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Cyclophanes

1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube**

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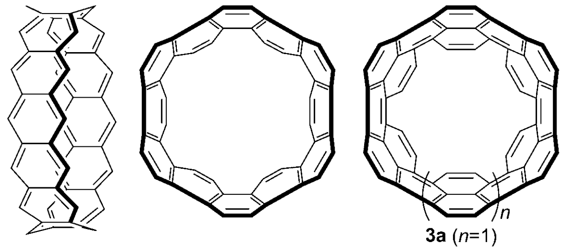
Dedicated to Professor Reginald Mitchell on the occasion of his 65th birthday

Cyclacenes, for example, [12]cyclacene (**1**; Figure 1), and cyclophenacenes, for example, cyclo[12]phenacene (**2**), are aromatic belts that map onto the surfaces of various fullerenes and single-walled carbon nanotubes (SWCNTs).[1] Indeed, they can be viewed as the shortest possible open-ended (uncapped) zig-zag and armchair single-walled carbon nanotubes, respectively.[1e] Although interest in the synthesis of aromatic belts, especially cyclacenes, predates the discovery of the fullerenes[2] and SWCNTs[3] by decades,[4] the discovery of SWCNTs and their homology to aromatic belts has engendered more intense synthetic and theoretical interest, not only in cyclacenes[5] and cyclophenacenes,[6] but also in related aromatic/conjugated belts.[7] Of particular interest to us are the Vögtle belts,[8] for example, **3**, which are armchair SWCNT segments having a pyrenoid or rylenoid motif, depending upon one's perspective.



1
[12]cyclacene
(the shortest (12,0) zig-zag SWCNT)

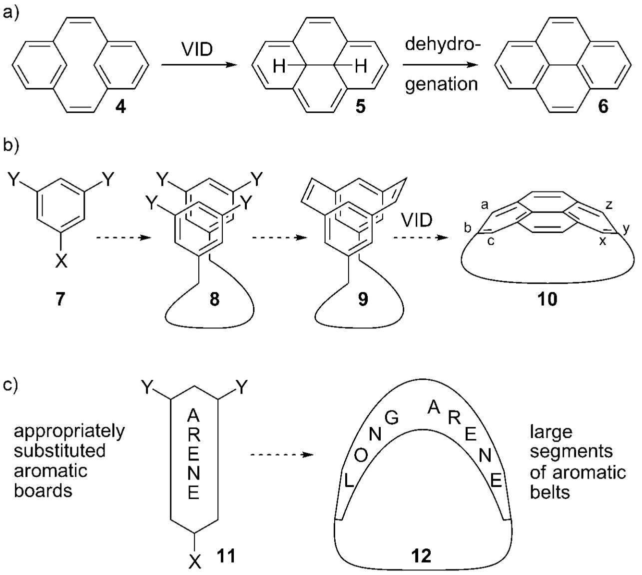
2
cyclo[12]phenacene
(the shortest (6,6) armchair SWCNT)

3a (n=1)
3b (n=2)
3c (n=3)
Vögtle belts
(short armchair SWCNTs)

Figure 1. [12]Cyclacene (**1**), cyclo[12]phenacene (**2**), and Vögtle belts **3a–c**.

A recurring theme in the numerous unsuccessful attempts to synthesize aromatic belts is the inability to aromatize partially saturated belt precursors. The interplay of two major energetic factors, strain and aromaticity, is at the heart of the problem.[9] The generation of a nonplanar aromatic system from a non- or partially aromatic precursor is inherently disfavored by the build-up of strain, but favored by the aromatic stabilization energy (ASE) of the aromatic system being formed. Increasing the distortion from planarity causes the strain energy to become larger and the ASE to become smaller. As a result, strain ultimately becomes dominant and aromatization, by standard methods such as the elimination of water, can become unfavorable. For example, the addition of water (2 equiv) to Schlüter's "double-stranded cycle" has been calculated to be exothermic by 42.2 kcal mol^{-1}.[7b] Therefore, if any approach to aromatic belts is ultimately going to be successful it will not only have to target a relatively stable structural motif, but also rely upon methodology that is capable of generating highly nonplanar aromatic systems under relatively mild conditions.

