounts of products derived by C−C bond cleavage, triphenylene and *o*-terphenyltriphenylene, with no indication of dehydrogenative C−C bond formation.[31b]

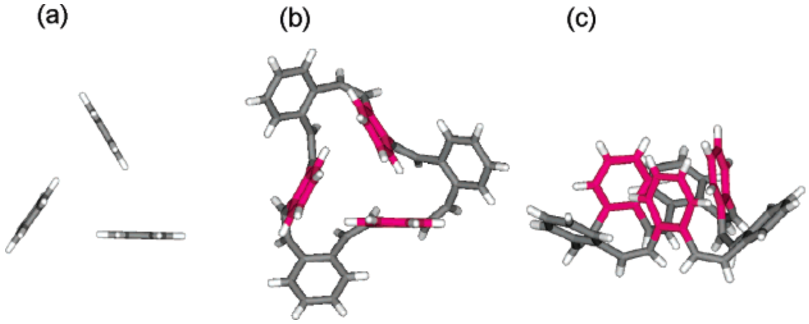
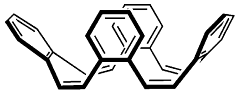


Figure 5. (a) Arrangement of benzene trimer optimized by B3LYP/6-31G*.[39b] (b) Top view and (c) side view of the X-ray crystallographic structure of hexabenzo[24]annulene **31**[33] reproduced from the data provided by courtesy of Professors M. Iyoda and Y. Kuwatani.

Tetrabenzo[16]annulene **29**, pentabenzo[20]annulene **30**, and hexabenzo[24]annulene **31** were similarly synthesized by the intramolecular pinacol coupling method.[25,33] Formation of silver complexes of **29** and **30** were also reported.[34] The structures of these large annulenes do not maintain the crown-like shape any more; the temperature-dependent ^{1}H NMR spectra of **29** indicate that it is in slow equilibrium between C_{2v}-symmetric forms at −50 °C which is time-averaged at higher temperatures.[25] The activation energy for the dynamic process was estimated to be 12.7 kcal·mol^{-1}. X-ray single-crystal analysis of **29** also showed that it possesses a C_{2v}-symmetric structure with a pair of facing benzene rings stacked at a distance of 3.4 Å.[25] Despite the structures seeming suited for C−C bond formation between the benzene rings, attempts at ring formation of **29** and **30** by chemical or photochemical activation failed to produce cyclo[8]- and cyclo[10]phenacenes, respectively.[35] In the laser desorption mass spectrum of **29**, however, a relatively weak peak attributed to the cyclo[8]phenacene cation formed by loss of eight molecular hydrogens from **29** was detected, indicating that the dehydrogenative aromatization would not be impossible.[35] Pentabenzo[20]annulene **30** is more flexible and possesses a time-averaged C_{5v}-symmetric structure in solution.[25] The molecular structure of crystalline hexabenzo[24]annulene **31** was found to be C_3 symmetric.[33] The three benzene rings are projected outward, while the remaining aromatic rings were assembled inside, with dihedral angles of ca. 60° relative to each other. The theoretically optimized structure of **31** (MP2/6-31G*) also exhibits a folded C_3 conformation with close contact between three benzene rings (Figure 5). Interestingly, this unexpected structural feature is similar to the arrangements of benzene trimer observed in gas-phase experiments[36] and obtained from theoretical calculations (MP2/6-31G*).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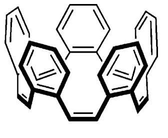
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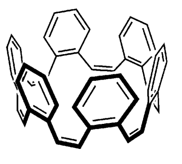
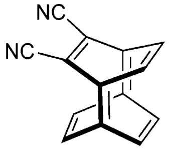

31

2.2.2. Bridged All-cis-[n]annulenes

Bridging any 1,4-position(s) of all-*cis*-[*n*]annulene would fix the conformation at least partly into the crown-like shape. The smallest molecule of this type, tricyclo[4.2.2.$2^{2,5}$]-dodecahexaene (**32**), a reactive intermediate intercepted with 1,2-dimethylenecyclopentane, was investigated by Tsuji et al. as part of his work on strained paracyclophanes since it can also be regarded as a bis(quinodimethane) form of [0_2]paracyclophane.[37] Tetrabenzo derivative **33** of **32**, first synthesized by Greene et al., is known for its stability.[38] Though this compound can be viewed as a bisquinoidomethane form of (1,9)[0_2]anthracenophane, it does not have a benzenoid structure and the two double bonds are located at the linkage between the two anthracene rings. Even though it is a bridged dibenzocyclooctatetraene derivative, there is little overlap between the p orbitals. On the other hand, in larger [0_n]paracyclophanes, effective cyclic conjugation can be attained. With increasing number of *n*, the quinodimethane form would become less favorable relative to the benzenoid form. Indeed, in the theoretical study of [0_n]paracyclophanes (n = 4, 5, and 6) it was found that [0_4]paracyclophane prefers to have the quinodimethane structure rather than the benzenoid structure whereas [0_5]paracyclophane has a D_{5d}-symmetrical benzenoid structure (Figure 6).[39] Since the phenylene units are twisted, [0_6]paracyclophane has a S_6-symmetrical structure which is 4.5 kcal·mol^{-1} lower in energy than the D_{6d}-symmetrical structure. Despite the several synthetic approaches to [0_n]paracyclophanes proposed by Vögtle,[40] only the quinodimethane form of benzoannelated [0_4]paracyclophane, “picotube” **34**, has so far been realized.



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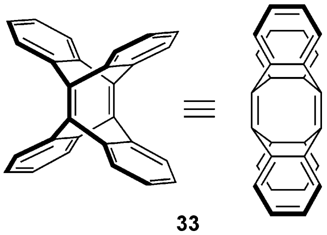
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Herges et al. used compound **33** as a starting material for the synthesis of a series of fascinating belt-shaped molecules by ingeniously exploiting the reactivity of its bridgehead double bonds (Scheme 2).[2f,41] Diels−Alder addition of **33** with a cyclobutadiene equivalent, α-pyrone or 1,2-diazine, followed by thermal electrocyclic ring opening afforded bridged all-*cis*-[12]annulene **35**.[42] X-ray crystal structure

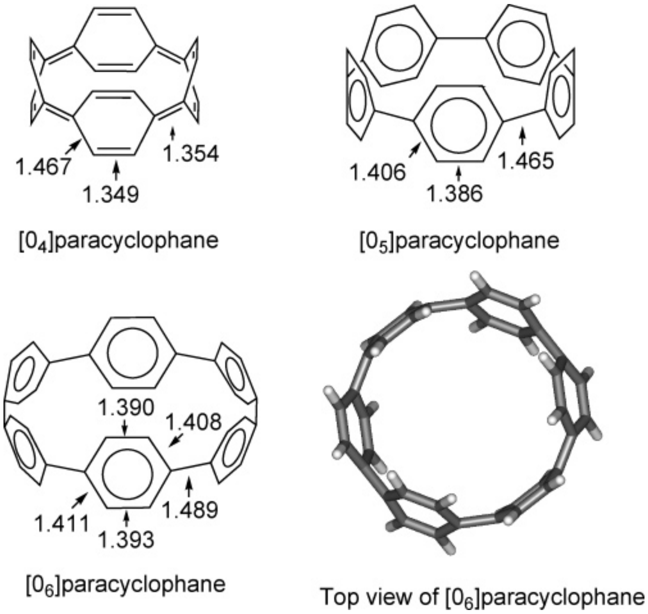
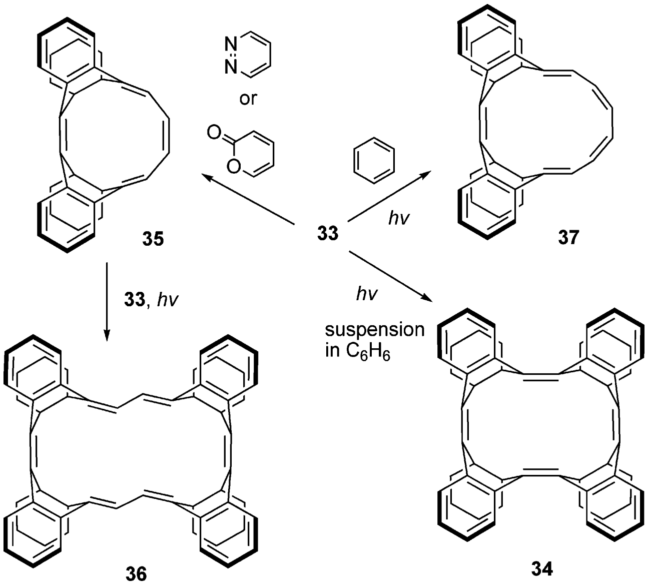


