Figure 1.
Symmetry-forbidden conrotatory electrocyclizations of (a) 14π vinylogous sesquifulvalene and (b) the related 18π fulvene–hendecafulvene system reported by Prinzbach. Reactions were performed in benzene. Energetics were measure by Prinzbach.[1,2]

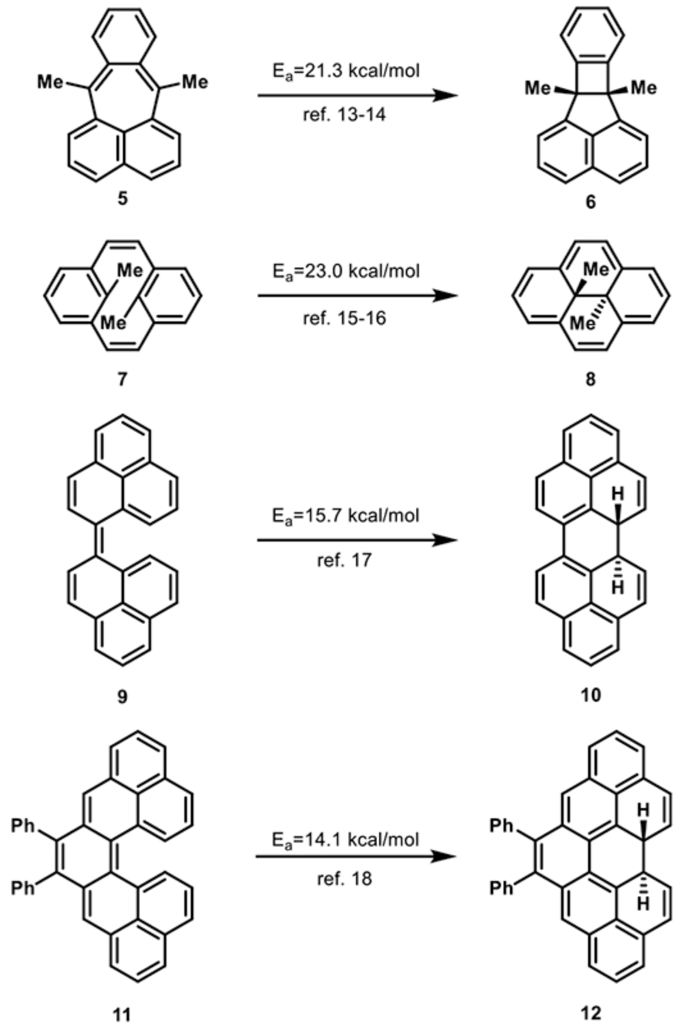


Figure 2.
Experimental activation energies for energetically preferred, symmetry-forbidden electrocyclizations.

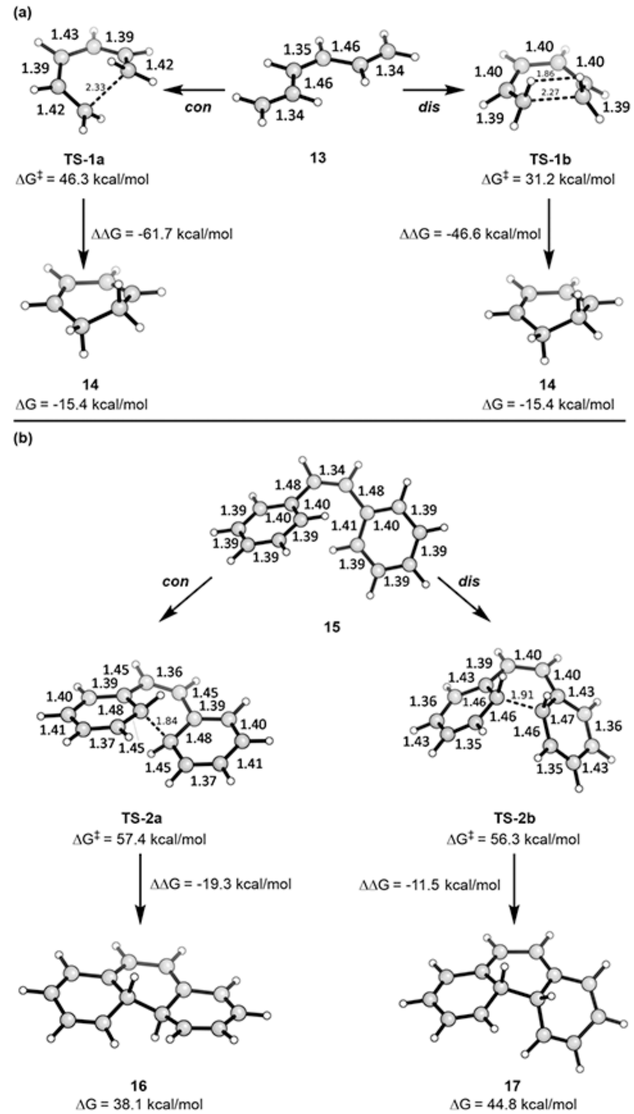


Figure 3.

