Electrocyclic Reactions of 1-Substituted 1,3,5,7-Octatetraenes. An ab Initio Molecular Orbital Study of Torquoselectivity in Eight-Electron Electrocyclizations

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Received June 8, 1992

Abstract: The effects of substituents on the conrotatory electrocyclizations of 1-substituted *cis,cis*-1,3,5,7-octatetraenes have been studied with ab initio molecular orbital theory. The results are compared to the conrotatory electrocyclic ring openings of 3-substituted cyclobutenes. Geometry optimizations employed restricted Hartree–Fock calculations and the 3-21G basis set. Electron correlation energies were calculated using second-order Møller–Plesset theory and the 6-31G* basis set. The transition structure for the conrotatary electrocyclization of *cis,cis*-1,3,5,7-octatetraene has a helical structure. The steric effects of the substituents direct the stereoselectivities of conrotatory electrocyclizations of 1-substituted *cis,cis*-1,3,5,7-octatetraenes. This contrasts to the conrotatory ring openings of 3-substituted cyclobutenes, where the electronic nature of the substituent directs the stereoselectivities of the conrotatory ring openings.

Introduction

The electrocyclic reactions of polyenes involve the rotation of the terminal double bonds. For butadiene-cyclobutene interconversions, we have shown how the electronic nature of the substituent influences the direction of rotation of the termini.[1] Here we extend the study of substituent effects to the electrocyclizations of 1-substituted *cis,cis*-1,3,5,7-octatetraenes.

The interconversion of *cis,cis*-1,3,5,7-octatetraene and *cis,cis,cis*-1,3,5-cyclooctatriene is an example of an eight-electron conrotatory electrocyclic process according to the Woodward-Hoffmann rules.[2] In a previous study of this process, we showed that the

transition structure has a helical geometry.[3] This electrocyclization is fast at room temperature[4] with a measured activation energy of 17.0 kcal/mol.[5] Ab initio molecular orbital calculations overestimate the activation energy at the RHF level (32.8 kcal/mol by RHF/6-31G* optimization) and underestimate the activation energy at the MP2 level, giving a value of 8.4 kcal/mol at the MP2/6-31G*//RHF/6-31G* + ZPE level of theory.[3]

The electrocyclic interconversions of several 1-substituted 1,3,5,7-octatetraenes and 7-substituted 1,3,5-cyclooctatrienes have been studied experimentally.[6] Generally, the equilibrium lies toward the cyclooctatriene, although conjugating substituents move the equilibrium toward the octatetraene. The rates and stereochemistries of most of these electrocyclic reactions are not known. Marvell and Seubert reported indirect evidence that *tcct*-