Figure 6. Optimized geometries and bond lengths (Å) (B3LYP/6-31G*) of [0_n]paracyclophanes of $n = 4, 5, 6$ (cyclic paraphenylenes).[39b]

Scheme 2



analysis of **35** revealed strong bond length alternation with 1.325−1.334 Å for double bonds and 1.478−1.479 Å for single bonds. In addition, since the double bonds of the 1,3,5-hexatriene unit are nearly orthogonal with a dihedral angle of 94.3° between the two vinyl hydrogen atoms, conjugation between the double bonds is not significant. Irradiation of **35** with **33** gave a [2 + 2] cycloadduct, which subsequently ring opened to furnish bridged all-*cis*-[20]annulene **36**, in which the 1,3-butadiene unit should have s-trans conformation.[42] Similarly, photochemical [2 + 2] cycloaddition of **33** with benzene in solution and subsequent ring opening gave bridged all-*cis*-annulene **37** with 14 conjugated π electrons in the perimeter.[43] Compound **37** was assumed to have a C_2-symmetric structure with its octatetraene unit adopting s-cis/s-trans conformation on the basis of the NOE experiments. Irradiation of **33** with tricyclo[4.2.0.0^{2,4}]octadiene, a cyclooctatetraene equivalent, gave two stereoisomeric products **38** derived from initial [2 + 2] cycloaddition followed by two successive electrocyclic ring openings. Finally, irradiation of **38** gave five isomers of bridged [16]annulenes from which two isomers with Möbius geometry (C_1 and C_2 symmetry) and one (compound **39**) with Hückel geometry (C_s symmetry) were isolated (Scheme 3).[44] X-ray crystal structure analysis of the C_s isomer **39** revealed considerable bond length alternation with 1.342−1.390 Å for double bonds and 1.455−1.486 Å for single bonds, presumably because of the large twisting of the π system and the benzoannelation effect. The geometrical, thermodynamic, and magnetic parameters calculated for the theoretical structure optimized by the DFT method (B3LYP/6-31G*) indicate that the Hückel isomer **39** is nonaromatic.[44]

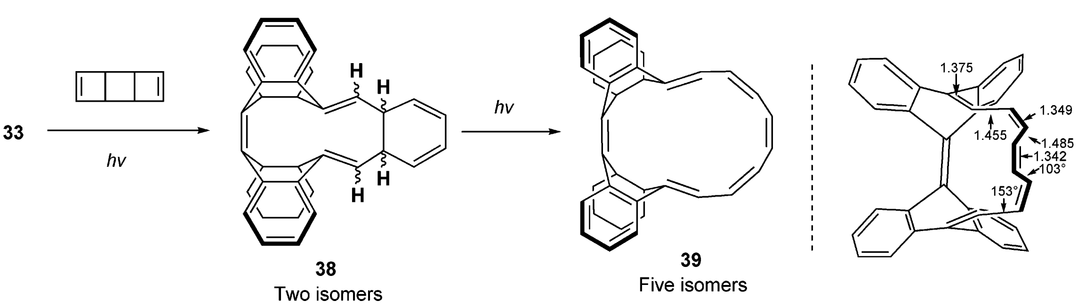
This approach was extended to the synthesis of [0_4]paracyclophane **34**, named “picotube”, which was synthesized by [2 + 2] dimerization of **33** by irradiation of solid **33** as a suspension in benzene (Scheme 2).[45] According to the X-ray single-crystal analysis and NMR spectra, picotube **34** adopts D_{4h} symmetry and its cavity has a diameter of 5.4 Å and length of 8.2 Å. However, theoretical calculations as well as low-temperature IR spectra measured at 12 K in an Ar matrix indicated that there is equilibrium between two D_{2h}-symmetrical structures (Scheme 4).[46] Under Friedel−Crafts conditions, picotube **34** reacted with ^{t}BuCl to afford octaalkylated compounds as a mixture of two regioisomers, chiral D_4- and achiral C_{4h}-symmetric isomers.[47] The enantiomer of the D_4 isomer, chiral picotube, was separated by chiral HPLC. Reaction of picotube **34** with lithium metal gave its tetraanion.[48] NMR spectra and DFT calculations indicated that the tetraanion of time-averaged D_2 symmetry is in rapid equilibrium between two C_2-symmetric structures and that two of the lithium ions coordinate to the localized double bonds within the inner domain of picotube.[48] Attempts were made for cyclodehydrogenation of picotube **34** leading to complete closure of the tube walls and formation of a short piece of a [4,4]armchair carbon nanotube.[49] However, oxidative dehydrogenation resulted in formation of polymeric materials. Dehydrogenation of **34** was also attempted by flash vacuum pyrolysis. At 800 °C, anthracene, bianthryl, tetraanthryl, and rearrangement product **40** were formed, but the purported cyclodehydrogenation product was not detected (Scheme 5).

2.3. Cyclo[*n*]carbons

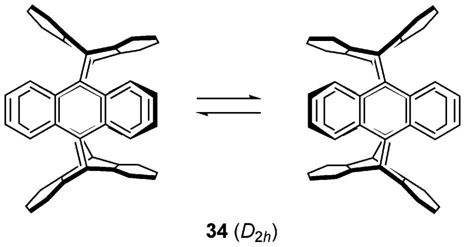
Monocyclic all-carbon molecules, known as cyclo[*n*]carbons (Figure 2), have been attracting a great deal of interest from several points of view, including molecular structure, electronic properties, astrophysical aspects, and mechanism of fullerene formation. Since this topic has been reviewed in several articles previously, only the issues relevant to molecular loops are described here.[50]

Cyclo[*n*]carbons are involved in the small carbon clusters generated by laser vaporization of graphite. Carbon clusters of the size regime of C_{10}−C_{30} are believed to have monocyclic structures on the basis of theoretical assessment, mass chromatographic behavior, and spectroscopic investigations of the mass-selected species, although the size regime differs slightly depending on whether they are neutral or positively or negatively charged.[51] Cyclo[*n*]carbons are also generated from relatively stable organic precursors of well-defined structures by their laser-induced fragmentation reactions. Figure 7 shows representative precursors developed by the groups of Diederich and Tobe. Precursor **41** was synthesized by Diederich et al., which lost three anthracene units by retro-Diels−Alder reaction, generating C_{18}^+ upon laser irradia-