Bond lengths and free energies of the transition states of (a) *cis*-hexatriene (*con* TS is open-shell) and (b) *cis*-stilbene (*con* TS is open-shell).

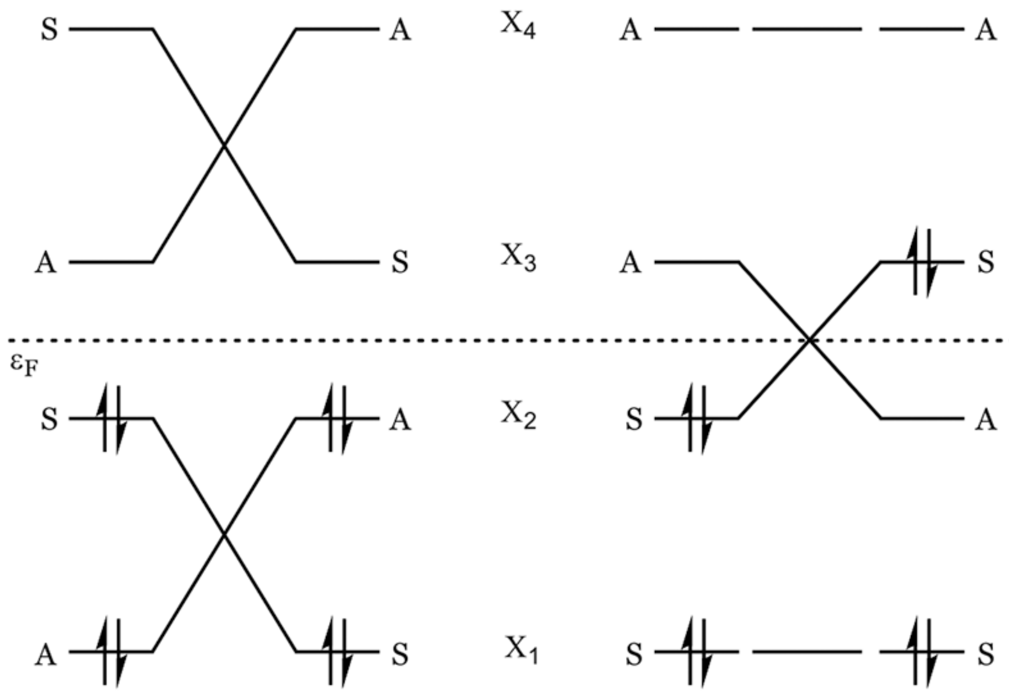


Figure 4.

Typical correlation diagrams for allowed (left) and forbidden (right) reactions. In the forbidden reactions, the crossing of HOMO and LUMO results in a diradical state (one electron in each of two degenerate orbitals).

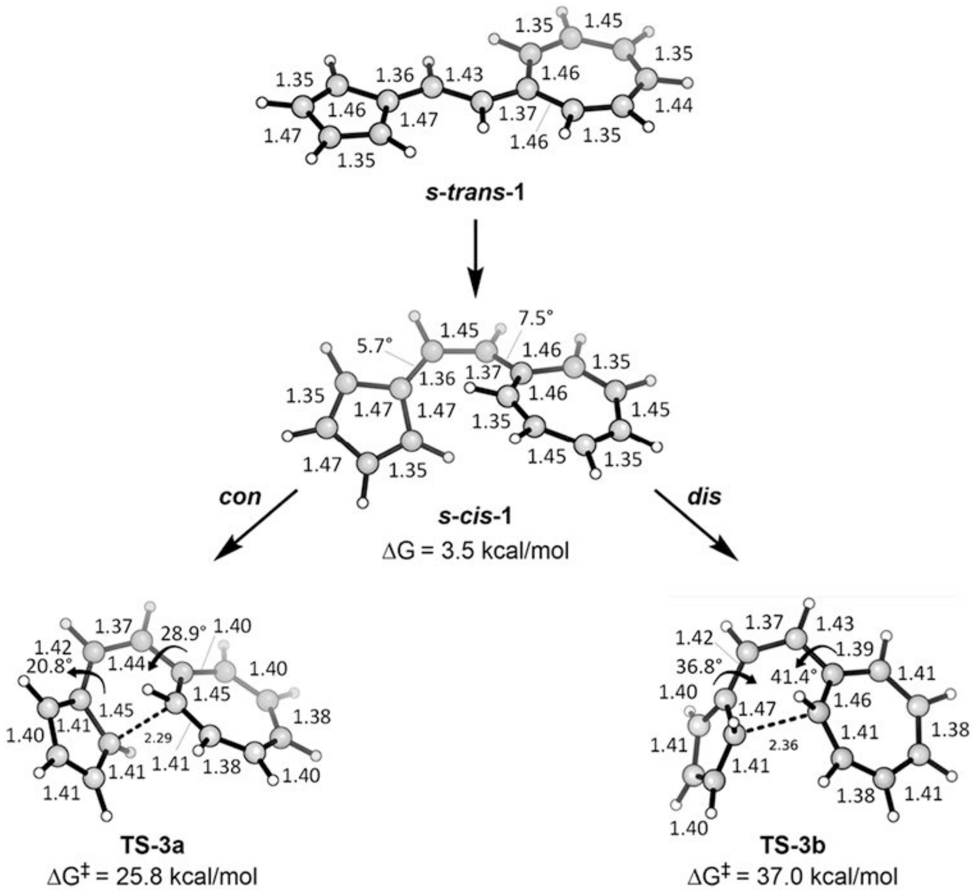


Figure 5.