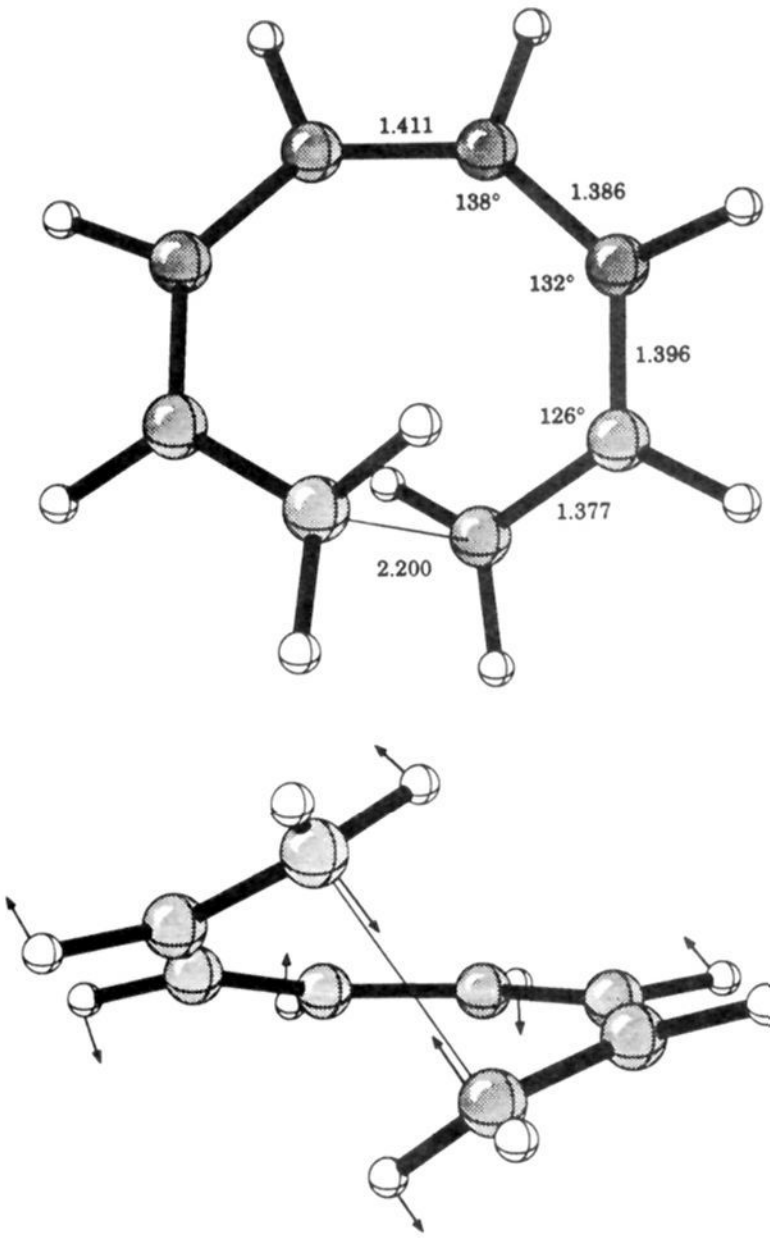

Figure 1. RHF/6-31G* conrotatory transition structure for the electrocylic interconversion of 1,3,5-cyclooctatriene and *cis,cis*-1,3,5,7-octatetraene. The transition vector is shown. Bond lengths are in angstroms and bond angles are in degrees.

and *ccct*-2,4,6,8-decatetraene cyclize form *trans*- and *cis*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene, respectively.[7] Subsequently, Huisgen and co-workers published a series of papers on the rates of electrocyclizations of *tcct*-, *tccc*-, and *cccc*-2,4,6,8-

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Table I. Total Energies of Reactants, Transition Structures, and Products for the Electrocyclizations of 1-Substituted 1,3,5,7-Octatetraenes[a]

structure	AM1	RHF/3-21G	ZPE	IMF	RHF/6-31G* [b]	MP2/6-31G* [b]
1,3,5,7-octatetraene	0.092 46	−306.972 17	103.8		−308.690 33	−309.692 95
cis-1-fluoro-1,3,5,7-octatetraene	0.012 11	−405.294 11	99.2		−407.538 80	−408.710 88
trans-1-fluoro-1,3,5,7-octatetraene	0.011 47	−405.291 06	98.9		−407.537 93	−408.709 72
cis-1-methyl-1,3,5,7-octatetraene	0.078 14	−345.792 36	122.8		−347.726 81	−348.861 49
trans-1-methyl-1,3,5,7-octatetraene	0.076 19	−345.795 30	122.6		−347.729 94	−348.864 27
cis-1-formyl-1,3,5,7-octatetraene	0.041 29	−419.062 79	111.1		−421.416 50	−422.717 34
trans-1-formyl-1,3,5,7-octatetraene	0.039 24	−419.064 75	110.9		−421.421 94	−422.721 77
1,3,5-cyclooctatriene	0.059 52	−306.988 38	106.2		−308.706 39	−309.718 56
1-fluoro-1,3,5-cyclooctatriene	−0.009 48	−405.310 84	101.4		−407.559 21	−408.738 88
1-methyl-1,3,5-cyclooctatriene	0.052 73	−345.809 24	125.1		−347.740 82	−348.887 19
1-formyl-1,3,5-cyclooctatriene	0.015 34	−419.073 40	112.5		−421.426 33	−422.737 80
TS (parent)	0.122 38	−306.928 99	104.5	755.9*i*	−308.637 96	−309.679 39
TS (fluoro in)	0.055 00	−405.244 73	99.5	815.2*i*	−407.481 10	−408.696 23
TS (fluoro out)	0.042 86	−405.248 23	99.3	815.6*i*	−407.485 29	−408.696 84
TS (methyl in)	0.118 27	−345.743 19	123.5	751.0*i*	−347.667 40	−348.846 97
TS (methyl out)	0.109 75	−345.750 41	123.3	768.4*i*	−347.675 08	−348.851 28
TS (formyl in)	0.078 60	−419.011 73	111.1	759.9*i*	−421.359 84	−422.703 31
TS (formyl out)	0.071 66	−419.021 00	111.3	751.4*i*	−421.367 13	−422.708 57