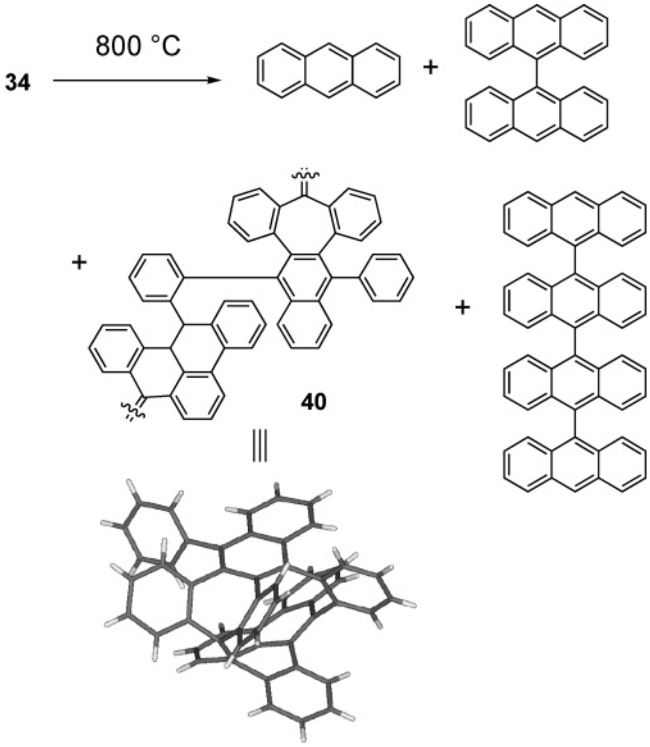
Scheme 3



Scheme 4



Scheme 5



tion.[52] Similarly, multistep decarbonylation of precursors **42a−c** having cyclobutenedione units took place in the positive and negative modes of the laser-desorption Fourier transform mass spectra, producing C_{18}, C_{24}, and C_{30} ions.[52b,53] While photoirradiation of **42a** in a low-temperature glass matrix resulted in formation of ketene intermediates and subsequent loss of carbon monoxide, definite spectroscopic evidence for formation of monocyclic C_{18} was not obtained.[52b] Dehydroannulenes **43a−c** and **44a**,**b**, having propellane units, were synthesized by Tobe et al. as precursors of cyclo[*n*]carbons of $n = 12$, 16, 18, 20, and 24.[54] In their negative-mode laser-desorption time-of-flight (LD TOF) mass spectra, they formed cyclo[*n*]carbon anions ($n = 12$, 16, 18, 20, 24) by expulsion of the Indane fragments. The structures of the carbon cluster anions (C_{12}^-, C_{16}^-, C_{18}^-, C_{20}^-, and C_{24}^-) were confirmed by comparison of the ultraviolet photoelectron spectra (UPS) with those of the mass-selected anions generated by laser vaporization of graphite.[55] Tobe et al. also utilized [2 + 1] fragmentation of radialenes **45a−d** having bicyclo[4.3.1]deca-1,3,5-triene units to produce cyclo[*n*]carbons ($n = 18$, 24, 30, 36) through isomerization of the corresponding vinylidene intermediates generated by loss of Indane fragments.[56] The negative-mode LD TOF mass spectra of **45a−d** exhibited peaks due to the corresponding carbon anions (C_{18}^-, C_{24}^-, C_{30}^-, and C_{36}^-), though their structures were not yet confirmed.

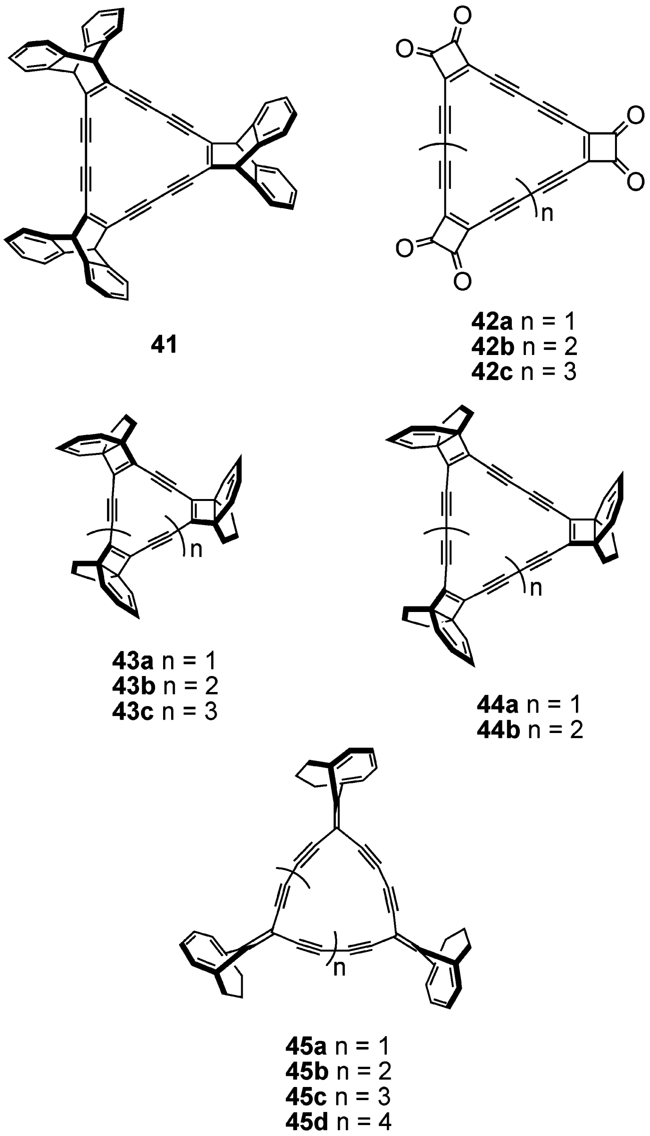


Figure 7. Structurally well-defined precursors **41**, **42a−c**, **43a−c**, **44a**,**b**, and **45a−d** of cyclo[*n*]carbons.

Table 2. Values Predicted for Magnetic Properties of [*n*]Cyclacenes[a]

n	NICS[b]	δ ^{1}H[c]
	singlet	
5	−9.6	2.6
7	−10.4	1.7
9	−6.4	1.7
11	−2.3	1.3
13	−1.7	−1.3
	singlet	
6	−32.1	2.5
8	−31.8	1.2
10	−30.0	0.6
12	−27.7	0.4
14	−25.4	0.4
	triplet	
6	−16.1	4.5
8	−17.0	3.4
10	−16.7	2.8
12	−15.8	2.5
14	−4.6	2.3

[a] Reference 67. [b] NICS (ppm) at the geometric midpoint. [c] Relative to tetramethylsilane (^{1}H = 31.0 ppm).

Cyclo[*n*]carbons possess a pair of orthogonal p orbitals: one aligning in plane and the other out of plane with respect to the molecular plane. Both types of π orbitals obey the Hückel rule and have similar level patterns of molecular orbitals. Namely, HOMOs and LUMOs of in-plane and out-of-plane π orbitals of cyclo[*n*]carbons with $n = 4k + 2$ are degenerate, whereas in the case of $n = 4k$, HOMOs and LUMOs of both types of π orbitals are nondegenerate. This also indicates that cyclo[*n*]carbons with $n = 4k + 2$ possess cumulenic structures while those with $n = 4k$ possess acetylenic forms.[50f,57] Despite their interest, spectroscopic characterization of cyclo[*n*]carbons is limited because of the difficulty in selective formation and their high reactivity. The structures of cyclo[*n*]carbons were established for the anions observed by UPS, which provides information on the electron affinity and electronic and vibrational structures of the corresponding neutral species.[51a,58] Little has been done, however, on the electronic and vibrational spectroscopy of cyclo[*n*]carbons in the gas phase or under matrix isolation,[59] even though much study has been done for linear carbon clusters smaller than C_9.[60]

3. Double-Stranded π Systems: Molecular Belts

3.1. [*n*]Cyclacenes

Heilbronner proposed for the first time a hypothetical hoop-shaped benzenoid “cyclacene” (Figure 2) and calculated the molecular orbital eigenvalues by the linear combination of atomic orbitals (LCAO) method.[61] Since then, structure,[2g,62] molecular orbitals,[2g,63] aromaticity,[64] and material properties[65] of this type of unique cyclic benzenoids have been studied. Recently, Houk et al.[66] and Kim et al.[67] independently predicted based on the DFT method (B3LYP/6-31G* and UB3LYP/6-31G*) that cyclacenes possess a double trannulene structure. Namely, bond length alternation (BLA) of the peripheral bonds is very small (within 0.01 Å), whereas that in the benzene ring is significantly large (0.3−0.6 Å), indicating the existence of trannulene conjugation along the peripheral edges and absence of aromaticity in the benzene rings. They also reported unusual magnetic properties of [*n*]-cyclacenes which are associated with the number of fused benzene rings (*n*) as compiled in Table 2. Figure 8 shows energetic and magnetic properties of [*n*]cyclacenes as a function of *n*. The singlet−triplet energy gaps (ΔE_{st}) are nearly constant and approximately zero for [*n*]cyclacenes when *n* = even. On the other hand, [*n*]cyclacenes with an odd *n* numbers favor the triplet state more than the singlet