Geometries of *s-trans* and *s-cis* reactants and transition state geometries for conrotatory and disrotatory 14*π* electrocyclizations.

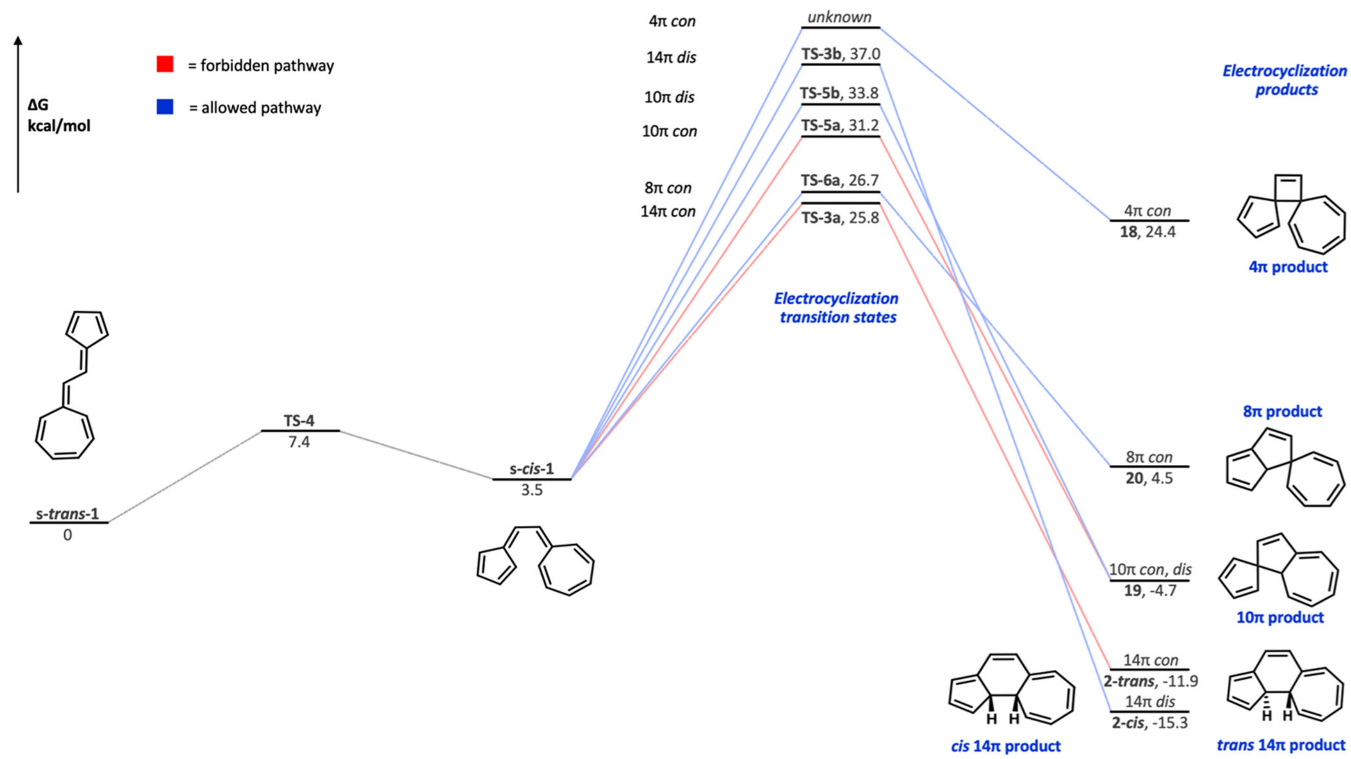


Figure 6.

Free energy diagram for electrocyclization of *s-cis*-**1** via 4π, 8π, 10π, and 14π conrotatory and disrotatory pathways. All structures have closed-shell wave functions except for **TS-5a**.