The valence isomerization/dehydrogenation (VID) reaction of [2.2]metacyclophane-1,9-diene (**4**) to give pyrene **6** is such a method (Scheme 1 a),[10] and it has been used for the synthesis of [n](2,7)pyrenophanes containing nonplanar



Scheme 1. The parent VID reaction of [2.2]metacyclophane-1,9-diene (**4**) to give pyrene (**6**), its use in the synthesis of [n](2,7)pyrenophanes (**10**) and a strategy for the synthesis of large [n]cyclophanes (**12**).

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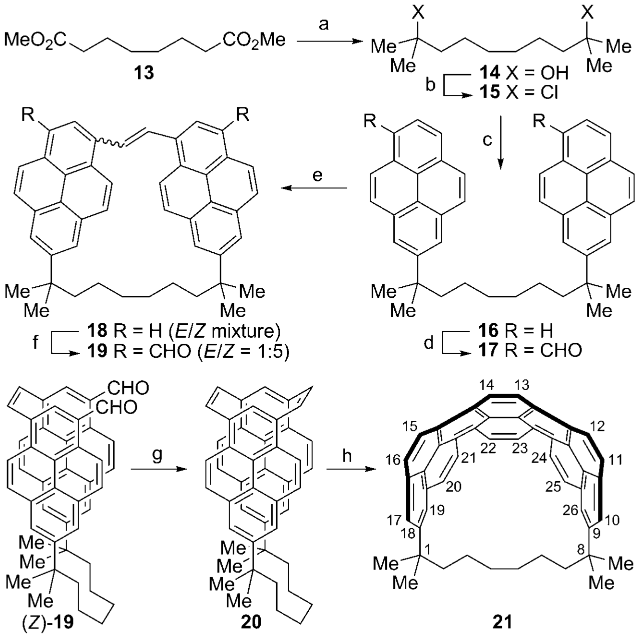
pyrene systems having deviations from planarity ranging from slight to severe.[11] The large ASE of pyrene (74 ± 1 kcal mol^{-1})[12] and the retention of the majority of this ASE,[9,11b] even in the most highly distorted geometries, are keys to the success of these reactions.

The general strategy for the synthesis of [*n*](2,7)pyrenophanes (Scheme 1 b) involves the tethering of two appropriately substituted benzene rings (**7**) to afford the tetrafunctionalized system **8**, which is then converted into the tethered *syn*-[2.2]metacyclophane-1,9-diene **9**. The VID reaction then affords the [*n*](2,7)pyrenophane **10**. Similarly, the use of an appropriately substituted aromatic "board" (**11**) would be expected to afford large [*n*]cyclophanes (**12**) containing elongated aromatic systems, which structurally resemble large segments of the Vögtle-type aromatic belts **3** and armchair SWCNTs (Scheme 1 c).

Pyrene (**6**) was identified as a viable substrate for the synthesis of an appropriately substituted aromatic board because of its predictable substitution chemistry. Specifically, electrophilic aromatic substitution occurs with very high selectivity at the 1-, 3-, 6-, and 8-positions in the vast majority of cases.[13] The one clear exception is Friedel–Crafts *tert*-butylation, which occurs exclusively at the 2- and 7-positions.[14] Both of these characteristics were exploited in the synthesis of the title compound.

The first synthetic task was to tether two pyrene units at their 2-positions, which required a dichloroalkane wherein both halides were tertiary. Dimethyl suberate (**13**) was reacted with MeMgBr to afford 2,9-dimethyldecane-2,9-diol (**14**; 86 % yield),[15] which was then treated with a concentrated aqueous HCl solution to give 2,9-dichloro-2,9-dimethyldecane (**15**; 91 % yield; Scheme 2).[16] Friedel–Crafts alkylation of pyrene (**6**) with dichloride **15** in the presence of $AlCl_3$ then furnished 2,9-dimethyl-2,9-bis(2-pyrenyl)decane (**16**; 62 % yield).