[a] Energies are in hartrees, zero-point energies in kcal/mol, and imaginary vibrational frequencies in cm^{-1}. [b] Single-point energy evaluation on the optimized RHF/3-21G geometries.

Table II. Relative Energies (kcal/mol) of the Reactants, Transition Structures, and Products for the Electrocyclizations of 1-Substituted 1,3,5,7-Octatetraenes

structure	AM1	RHF/3-21G	RHF/6-31G* [a]	MP2/6-31G* [a]	MP2/6-31G* [a] + ZPE
1,3,5,7-octatetraene	0.0	0.0	0.0	0.0	0.0
TS	18.8	27.1	32.9	8.5	9.2
1,3,5-cyclooctatriene	−20.7	−10.2	−10.1	−16.1	−13.7
cis-1-fluoro-1,3,5,7-octatetraene	0.0	0.0	0.0	0.0	0.0
TS (fluoro in)	26.9	31.0	36.2	9.2	9.5
7-fluoro-1,3,5-cyclooctatriene	−13.5	−10.5	−12.8	−17.6	−15.4
trans-1-fluoro-1,3,5,7-octatetraene	0.0				
TS (fluoro out)	19.7	26.9	33.0	8.1	8.5
7-fluoro-1,3,5-cyclooctatriene	−13.1	−12.4	−13.4	−18.3	−15.8
cis-1-methyl-1,3,5,7-octatetraene	0.0	0.0	0.0	0.0	0.0
TS (methyl in)	25.2	30.9	37.3	9.1	9.8
7-methyl-1,3,5-cyclooctatriene	−15.9	−10.6	−8.8	−16.1	−13.8
trans-1-methyl-1,3,5,7-octatetraene	0.0	0.0	0.0	0.0	0.0
TS (methyl out)	21.1	28.2	34.4	8.2	8.9
7-methyl-1,3,5-cyclooctatriene	−14.7	−8.8	−6.8	−14.4	−11.9
cis-1-formyl-1,3,5,7-octatetraene	0.0	0.0	0.0	0.0	0.0
TS (formyl in)	23.4	32.0	35.6	8.8	8.8
7-formyl-1,3,5-cyclooctatriene	−16.3	−6.7	−6.2	−12.8	−11.4
trans-1-formyl-1,3,5,7-octatetraene	0.0	0.0	0.0	0.0	0.0
TS (formyl out)	22.9	27.5	34.4	8.3	8.7
7-formyl-1,3,5-cyclooctatriene	−15.0	−5.4	−2.8	−10.1	−8.5

[a] Single-point energy evaluation on the optimized RHF/3-21G geometries.

decatetraene.[8] The tcct isomer cyclizes fastest, the tccc isomer next, and the cccc isomer the slowest.[8] In cases where the stereochemistry of an electrocyclic ring opening of a 7-substituted cyclooctatriene is known, the substituent predominately rotates outward.[9-11]