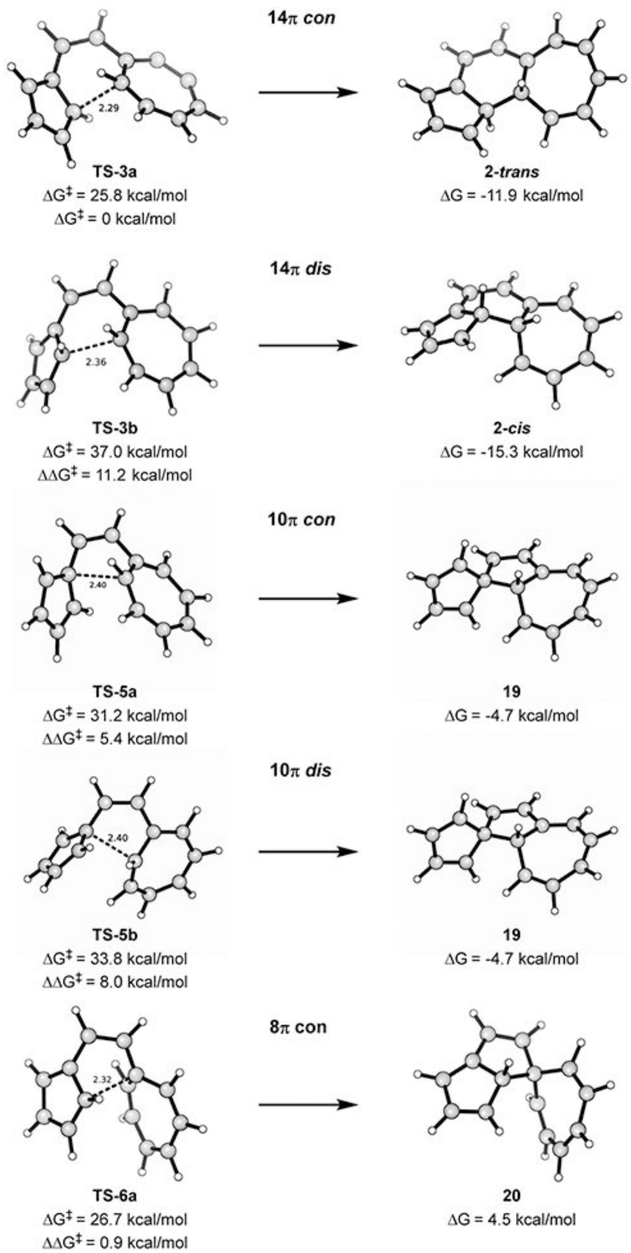
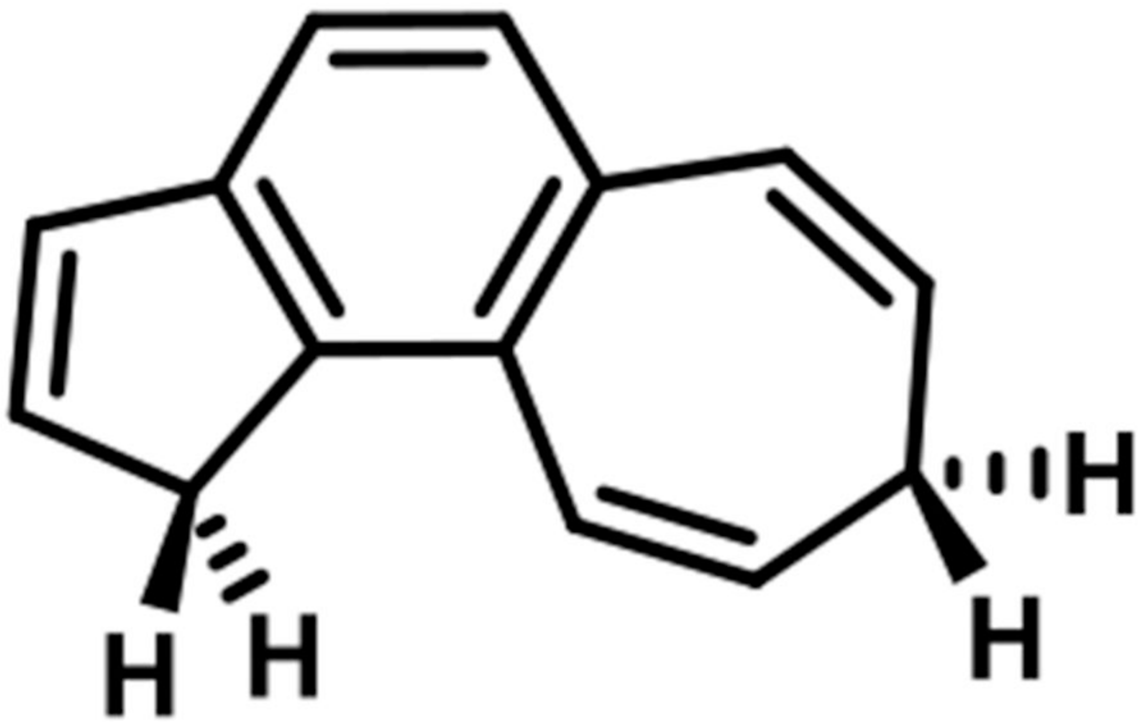


Figure 7.

Transition states of 14π-, 10π-, and 8 π-electron electrocyclizations of *s-cis*-**1**.



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$\Delta G = -42.3$ kcal/mol

Figure 8.
Final product formed by thermolysis of **2**-*trans*.