The next objective was to functionalize the pyrene units and then use the functionality to form a cyclophanediene. Although the original plan to achieve this goal involved twofold functionalization of both pyrene units, it was ultimately discovered that a stepwise functionalization/bridge-formation approach was more effective. Furthermore, the discovery that McMurry reactions could be used to directly install the *Z*-configured alkene bridges obviated the need to proceed through one or more thiacyclophane intermediates, as is the case for the [*n*](2,7)pyrenophanes.[17] Rieche formylation of **16** afforded dialdehyde **17** (88 % yield), which was subjected to an intramolecular McMurry reaction to afford [8.2](7,1)pyrenophane **18** as an inseparable mixture of *E* and *Z* isomers.[18] This structure is the first example of a pyrenophane having a (1,7)-bridging motif.[19] Rieche formylation of this mixture delivered a chromatographically separable mixture of enedialdehydes **19** [(*Z*)-**19** (57 % yield), (*E*)-**19** (11 % yield) over 2 steps]. Subjection of (*Z*)-**19** to another intramolecular McMurry reaction then led to the formation of the desired cyclophanediene **20** (41 % yield). Finally, treatment of **20** with DDQ in *m*-xylene at 145 °C brought about an efficient VID reaction, from which 1,1,8,8-tetramethyl[8](2,11)teropyrenophane (**21**) was isolated in 95 % yield as a stable and hexanes-soluble orange solid. At just eight steps from dimethyl suberate (**13**) and 10 % overall yield, the synthesis of **21** is considerably shorter than all reported syntheses of [*n*](2,7)pyrenophanes ($\geq$ 12 steps) and comparable in efficiency.



Scheme 2. Synthesis of 1,1,8,8-tetramethyl[8](2,11)teropyrenophane (**21**). Reagents and conditions: a) MeMgBr, THF, 0 °C to reflux, 10 h, 86 %; b) 12 M HCl (aq), RT, 2 h, 91 %; c) pyrene (**6**), $AlCl_3$, CH_2Cl_2, 0 °C to RT, 4 h, 62 %; d) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2, 0 °C to RT, 2 h, 88 %; e) $TiCl_4$, Zn, pyridine, THF, 0 °C to reflux, 5 h; f) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2, 0 °C to RT, 2 h, 11 % (*E*)-**19**, 57 % (*Z*)-**19**; g) $TiCl_4$, Zn, pyridine, THF, 0 °C to reflux, 4 h, 41 %; h) DDQ, *m*-xylene, 145 °C, 48 h, 95 %. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

In addition to the remarkable structural characteristics discussed below, teropyrenophane **21** is noteworthy because it is just the second teropyrene system to have been synthesized,[20] and also because teropyrene is now the largest aromatic system to have been incorporated into an [*n*]cyclophane (i.e. one aromatic system and one bridge).[21] The teropyrene system (36 carbon atoms) in **21** contains more than half of the carbon atoms in the D_{6h}-symmetric Vögtle belts **3a** (60 carbon atoms) and **3b** (70 carbon atoms). However, as outlined below, its structure (including the benzylic carbon atoms) more closely resembles a substructure of the D_{8h}-symmetric Vögtle belt **3c** (80 carbon atoms), which is, in turn, a segment of an (8,8) SWCNT.

A single-crystal X-ray structure determination of **21** revealed two independent molecules in the asymmetric unit, one of which is shown in Figure 2 (see the Supporting Information for other views).[26] In the packing diagram (see the Supporting Information) molecule A sits in pairs with a face-to-face orientation of the aliphatic chains, whereas molecule B does not. As dictated by the eight-atom bridge, each independent molecule has a highly nonplanar teropyrene unit. In the [*n*](2,7)pyrenophanes, the nonplanarity of the pyrene system is most commonly characterized by the angles formed by the adjacent planes of atoms and, more generally, by the angle (θ)[11d] formed between the two terminal planes

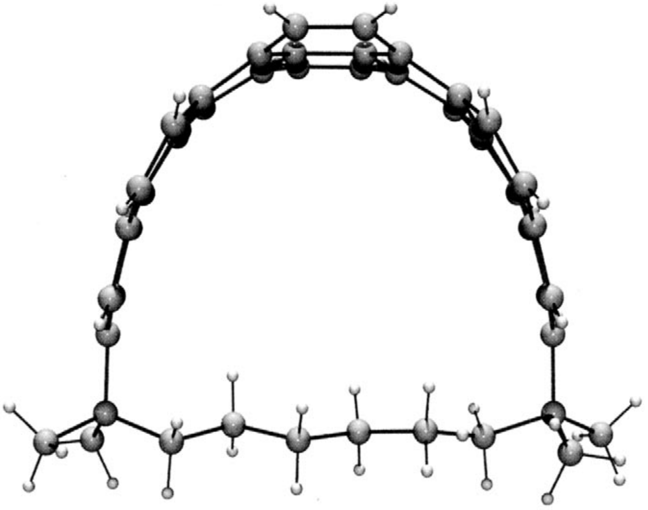


Figure 2. POV-Ray ball-and-stick representation of molecule B of 1,1,8,8-tetramethyl[8](2,11)teropyrenophane (**21**) in the crystal.