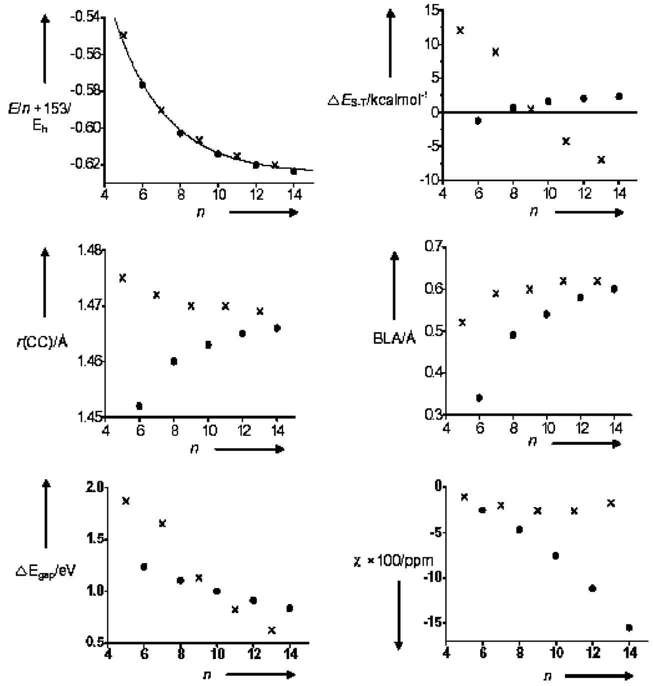
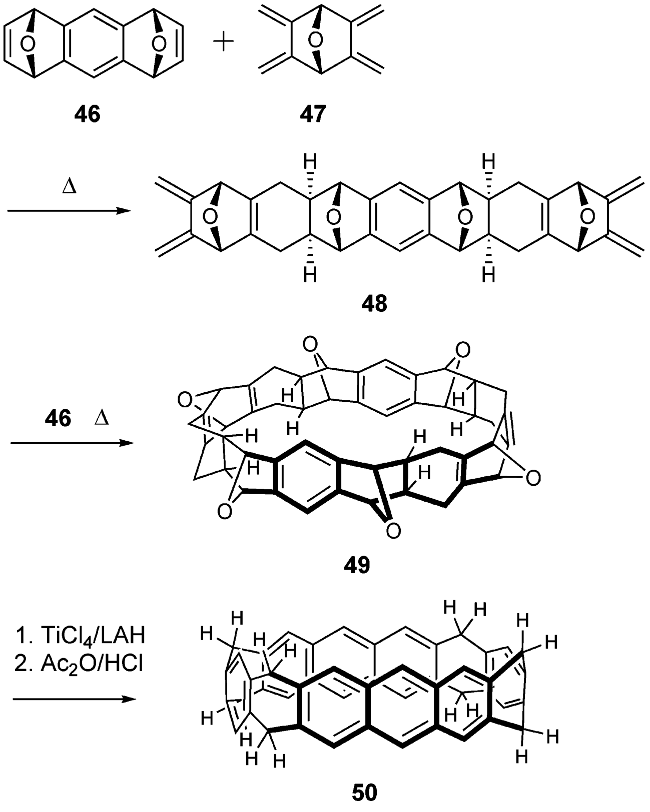
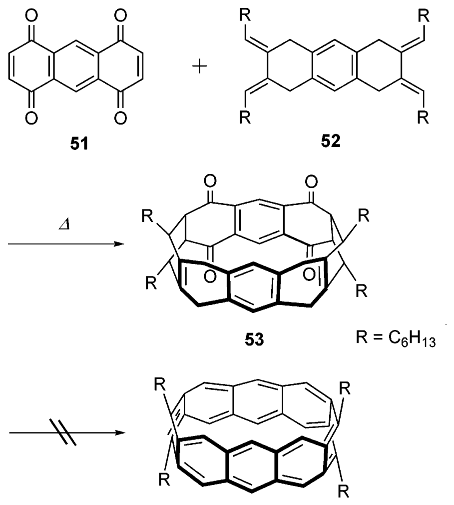


Figure 8. Building unit energy *E*/*n* (in hartree, E_h), singlet−triplet energy gap (ΔE_{S-T}), C−C bond length (*r*(CC), C denotes a carbon atom bonded to other three carbon atoms), bond length alternation (BLA), HOMO−LUMO energy gap (ΔE_{gap}), and magnetic susceptibility (χ) of [*n*]cyclacenes.[67] Reprinted with permission from ref 67. Copyright 1999 Wiley-VCH.

Scheme 6

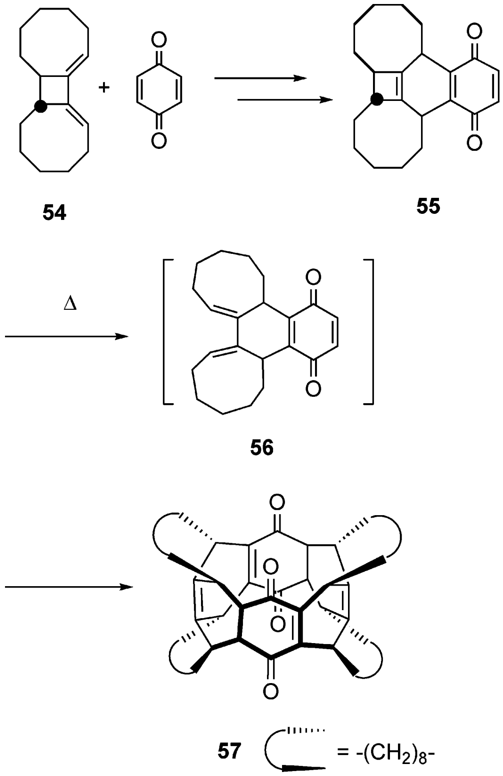


Scheme 7

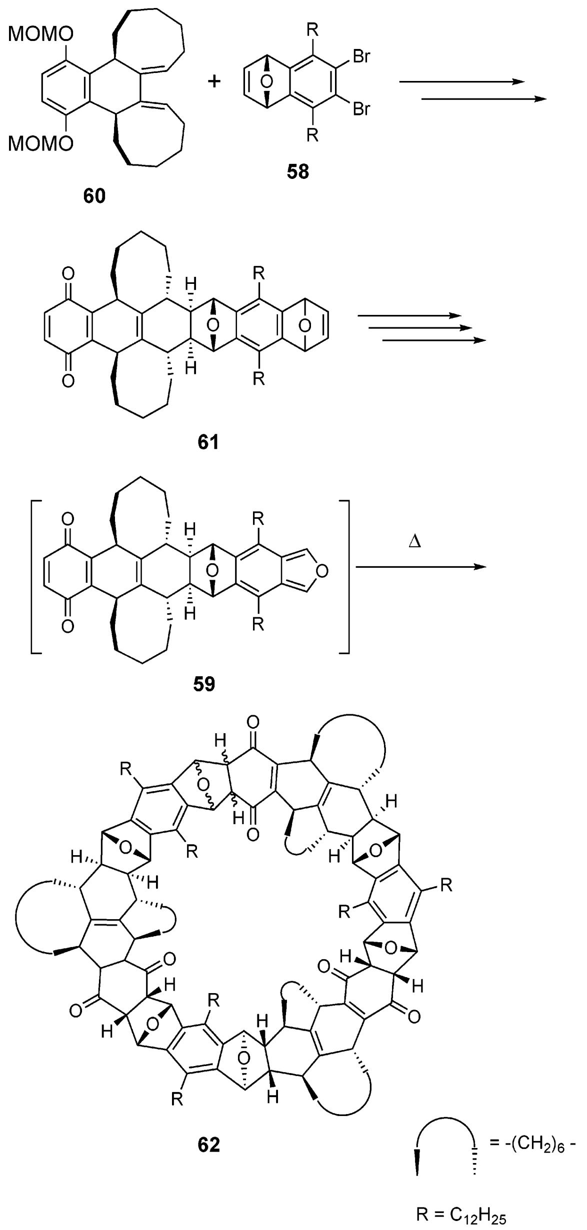


as *n* increases, while those with even *n* numbers slightly favor the singlet state. The HOMO−LUMO gap (ΔE_{gap}) of [*n*]cyclacenes with odd *n* numbers decreases rapidly (ca. 2.0 eV for $n = 5$ and ca. 0.6 eV for $n = 13$), while those of [*n*]cyclacenes with even *n* numbers decrease very slowly (ca. 1.0 eV for $n = 6-14$). Regarding the magnetic properties, [*n*]cyclacenes with $n =$ even shows more negative magnetic susceptibility (χ) and NICS values than those with $n =$ odd as shown in Table 2 and Figure 8. The susceptibility (χ) of even-number [*n*]cyclacenes decreases dramatically with increasing number of *n*, while those of odd-number [*n*]-cyclacenes are almost constant. These results indicate that odd-number [*n*]cyclacenes are nonaromatic because the aromaticity of the two constituent [$4k + 2$]trannulene units is canceled. On the other hand, triplet [*n*]cyclacenes with n = even possess aromaticity like the two constituent [$4k$]-trannulene units. The singlet [*n*]cyclacenes with $n =$ even have aromaticity nearly twice as large as those of the constituent triplet [$4k$]trannulenes, indicating that the aromaticity of the latter is concerted.