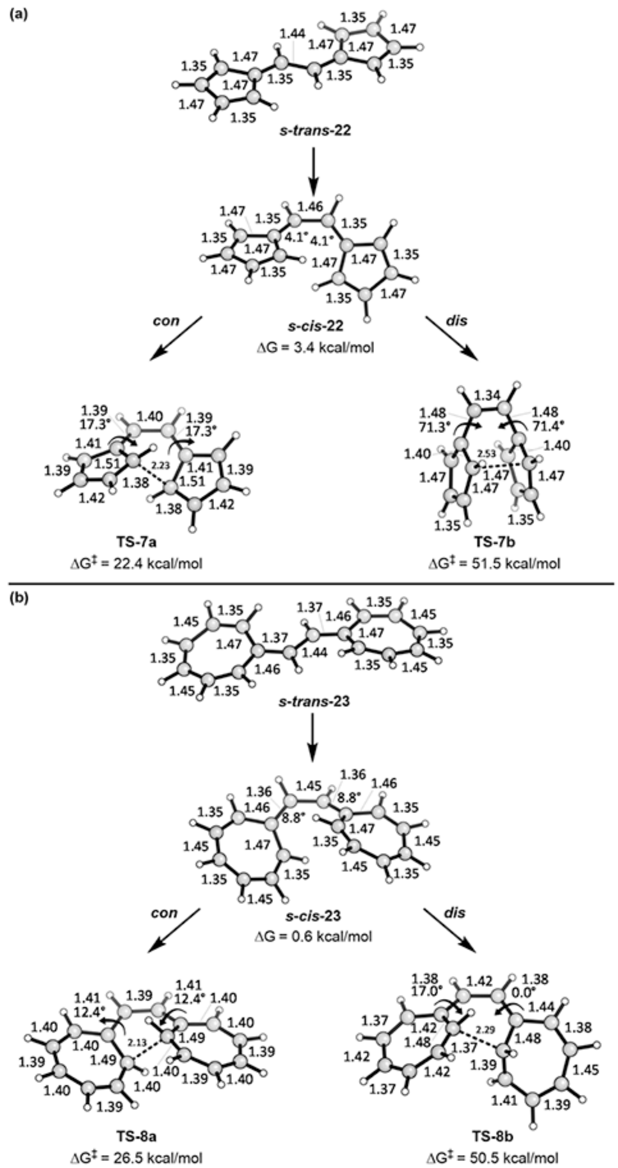

Figure 9.

Bond lengths and torsion angles of (a) vinylogous pentafulvalene and (b) vinylogous heptafulvalene along with transition states for their electrocyclizations. All are closed-shell wave functions.

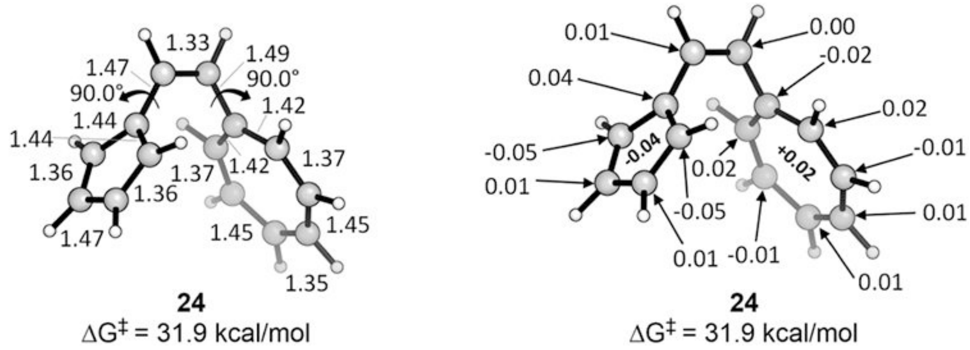

Figure 10.

Diradical structure formed from the vinylogous sesquifulvalene by rotating both rings to 90° relative to the connecting ethylene moiety. Geometries and Hirshfeld charges (Hs summed into Cs) are shown.

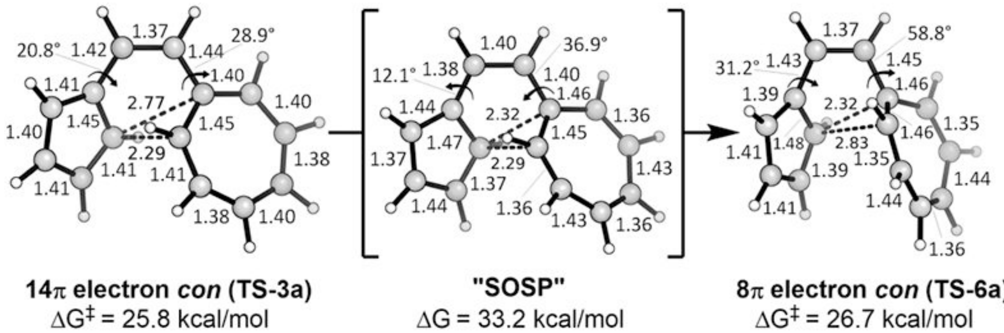

Figure 11.