Table 1: Structural data for **21** (see Figure 3).

Metric	Molecule A	Molecule B
β_1 [°]	5.2	6.1
θ_1 [°]	68.0	67.5
θ_2 [°]	95.9	92.8
θ_3 [°]	69.8	70.4
β_2 [°]	4.7	6.5
θ_{tot} [°]	167.6	166.4
overall bend [°]	178.5	179.0
d_1 [Å]	9.033(4)	9.084(4)
d_2 [Å]	9.101(5)	9.082(4)
d_3 [Å]	9.067(6)	9.082(5)
d_4 [Å]	6.19(2)	6.12(2)

of atoms (C(a)-C(b)-C(c) and C(x)-C(y)-C(z) in **10**).[22] An analogous analysis can be applied to **21**, in which three pyrene substructures can be identified. Thus three angles (θ_1 and θ_3 for the terminal pyrene units and θ_2 for the central pyrene unit) and a total bend angle (θ_{tot} = the angle formed by the two terminal planes of atoms in the teropyrene system, that is, (C9-C10-C26 and C17-C18-C19 in 21; Figure 2) can be measured (Figure 3, Table 1). The angles (β)[23] formed by the $C_{bridgehead}$–$C_{benzylic}$ bonds and the terminal planes of the teropyrene system have also been included in the analysis for the calculation of the overall bend in the system (see the Supporting Information for a full list of angles between planes). Key distances (Figure 3, Table 1) are d_1 (distance between the bridgehead carbon atoms), d_2 (distance between the benzylic carbon atoms), d_3 (distance between the centroids of the $C_{bridgehead}$–$C_{benzylic}$ bonds), and d_4 (distance between the centroid of d_3 and the centroid of the central bond of the central pyrene unit of the teropyrene system).

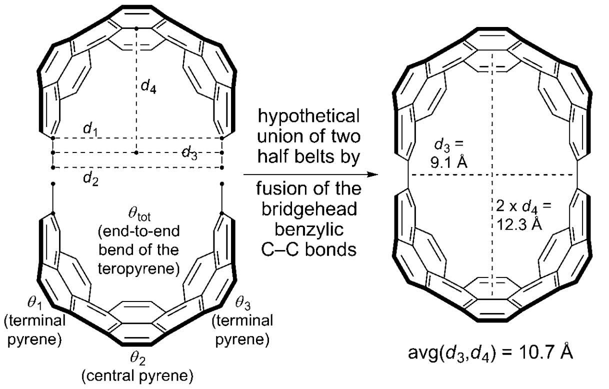


Figure 3. Parameters used to describe the structure of **21** and the hypothetical joining of two half belts to afford an ellipsoidal segment of an (8,8) armchair SWCNT.

The two independent molecules of **21** have some small local differences in their structures, but the general features are essentially the same. The teropyrene system is not far from being bent through 180° (θ_{tot} = 166.4–167.6°), which invites comparison to a Vögtle belt or an armchair SWCNT. It is useful to include the benzylic carbon atoms in the analysis. In the D_{8h}-symmetric Vögtle belt **3c** (or an (8,8) SWCNT), the bonds corresponding to the two $C_{bridgehead}$–$C_{benzylic}$ bonds in **21** are parallel. In **21**, the observed overall bend ($\theta_{tot} + y_1 + y_2 = 178.5°$ and 179.0° for molecules A and B, respectively) is indeed very close to 180°. This near-parallel orientation is also reflected in the values of d_1, d_2, and d_3 (range = 9.03–9.08 Å), which should be identical in a parallel orientation.