Scheme 8



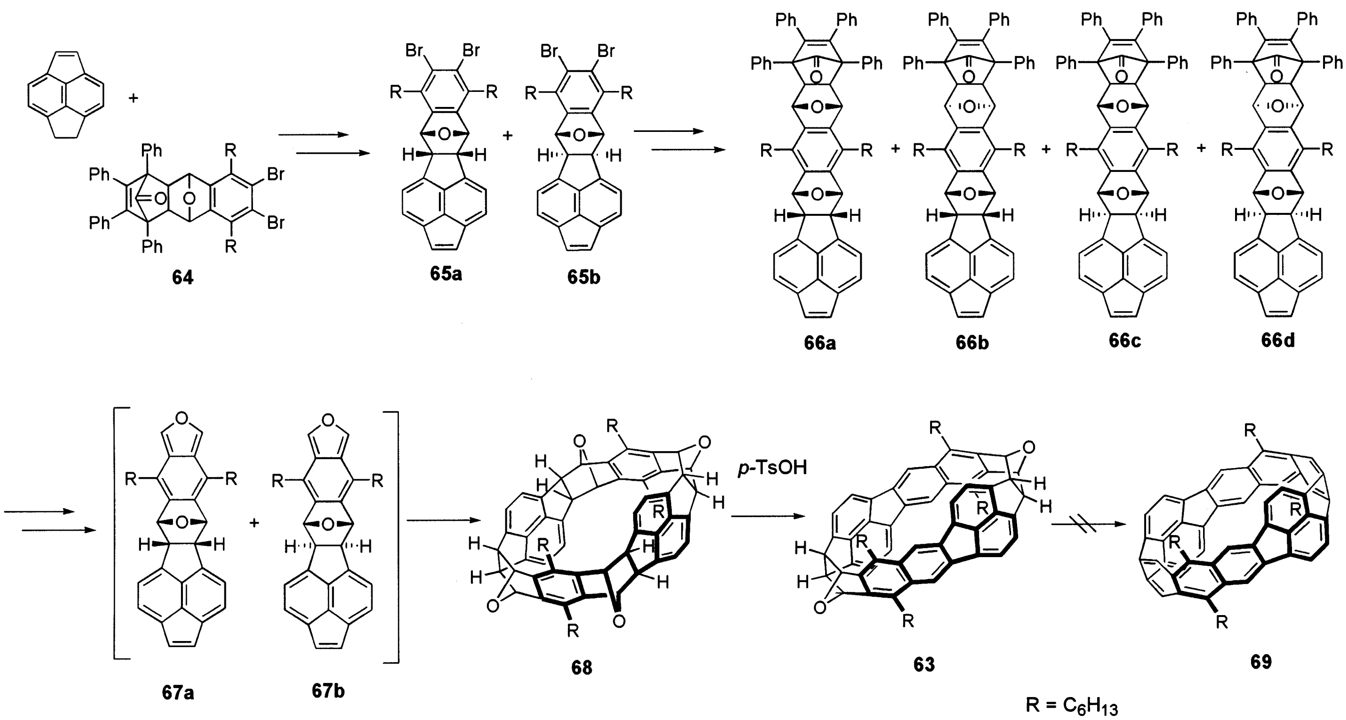
Scheme 9



In connection with the fact that [*n*]cyclacenes are considered as the shortest part of carbon nanotubes (CNTs), cyclacenes are now also a subject of interest for the broader scientific community, and a number of theoretical works have been done for tubular analogues of [*n*]cyclacenes.[65b,68]

[*n*]Cyclacenes have been one of the most fascinating yet unrealized target molecules for synthetic chemists. Synthesis of cyclacene has been attempted by the groups led by Stoddart, Cory, and Schlüter. The first two groups employed two-component Diels−Alder reaction as the key step in the construction of the belt-shaped molecular framework. Thus, Stoddart used building blocks **46** and **47**, taking advantage of the exo and endo stereoselectivity in the Diels−Alder addition of oxanorbornadiene unit of **46** and the dimethyleneoxanorbornane unit of **47**, respectively (Scheme 6).[69] Thus, 1:2 cycloadduct **48** obtained from **46** and **47** in 80% yield was reacted with another molecule of **46** in xylene under high pressure at 18 kbar to afford **49** having a [12]-

Scheme 10

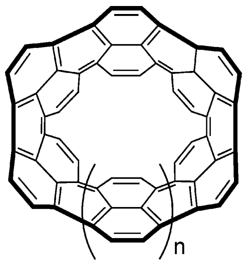


cyclacene framework in 47% yield. Deoxygenation of **49** with a low-valent titanium reagent followed by acid-catalyzed dehydration gave **50**, octahydro[12]cyclacene. Cory's approach made use of bisquinone **51** and tetramethylenetetrahydroanthracene **52**, which afforded in refluxing dioxane 1:1 adduct **53** having a [8]cyclacene framework in 67% yield (Scheme 7).[70] However, both groups have had difficulties in their attempts toward complete dehydrogenation of the above precursors of cyclacenes, and synthesis of fully conjugated belts has not been achieved.

Conversely, Schlüter et al. developed single-component Diels−Alder reactions to construct the cyclacene framework. He designed tricyclic diene **54** derived by [2 + 2] cycloaddition of cycloocta-1,2-diene as the diene part of the Diels−Alder reaction with *p*-benzoquinone (Scheme 8). Quinone **55** derived from the initial [4 + 2] adduct produced diene **56** by [2 + 2] cycloreversion upon thermolysis at 110 °C, which underwent cyclodimerization under high dilution, furnishing cycloadduct **57** possessing a [6]cyclacene framework.[71] He also designed dibromobenzooxanorbornadiene **58** which served as a precursor of "diene-dienophile" **59** (Scheme 9). Thus, reaction of **58** with diene **60** followed by treatment with butyllithium (to generate a benzyne derivative) and furan gave **61**.[72] [4 + 2] addition of tetraphenylcyclopentadienone (tetracyclone) followed by hydrolysis, oxidation, and thermolysis in refluxing toluene produced **59** having a reactive isobenzofuran moiety by retro-Diels−Alder fragmentation. This intermediate **59** underwent cyclotrimerization, furnishing **62** having a [18]cyclacene skeleton in low yield together with acyclic oligomers (7mer−14mer). Interestingly, the oligomers were in thermal equilibrium with **62**; the maximum yield of **62** (45% by NMR) was reached when oligomers were heated in Decalin.[72]

This masked "diene-dienophile" Diels−Alder strategy was also employed for synthesis of the partially unsaturated belt **63** having a central structure of D_2-symmetrical [84]fullerene (Scheme 10).[73] Here compound **64** served as a precursor of "diene-dienophile". Thus, Diels−Alder reaction of isobenzofuran generated from **64** with dihydropyracylene followed by dehydrogenation gave products **65a** and **65b**, which were converted to **66a**−**d** by cycloaddition with furan followed by tetracyclone. Retro-Diels−Alder reaction of each of the four isomers of **66a**−**d** gave the same macrocycle **68** formed via the in-situ-generated isobenzofuran derivatives **67a** and **67b**. Acid-catalyzed dehydration of **68** gave partially aromatized belt **63**. While conversion into perfect belt **69** has not been achieved, the goal does not seem too far.

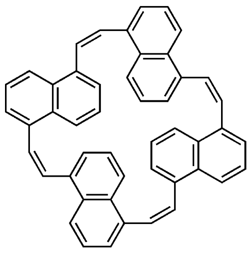
In connection with the deformed pyrenophanes, Bodwell suggested approaches to molecular belts **70a** and **70b**, also called "Vögtle belts", which represent the equators of D_{5h} [70]fullerene or D_{5d} [80]fullerene and D_{6h} [84]fullerene, respectively.[74]



70a n = 0
70b n = 1

3.2. Cyclo[*n*]phenacenes

Another type of double-stranded π system, cyclo[*n*]-phenacenes (Figure 2), has also been a synthetic targets. They are expected to be fairly stable on the basis of simple Clar's aromatic sextet rules, and it was confirmed by assessment of the topological resonance energy[64b] and semiempirical calculations.[75] Indeed, cyclo[10]phenacene, for example, manifests itself as a partial structure of [60]fullerene or single-wall [5,5] carbon nanotube, indicating the parent hydrocarbon may well exist as a stable entity. However, synthesis of cyclo[*n*]phenacenes from flat precursors must be difficult due to the large strain associated with the structural deformation. As described in section 2.2.1, attempts to synthesize cyclophenacenes from benzoannelated all-*cis*-annulene derivatives failed. Attempts have also been made by the group led by Scott to prepare precursors **71** and **72** that would be converted to cyclo[12]phenacene by flash vacuum pyrolysis.[76] Despite these attempts, none of the parent cyclo[*n*]phenacene has been synthesized yet.