Bond lengths, torsion angles, and energies of **TS-3a**, approximate second-order saddle point **"SOSP"**, and **TS-6a**.

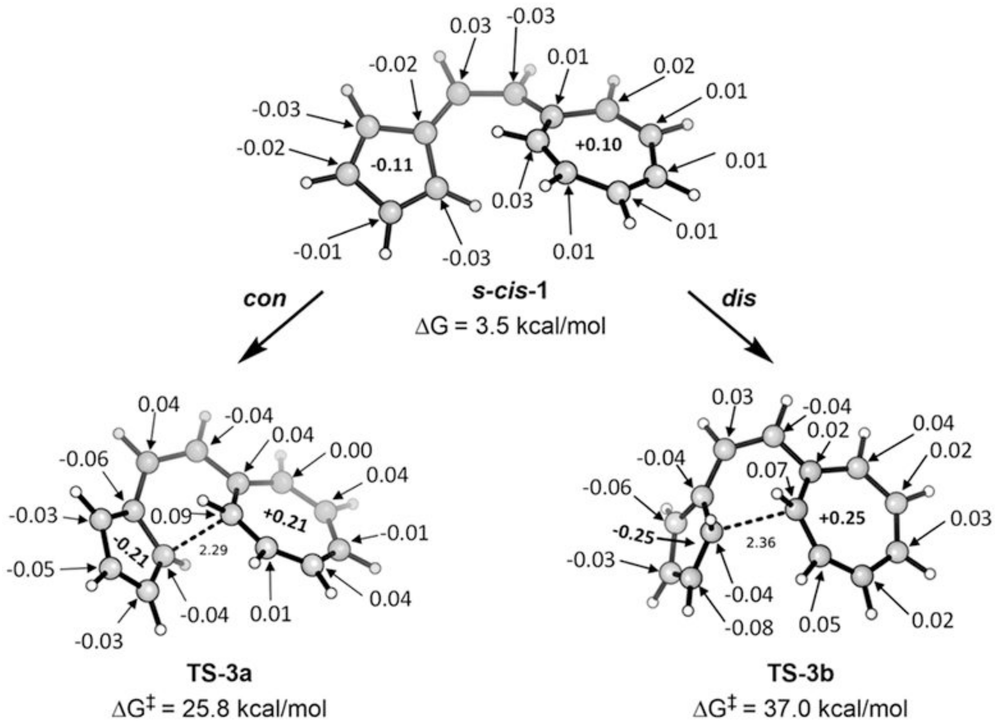

Figure 12.

Charges in *s-cis* vinylogous sesquifulvalene and the forbidden and allowed 14π transition states.

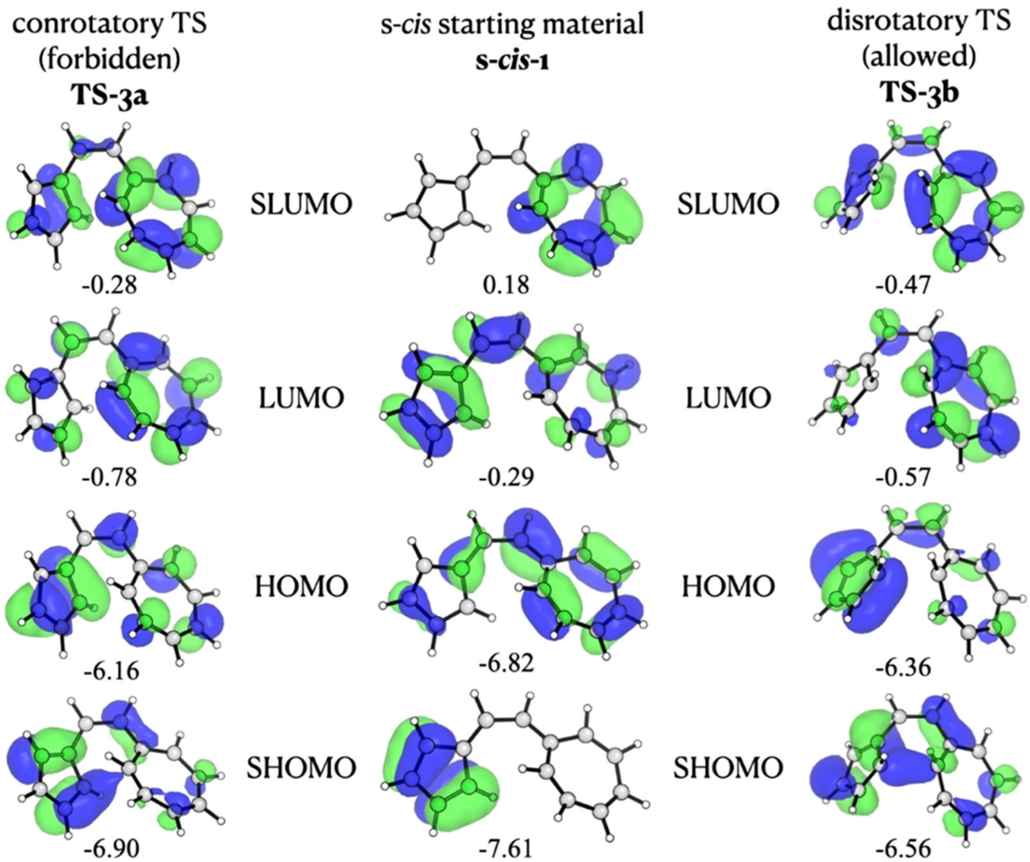

Figure 13.