The two terminal pyrene units of the teropyrene system are less severely bent (θ_1 and θ_3 = 67.5–70.4°) than the central pyrene unit (θ_2 = 92.8–95.9°), which means that the cross section of the teropyrene system more closely resembles a portion of an ellipse rather than that of a circle. In fact, the hypothetical union of two half-belt systems (teropyrene + $2C_{benzylic}$) by fusion of the $C_{bridgehead}$–$C_{benzylic}$ bonds (Figure 3) affords an ellipsoidal segment of **3c** or an (8,8) SWCNT. The short axis of the ellipse measures 9.08 Å (the average value of d_3) and the long axis measures 12.3 Å (double the average value of d_4). The average of these distances is 10.7 Å, which is very close to the calculated value for an (8,8) SWCNT (10.86 Å).[24] Thus the cross section of the half-belt system corresponds to the more curved half of an ellipse. This is also reflected in the angles between planes of atoms in **21** that correspond to angles between planes related by the eight-fold symmetry in **3c** or an (8,8) SWCNT. In **21**, these angles range from 34.7° to 65.4° and average 52.1° and 52.0° for molecules A and B, respectively (see the Supporting Information), which exceed the 45° angle dictated by the eight-fold symmetry.

The ^{1}H NMR spectrum of **21** contains a set of low-field signals at δ = 8.62 (H13, H14, H22, H23), 8.39 (H12, H15, H21, H24), 7.71 (H11, H16, H20, H25) and 7.42 ppm (H10, H17, H19, H26) for the aromatic protons and a set of high-field signals at δ = 1.32 (CH_3), 0.72 (H2, H7), −0.26 (H4, H5), and −0.67 ppm (H3, H6) for the aliphatic protons. As with the [*n*](2,7pyrenophanes,[11] the anisotropic effect of the aromatic π system in **21** causes the aliphatic protons to resonate at unusually high field.

The absorption spectrum of **21** in acetonitrile (Figure 4) exhibits three major bands, each one having some fine structure. The longest wavelength maximum is observed at 489 nm. By comparison, the longest wavelength absorption maximum of teropyrene (in 1,2,4-trichlorobenzene) is reported to be at 537 nm,[20] which may suggest that, in contrast to what is observed in the [*n*]paracyclophanes[25] and [*n*](2,7)pyrenophanes,[11f] bending the teropyrene system causes a significant blue shift. The fluorescence spectrum (Figure 4, excitation at 370 nm) shows what appears to be two overlapping bands with $\lambda_{max} = 509$ and 530 nm. The fluorescence quantum yield (ϕ_{em}) is 0.11. More substantial commentary on the effect of bending the teropyrene system out of planarity on its spectroscopic properties will have to await the synthesis of other homologs of **21** or a more suitable model compound, for example, 2,11-di-*tert*-butylteropyrene, neither of which has yet been achievable in our hands using the approach described herein.

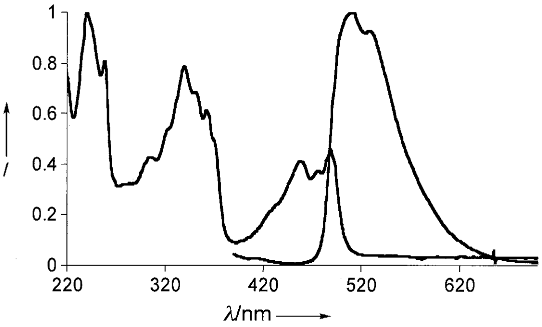


Figure 4. Normalized absorption and emission spectra of 1,1,8,8-tetramethyl[8](2,11)teropyrenophane (**21**) (9.8×10^{-6} M in CH_3CN).

In summary, a teropyrene system that structurally resembles a segment of an (8,8) armchair SWCNT has been generated by linking the 2- and 11-positions with an eight-atom aliphatic bridge. Noteworthy features of the synthesis are 1) its brevity and efficiency (eight steps from dimethyl suberate, 10% overall yield), 2) the first example of the use of a McMurry reaction to form a *syn*-[2.2]metacyclophane-1,9-diene system, 3) only the second example of a teropyrene system, 4) the first examples of (1,7) and (1,3,7) bridging motifs in pyrenophanes, and 5) the ability of the VID reaction to deliver such a large nonplanar polycyclic aromatic system. Indeed, the success of the VID reaction is cause for cautious optimism that this methodology will ultimately be capable of not only generating smaller homologs of **21**, but also complete aromatic belts that map onto the surfaces of (*n*,*n*) armchair SWCNTs. Work aimed at achieving these goals is being pursued actively in our laboratory.

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