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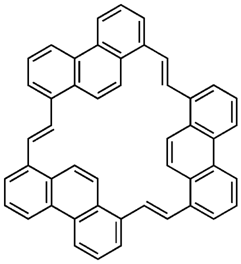

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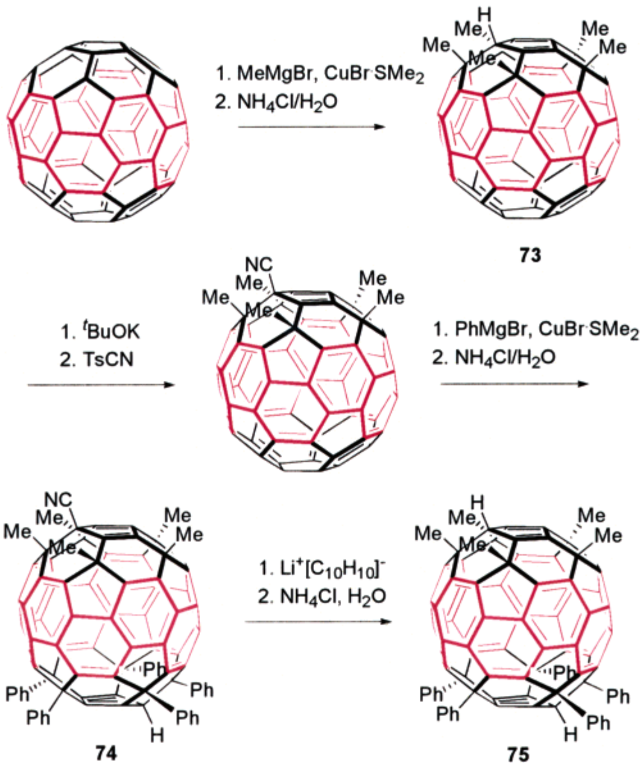
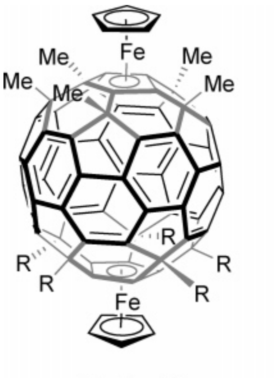
Just like the successful synthesis of [*n*]trannulene derivatives described in section 2.1, another way to create the belt-shaped conjugate system is to modify the spherical π system, i.e., fullerene structure, by regioselective, multiple addition reactions. Nakamura and Matsuo et al. succeeded in the first synthesis of cyclo[10]phenacene derivatives by the site-selective alkylation/arylation of [60]fullerene as shown in Scheme 11, where the cyclo[10]phenacene substructure embedded in the [60]fullerene framework is highlighted.[77] First, addition of the five methyl groups using an organcopper reagent to [60]fullerene took place selectively to produce $C_{60}Me_5H$ (**73**). The acidic cyclopentadienyl hydrogen was then protected with a cyano group for the subsequent manipulations. The southern pole of the fullerene cage was converted to the other cyclopentadiene structure by regioselective addition of five phenyl groups, resulting in formation of **74** having a fully conjugated, 40π-electron belt in the central part of the [60]fullerene framework. Then the cyano group was removed under reductive conditions to furnish cyclo[10]phenacene derivative **75**. The electronic absorption and emission spectra associated with this novel belt-like molecule **75** with radially orientated π orbitals were investigated.[77] It emits yellow fluorescence (λ_{max} = 560, 620 nm) with a quantum yield of 0.1. X-ray crystallographic analysis of **75** confirmed that the C(sp^2)−C(sp^2) bond lengths range from 1.37 to 1.44 Å, which agrees with the theoretical predictions derived from DFT calculations at the B3LYP/6-31G* level.[77b] The structural criteria for aromaticity and the NICS values calculated at the center of each hexagon of the cyclophenacene part of **75** (−11.46 to −11.99) and that of the parent cyclo[10]phenacene (−8.62) support that **75** as well as the parent molecule are aromatic. Similarly, the NICS values at the center of the hoops of **75** and the parent cyclo[10]phenacene are −11.58 and −7.25, respectively. The small difference in the NICS values between the two molecules is attributed to the effect of the σ skeleton.[77]

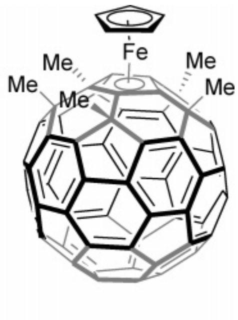
Scheme 11



Recently, “double-decker Buckyferrocenes” **76a** and **76b**, diferrocene derivatives linked by a cyclo[10]phenacene unit, were synthesized by the same group.[78] C_{5v}-symmetric **76a** was obtained from **74** or **75** by treatment with $[FeCp(CO)_2]_2$ at 185 °C, whereas D_{5d}-symmetric **76b** was prepared from monoferrocene **77**[79] by regioselective 5-fold methylation followed by metalation with $[FeCp(CO)_2]_2$. Complex **76a** exhibits two-electron oxidation waves in cyclic voltammetry at 0.08 and 0.36 V (vs Fe/Fe$^+$), the first oxidation taking place at the top iron atom surrounded by methyl groups and the second oxidation at the bottom one. The observed large difference between the first and second oxidation potentials is ascribed to electronic communication between the two ferrocene units and the electronic effect of the substituents. Decamethyl derivative **76b** exhibits oxidation waves at 0.06 and 0.17 V, supporting the above deduction. Chemical as well as electrochemical reduction of the cyclo[10]phenacene unit of **76a** took place, yielding mono- and dianions which were stable under anaerobic conditions.



76a R = Ph
76b R = Me

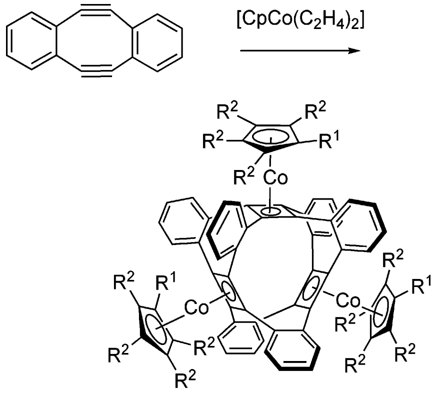


77

Subsequently, theoretical studies on a series of [5,5] and [6,6] armchair carbon nanotubes up to carbon number 210 have been performed.[80] The structure is critically dependent on the length of the tube. Analysis of the C−C bond lengths, HOMO−LUMO gaps, and NICS values indicates that their chemical properties change periodically as the tube is elongated by layer-by-layer addition of carbon atoms.

Synthesis of fully conjugated rigid belt-shaped molecules, consisting of 4π and benzoannelated 8π systems, was elegantly conducted by Gleiter et al. utilizing transition-metal-catalyzed [2 + 2] cyclodimerization of a cyclic diyne.[81] Reaction of highly reactive dibenzo[*a*,*e*]cyclooctadienediyne with $CpCo(CO)_2$ under irradiation of light afforded trimer **78a** in 14% yield (Scheme 12). By changing the cyclopentadienyl group to a pentamethylcyclopentadienyl group, the yield of trimer **78b** was improved (41%). The methyl ester or trimethylsilyl groups could also be introduced to the cyclopentadienyl group as in **78c** and **78d** by use of the corresponding cobalt complexes. Cyclic voltammogram measurement of cobalt complex **78b** showed two reversible redox processes at 0.59 and 0.84 V (vs Fe/Fe^+).