Two highest occupied and two lowest vacant orbitals of vinylogous sesquifulvalene in the *s-cis* conformation and in the 14π *con* and *dis* transition states.

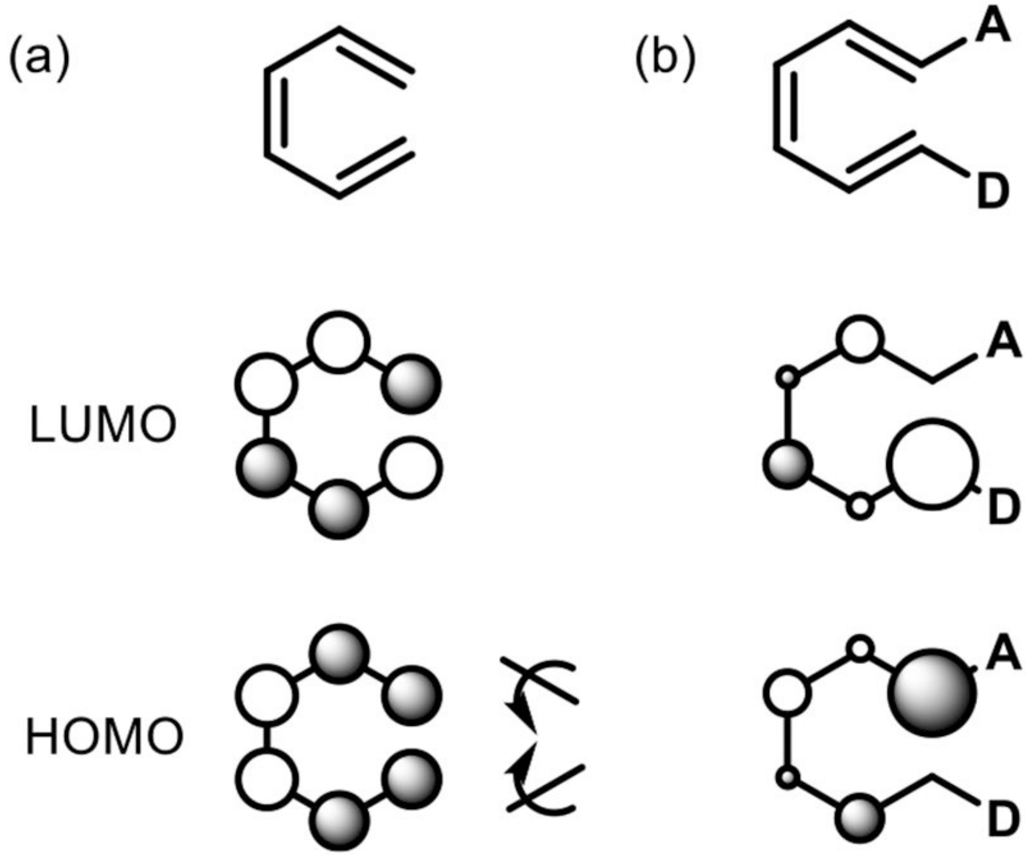

Figure 14.
HOMO and LUMO of (a) hexatriene and (b) a 1-D, 6-A substituted triene (D = strong donor; A = strong acceptor).