The stereoselectivities of electrocyclic reactions have been shown to be strongly influenced by the electronic properties of substituents. The ring openings of 3-substituted cyclobutenes provide many examples of this in both experimental[12,13] and theoretical[1] work. The electronic properties of substituents have also been shown to affect the stereoselectivities of the electrocyclizations of 1-substituted pentadienyl cations[14] and the electrocyclic ring openings of 2-substituted oxiranes and aziridines.[15] In the six-electron disrotatory electrocyclizations of 1-substituted 1,3,5-hexatrienes, steric factors become more important and electronic effects are less important.[16]

Computational Procedure

Ab initio molecular orbital calculations were performed with restricted Hartree–Fock theory using the GAUSSIAN 88 and 90 programs.[17] The 3-21G[18] basis set was employed for the RHF geometry optimizations.

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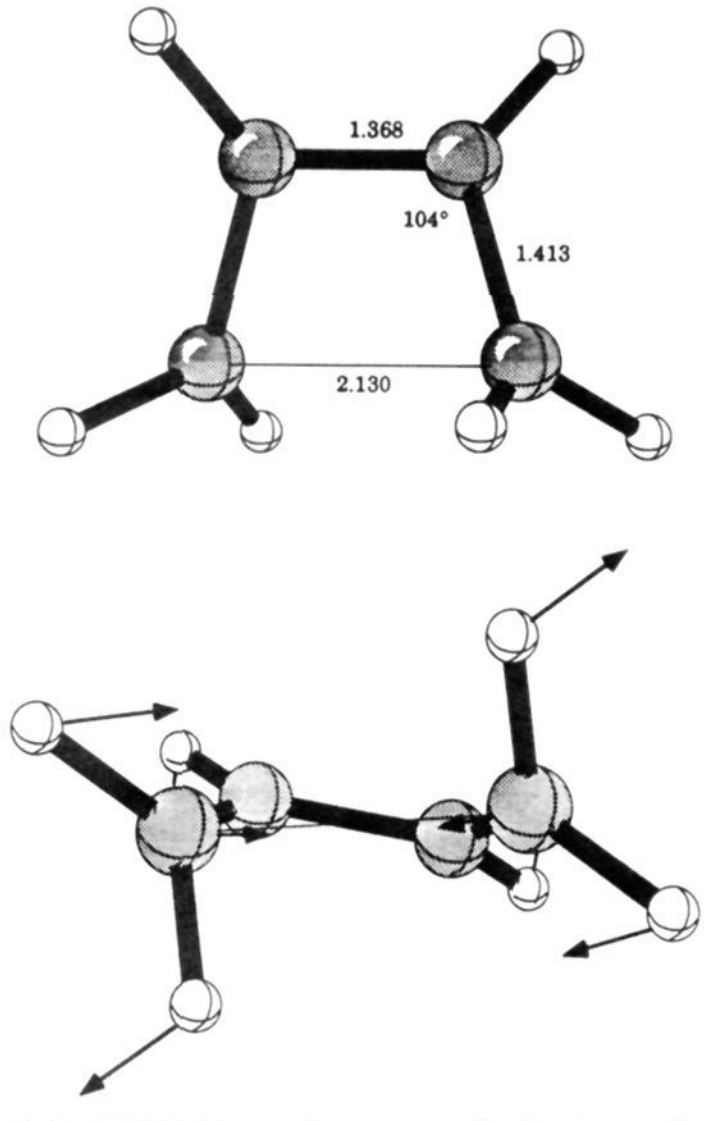


Figure 2. RHF/6-31G* transition structure for the electrocylic interconversion of cyclobutene and butadiene. The transition vector is shown.