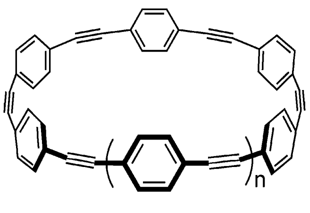
Scheme 12



78a $R^1 = R^2 = H$
78b $R^1 = R^2 = Me$
78c $R^1 = CO_2Me$, $R^2 = H$
78d $R^1 = SiMe_3$, $R^2 = H$

3.3. Cyclic Paraphenylene–Ethynylenes

Cyclic paraphenylene−ethynylenes are viewed as hybrids of cyclic paraphenylenes and cyclo[*n*]carbons, and the p orbitals align parallel to the molecular plane. Because of the pyramidalization of the sp^2 carbon atoms, the electron densities and electrostatic potentials between the inner and outer surfaces of the cyclic paraphenylene−ethynylenes are different. This property gives rise to unique supramolecular behavior of this class of compounds. Moreover, this type of molecule becomes highly reactive as the ethynylene chain lengths are elongated. Such molecules have been attracting interest as not only reactive intermediates but also precursors of carbon clusters.[50f]



79a n = 1
79b n = 3
79c n = 2
79d n = 4

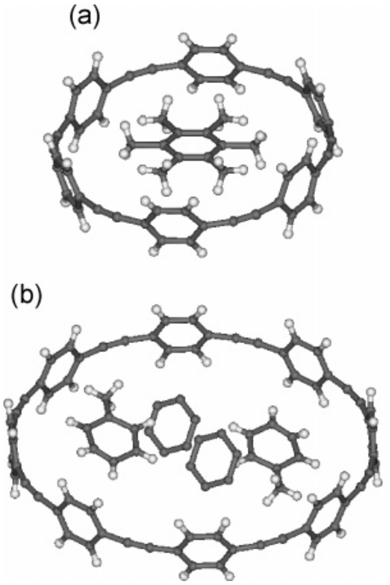


Figure 9. (a) X-ray crystallographic structures of [2_6]paracyclophyne **79a** containing hexamethylbenzene and (b) [2_8]paracyclophyne **79b** containing four molecules of toluene in their cavities.[83] Two methyl groups of the two toluene molecules are not shown because of disorder. Figures reproduced from data available from the Cambridge Crystallographic Data Centre.

Hexameric and octameric cyclic paraphenylene−ethynylenes, [2_6]- and [2_8]paracyclophynes **79a** and **79b**, respectively, were synthesized by Kawase and Oda et al. by bromination/dehydrobromination of the corresponding paracyclophenes, which were in turn obtained by the McMurry coupling of *p*-formylstyrene with a low-valent titanium reagent.[82a] An improved method for the synthesis of **79a**, **79b**, and their homologues **79c** and **79d** was also reported.[82b] X-ray crystal structure analyses of a complex of [2_6]-paracyclophyne **79a** with hexamethylbenzene and [2_8]paracyclophyne **79b** with four molecules of toluene were carried out to reveal that the diameter of the cavities of **79a** and **79b** are 1.32 nm (av.) and 1.73 nm (av.), respectively, as shown in Figure 9.[83] The benzene and the acetylene units of **79a** and **79b** are slightly deformed. The bending angles of the benzene ring of **79a** and **79b** are ca. 150° and ca. 160°, respectively, while the bond angles of the acetylene units are 164.4° (av.) and 168.8° (av.), respectively. The cavity size of **79a** should be slightly smaller than the best fit for [60]fullerene, taking into account the van der Waals distance between sp^2 carbon atoms. Indeed, X-ray analysis of the complex with a [60]fullerene derivative $C_{60}C(CO_2Et)_2$ revealed that the guest molecule is shifted from the center of the cavity to the floating position of **79a** as shown in Figure 10.[84] The mean distance between the closely located carbon atoms of **79a** and the guest is 3.4 Å, indicative of van der Waals contact between them. Moreover, the complex of **79a** with [60]fullerene is remarkably stable in solution. In benzene, the binding constant was determined to be $1.6 \times 10^4\ M^{-1}$.[84] In CD_2Cl_2, the C_{60} complex of **79a** exhibits dynamic NMR behavior with $\Delta G^{\neq} = 9.9$ kcal·mol^{-1} at −80 °C, which was ascribed to the shuttling motion of the [60]fullerene molecule between the upper and lower rims of the cavity of **79a**.[84] These strong attractive forces between the concave surface of **79a** and the convex surface of the [60]fullerene derivatives is attributed to polar electrostatic interactions due to deformation of the molecular framework of both components from planarity. That is, the electron-

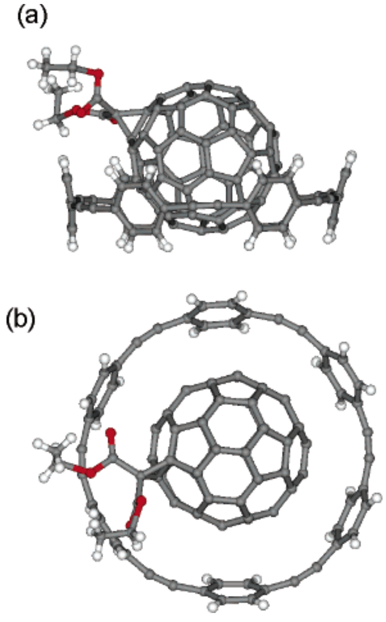
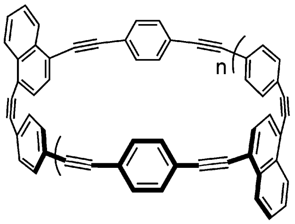
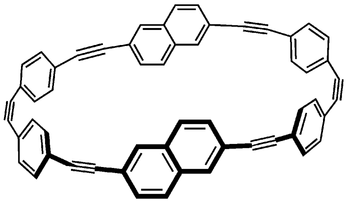


Figure 10. Side view of the X-ray crystallographic structure of the complex of [2_6]paracyclophyne **79a** with a [60]fullerene derivative.[84] Figure reproduced from data available from the Cambridge Crystallographic Data Centre.

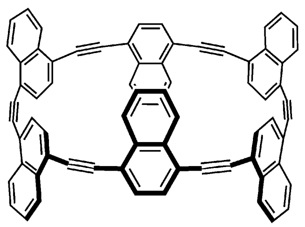
rich inner cavity of **79a** is complementary to the electron-deficient outer surface of [60]fullerene.



80a n = 1
80b n = 2



81



82

[2_6]Paracyclophynes **80a** and **81** possessing two 1,4- and 2,6-naphthylene units, respectively, were also synthesized.[85] While the cavity size of **80a** is equal to that of **79a**, the size of **81** (diameter 1.39−1.41 nm) should be larger than that of **79a**. The binding selectivity of **79a**, **79b**, **79c**, **80a**, and **81** toward [60]/[70]fullerenes was estimated by fluorescence quenching of the hosts by fullerenes.[85] The Stern−Volmer constants (K_{SV}) are listed in Table 3 together with the cavity diameter (Φ) estimated by AM1 calculations. As shown in Table 3, cyclophyne **80a** with the naphthalene units binds [60]- and [70]fullerenes more strongly than **79a**, presumably because of the increased area of van der Waals contact. However, the C_{70}/C_{60} selectivity is not significantly different because the cavity sizes are identical. The C_{70}/C_{60} selectivity of [2_7]cyclophyne **79c** is better than those of **79a** and **80a** because **79c** has a larger cavity that can accommodate [70]fullerene favorably. Most interestingly, cyclophyne **81** having 2,6-naphthylene units exhibits the largest C_{70}/C_{60} selectivity, which can be attributed to the large and slightly elliptical cavity of **81** which is complimentary to [70]fullerene. These results are consistent with the binding and dynamic behavior of **79a**, **80a**, and **81** with [60]- and [70]fullerenes observed by NMR and solid−liquid extraction.[85] The dynamic behavior of complexes of **79a** with [60]- and [70]fullerene derivatives was investigated in detail by variable temperature ^{1}H NMR, and steric and electrostatic effects of the guests on the complexation/decomplexation and shuttling motion were elucidated.[86] Interestingly, $\Delta G^{\neq}$ for the shuttling motion of C_{70} is larger than that of C_{60}, indicating the presence of "friction" at the molecular level.

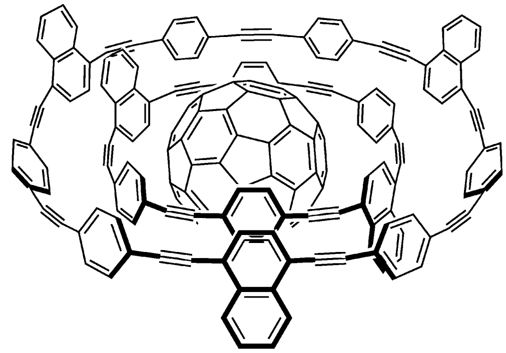
Recently, [2_6](1,4)naphthalenophyne **82** was also synthesized by the same group.[87] As expected, **82** binds fullerenes most strongly among the cyclic paraphenylene−ethynylenes studied by the group (Table 3). The Stern−Volmer constants (K_{SV}) of the complexes with [60]- and [70]fullerenes are ca. 40 and 30 times larger than those of the corresponding complexes of **80a**, respectively, as shown in Table 3.[87] Dynamic ^{13}C NMR spectra of the complex with ^{13}C-enriched [60]fullerene in $CDCl_3$ indicate that there are two dynamic processes, dissociation of the complex and interconversion between the rotational isomers of the host.[87] The barrier for dissociation ($\Delta G^{\neq} = 14.1$ kcal·mol^{-1}) is considerably larger than those of **79a** (9.9 kcal· mol^{-1}) and **80a** (10.8 kcal·mol^{-1}) in accordance with the larger stability of the **82**-[60]fullerene complex. The naphthylene units of **82** rotate freely. In contrast, in the complex with [60]fullerene, **82** adopts two major conformations, which are assumed to be $(up)_6$ and $(up)_5(down)_1$ on the basis of the ^{1}H NMR spectra (*up*/*down* indicate *up* and *down* conformations of the naphthylene unit).