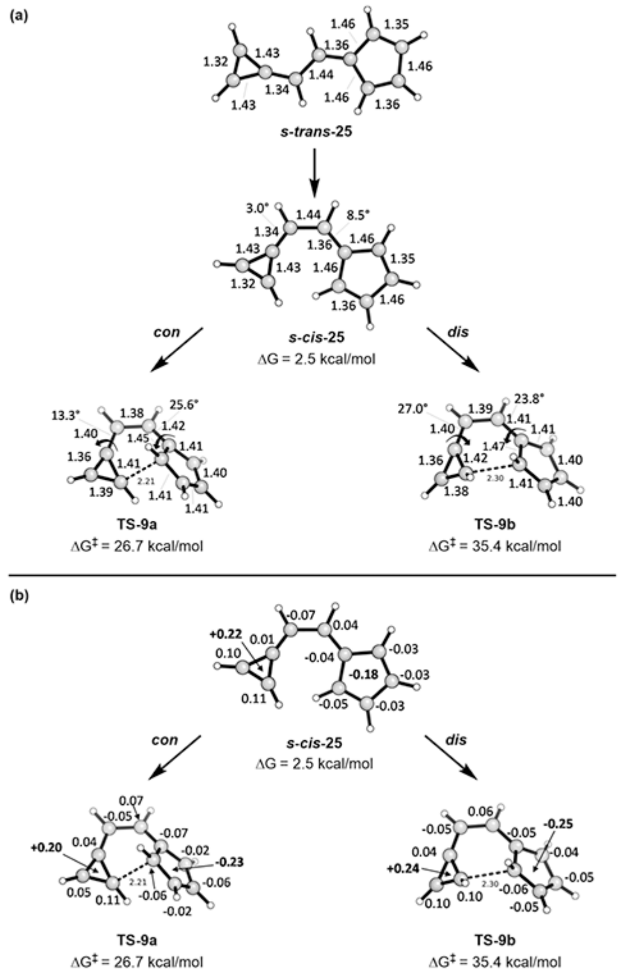

Figure 15.

Forbidden conrotatory and allowed disrotatory transition states for electrocyclization of 6-triafulvenylfulvene. In (a) geometries are shown. In (b) Hirshfeld charges are shown by each atom.

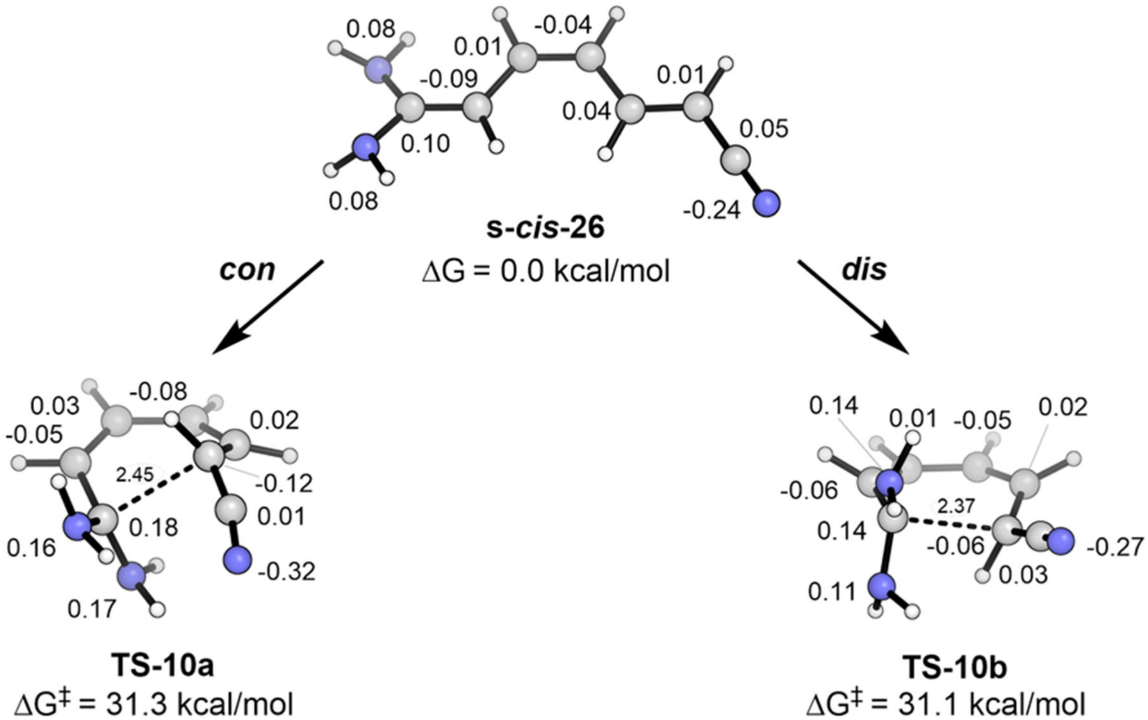

Figure 16.

Forbidden conrotatory and allowed disrotatory transition states for electrocyclization of *cis,trans*-1,1-diamino-6-cyanohexatriene. Hirshfeld charges are shown by each atom.

Table 1.

Energy Barriers for the Electrocyclization of Cethrene and Biphenalenylidene[a]

structure	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	ΔE_a (expt)
cethrene: *dis* TS	26.1	27.0	unknown
cethrene: *con* TS	17.4	18.7	14.1
biphenalenylidene: *con* TS	14.1	15.1	15.7

[a]All transition states listed have open-shell wave functions except for the cethrene *dis* TS.

Table 2.

Energy Barriers for the Electrocyclizations of *s-cis*-1 (in kcal/mol)

structure	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta\Delta G^{\ddagger}$
TS-3a	23.7	25.8	0
TS-3a (exp)	23.9 ± 0.5		
TS-3b	35.2	37.0	11.2
TS-5a	29.6	31.2	5.4
TS-5b	31.8	33.8	8.0
TS-6a	24.4	26.7	0.9
4π TS	unknown	unknown	unknown