Harmonic vibrational frequencies were calculated to confirm the nature of all stationary points. Single-point energy evaluations were performed on the RHF/3-21G-optimized geometries using the 6-31G* [19] basis set and second-order Møller–Plesset perturbation theory.[20] Preliminary calculations were carried out using the semiempirical AM1 method.[21]

There is concern that transition states may be poorly described by RHF wave functions. This is certainly true for reactions which form a biradical. However, we have investigated pericyclic reactions very extensively, including a comparison of RHF and MCSCF results.[3] For electrocyclizations, both produce very similar results. In our previous studies on the closely related cyclobutene ring opening, we have not found a significant change in the geometry of the calculated transition structures with change in the basis set or methodology.[22] Goddard et al. have studied the cyclobutene ring opening using CASSCF-level calculations.[23] The CASSCF transition structure is not very different from the MP2/6-31G*, RHF/6-31G*, and RHF/3-21G transition structures. The most significant difference is a lengthening of the breaking bond by 0.1 Å. A general discussion may be found in ref 3b.

Results and Discussion

The computed transition structure for the conrotatory electrocyclization of *cis,cis*-1,3,5,7-octatetraene is shown in Figure 1. The predicted activation energy is 8.4 kcal/mol, and the predicted energy of reaction is –14.2 kcal/mol at the MP2/6-31G*//RHF/6-31G* + ZPE level of theory.[3] The forming bond length is 2.20 Å, which is typical of pericyclic reactions.[3] This conrotatory process is quite different from that of the electrocyclic ring opening of cyclobutene. The transition vector of the 1,3,5,7-octatetraene ring closure is almost entirely composed of the motion of the two carbon termini toward each other as well as motions of the vinyl hydrogens at the 1, 2, 5, and 6 positions (Figure 1).[3] It is a conrotatory process that involves rotation about the CC bonds twice removed from the forming CC bond. By contrast, the transition vector for the conrotatory ring opening of cyclobutene primarily involves motion of the hydrogens attached to the carbon atoms of the breaking CC bond to produce a pronounced rotation of the developing CH_2 termini of the forming diene (Figure 2).

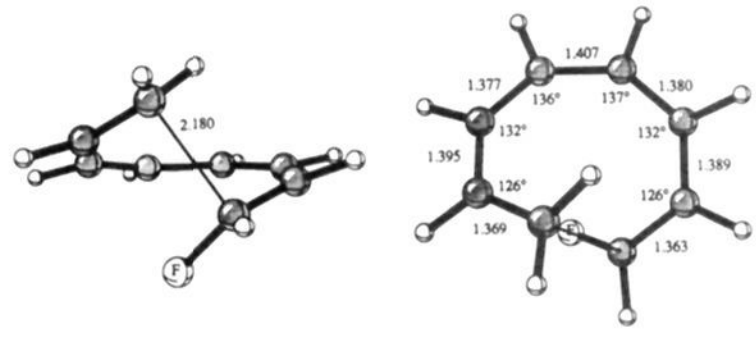
In the cyclobutene ring opening, the electronic contribution of the substituent is maximized while the steric effects are minimized. Upon inward rotation, the substituent orbitals overlap with the remote terminus of the breaking bond. When a substituent orbital is doubly occupied, this leads to a repulsive cyclic four-electron interaction. Consequently, outward rotation is favored. If the substituent orbital is vacant, then inward rotation is favored to maximize the cyclic two-electron stabilization.[1]

In the octatetraene cyclization, the inward and outward substituents have about the same relationship with the remote terminus of the forming bond. Consequently, a smaller electronic effect upon stereoselectivity is expected. The total and relative energies of the reactants, transition structures, and products for

Table III. Activation Energies and Relative Energies of the Transition Structures for Inward and Outward Rotation of the Substituent for the Ring Opening of 7-Substituted 1,3,5-Cyclooctatrienes[a]

substituent	basis set	E_a(in)	E_a(out)	ΔE_a[b]
F	AM1	40.5	32.8	7.7
	3-21G	41.5	39.3	2.2
	6-31G* [c]	49.0	46.4	2.6
	MP2/6-31G* [c]	26.8	26.3	0.4
	MP2/6-31G* [c] + ZPE	24.9	24.1	0.8
CH_3	AM1	41.1	35.8	5.3
	3-21G	41.4	36.9	4.5
	6-31G* [c]	46.1	41.3	4.8
	MP2/6-31G* [c]	25.2	22.5	2.7
	MP2/6-31G* [c] + ZPE	23.6	20.7	2.9
CHO	AM1	39.7	35.3	4.4
	3-21G	38.7	32.9	5.8
	6-31G* [c]	41.7	37.1	4.6
	MP2/6-31G* [c]	21.6	18.3	3.3
	MP2/6-31G* [c] + ZPE	20.2	17.1	3.1