Moreover, Kawase and Oda found that hexameric [2_6]-paracyclophynes **79a** and **80a** formed complexes **79d**⊃**79a** and **80b**⊃**80a** (**B**⊃**A** indicates inclusion of **A** in the cavity of **B**) with the corresponding nonameric [2_9]paracyclophynes **79d** and **80b**, respectively.[88] Namely, **79a** and **80a** were included in the cavity of **79d** and **80b**, the diameter of which (1.98 nm) fits nicely with the smaller cyclophynes **79a** and **80a**. Because of the low solubility and small complexation ability, the binding constant of **79a** with **79d** in $CDCl_3$ was only determined at −60 °C to be 340 M^{-1}. In contrast, the binding constant of **80a** with **80b** having naphthalene units is larger—340 M^{-1} at 30 °C and 11 000 M^{-1} at −60 °C—indicating the stronger $\pi-\pi$ interaction due to the larger π

Table 3. Diameters (Φ) of the Cavities of [2_n]Paracyclophynes 79a−c, 80a, 81, and 82 and Stern−Volmer Constants (K_{sv}) in Complexation with [60]- and [70]Fullerenes[a]

	79a[a]	**80a**[a]	**81**[a]	**79c**[a]	**79b**[a]	**82**[b]
Φ (nm)[c]	1.31	1.31	1.41	1.53	1.74	1.31[d]
K_{sv} C_{60} (M^{-1})[e]	7.0×10^4	2.7×10^5	2.6×10^5	5.6×10^4	$<10^4$	1.0×10^7
K_{sv} C_{70} (M^{-1})[e]	1.4×10^5	2.6×10^5	4.3×10^6	2.1×10^5	$<10^4$	7.7×10^6
K_{sv} C_{70}/K_{sv} C_{60}	2.0	1.0	16.5	3.7		0.77

[a] Reference 85a. [b] Reference 87. [c] Estimated from AM1 calculations. [d] Assumed to be the same as those of **79a** and **80a**. [e] In benzene.

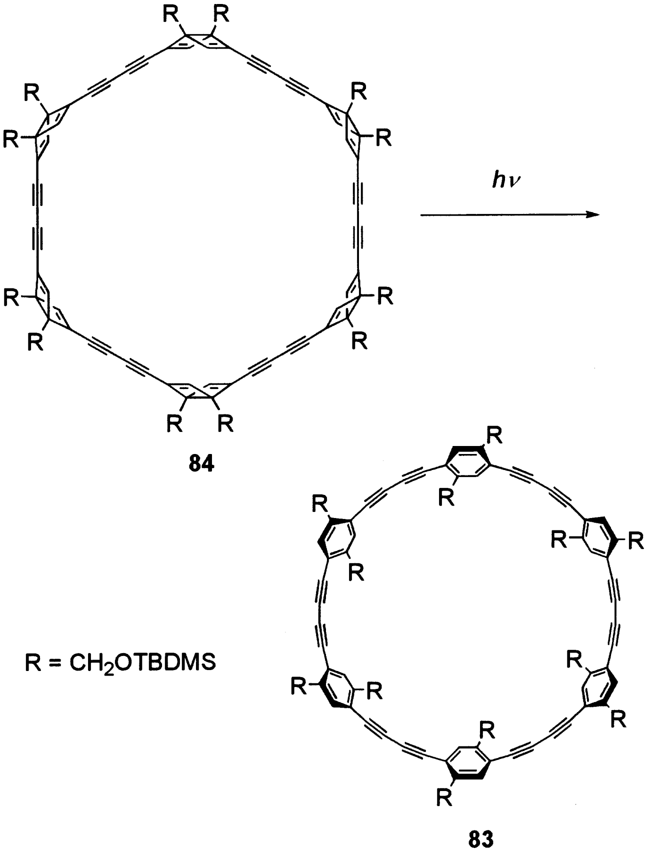


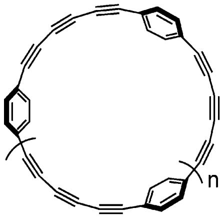
80b$\supset$**80a**$\supset$ C$_{60}$

surfaces. Moreover, complexes **79d**$\supset$**79a** and **80b**$\supset$**80a** formed double-inclusion complexes **79d**$\supset$**79a**$\supset$C$_{60}$ and **80b**$\supset$**80a**$\supset$C$_{60}$, respectively, containing [60]fullerene in the cavity of **79a** and **80a**.[88] The binding constant of **79d** with **79a**$\supset$C$_{60}$ (410 M^{-1} at -60 °C) was almost identical to that of **79d** with **79a**, indicating little effect of the included [60]-fullerene molecule on the electronic property of the convex surface of **79a**.

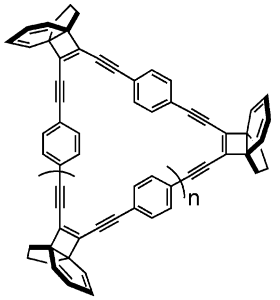
Regarding the [m_n]cyclophynes with larger cavities, Tsuji and Ohkita et al. prepared [4$_6$]paracyclophyne **83** having butadiyne units using valence isomerization of the corresponding Dewar benzene isomer **84**.[89] Thus, irradiation of **84** with a high-pressure mercury lamp gave **83** quantitatively (Scheme 13). The next larger homologues, [6$_n$]cyclophynes **85a**–**d** ($n = 3$–6), were only detected by laser desorption mass spectrometry of the corresponding precursors **86a**–**d** having propellane units which serve as the protective group of reactive hexatriyne units.[90] Upon laser irradiation, [2 + 2] fragmentation of the propellane units took place with expulsion of Indane fragments to produce the cyclophyne anions in the gas phase, which were detected by a TOF mass spectrometer.

Scheme 13



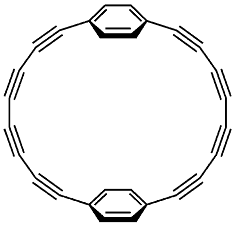


85a n = 3
85b n = 4
85c n = 5
85d n = 6

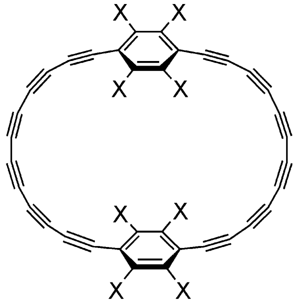


86a n = 3
86b n = 4
86c n = 5
86d n = 6

Paracyclophynes with even longer alkyne chains should be more reactive. Indeed, Haley's attempt to generate [8$_2$]-paracyclophyne **87** having octatetrayne bridges by oxidative degradation of the transition-metal complex was not successful.[91] The larger homologue **88a** having dodecahexayne bridges was generated in the gas phase from the corresponding precursor having propellane units by laser irradiation.[92] Since its octachloro derivative **88b** exhibited peaks down to C$_{36}^{-}$ due to loss of all chlorine atoms in the mass spectrum, it was assumed that the extremely reactive polyyne species was transformed into carbon cluster anion of specific molecular structure through C−C bond formation between the polyyne chains.



87



88a X = H
88b X = Cl

4. Conclusions

Recent advances in the theoretical study of molecular loops and belts have revealed new aspects of π systems exhibiting unusual topology. The experimental success/failure toward the synthesis of molecular loops and belts demonstrated that cage structures derived from fullerene frameworks which fix the π systems play a crucial role in stabilizing the otherwise elusive conjugated π systems such as trannulenes and cyclophenacenes. With knowledge of the strategy for the synthesis together with their characteristic properties in hand, it is convincingly expected that more previously unknown loops and belts would be realized soon, resulting in new potentials and applications in novel aromatic compounds.

5. Acknowledgment

We are grateful to Professor Lawrence T. Scott for valuable discussion and sending us the Ph.D. dissertations cited in ref 76 and to Professors A. Dieter Schlüter, Fritz Vögtle, and Kwang S. Kim for providing information. K.T. is grateful for a JSPS Research Fellowship for Young Scientists.

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