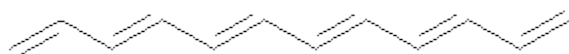


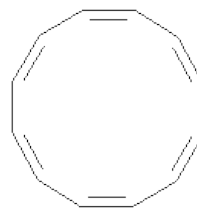
DENDRALENES

Conjugated alkenes have played a major role in conceptualizing organic chemistry. Linear and cyclic unbranched conjugated alkenes have been well studied; the latter class comprising the *aromatic* and *antiaromatic annulenes*. The cyclic branched conjugate alkenes are known as *radialenes* and have been subject of some study. But the last category, the linear branched conjugated alkenes have been overlooked. Paddon-Row and Sherburn¹ now report a general synthetic method for preparing these species, which they call *dendralenes*, see Scheme 1.

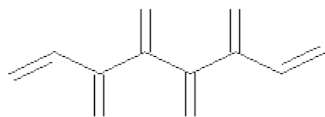
Scheme 1. Classes of conjugated alkenes



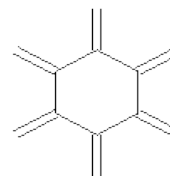
Linear unbranched



Cyclic unbranched (*annulenes*)



Linear branched (*dendralenes*)

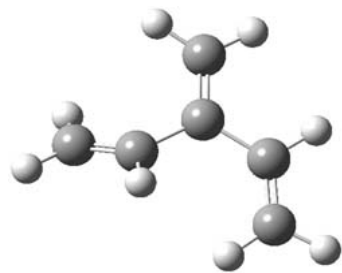


Cyclic branched (*radialenes*)

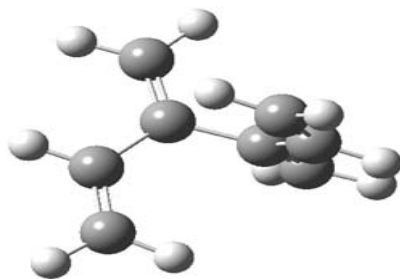
The dendralenes fall into two groups – those with an odd number of double bonds and those with an even number. While the UV/Vis absorption maximum redshifts

with increasing length, the molar extinction coefficients are relatively constant for the odd dendralenes but it increases by about 10,000 within the even dendralene family. The Diels-Alder chemistry is even more distinctive: the odd dendralenes react rapidly with an electron deficient dienophile (*N*-methylmaleimide), with rates decreasing slightly with increasing size, but the even dendralenes are significantly more sluggish.

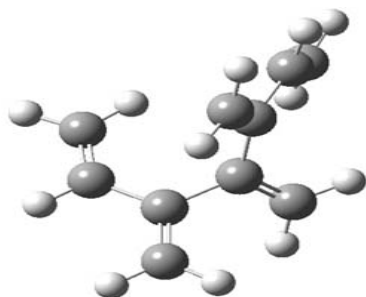
The optimized B3LYP/6-31G(d) geometries of the lowest energy conformers of the [3]- to [8]dendralenes are shown in Figure 1. There are three types of butadiene fragments present in these structures: (a) near planar *s-trans* arrangement, (b) near perpendicular arrangement of the two double bonds, and (c) *s-cis* arrangement with the dihedral angle about 40°. The even dendralenes have only the first two type: alternating planar butadiene fragment that are more-or-less orthogonal to each other. The odd dendralenes all have at least one *s-cis* arrangement. Paddon-Row and Sherburn suggest that since the *s-cis* arrangement is necessary for the diene component of the Diels-Alder reaction, the odd dendralenes are more reactive than the even ones since they have this arrangement in their ground state conformations, while the even dendralenes will have to react out of a higher energy conformation. This is a nice explanation readily formulated from simple computations.



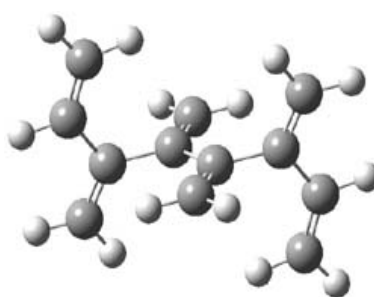
[3]dendralene



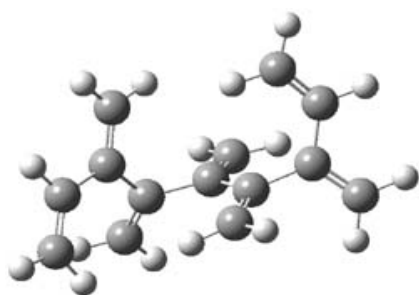
[4]dendralene



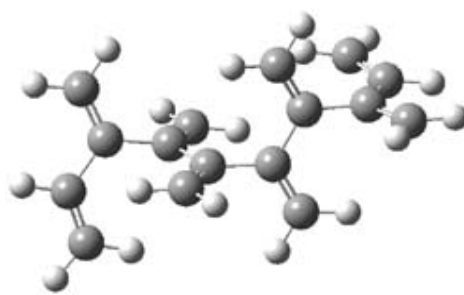
[5]dendralene



[6]dendralene



[7]dendralene



[8]dendralene

Figure 1. B3LYP/6-31G(d) optimized structures of [3]- to [8]dendralene.¹

Source: <http://comporgchem.com/blog/?p=304>