[a] Energies are in kcal/mol. [b] $\Delta E_a = E_{in} - E_{out}$. [c] Single-point energy evaluation on the optimized RHF/3-21G geometries.



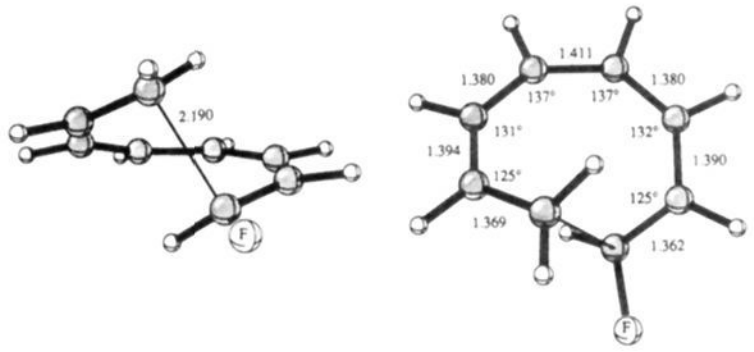


Figure 3. RHF/3-21G transition structures for the conrotatory electrocyclization of *cis*- and *trans*-1-fluoro-1,3,5,7-octatetraene. Two views of each transition structure are shown.

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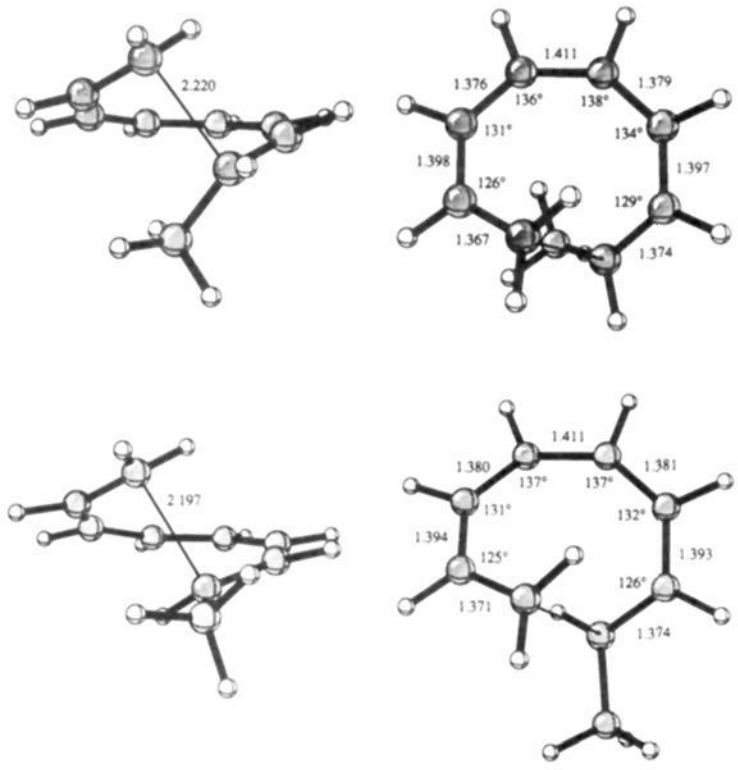

Figure 4. RHF/3-21G transition structures for the conrotatory electrocyclizations of *cis*- and *trans*-1-methyl-1,3,5,7-octatetraene. Two views of each transition structure are shown.

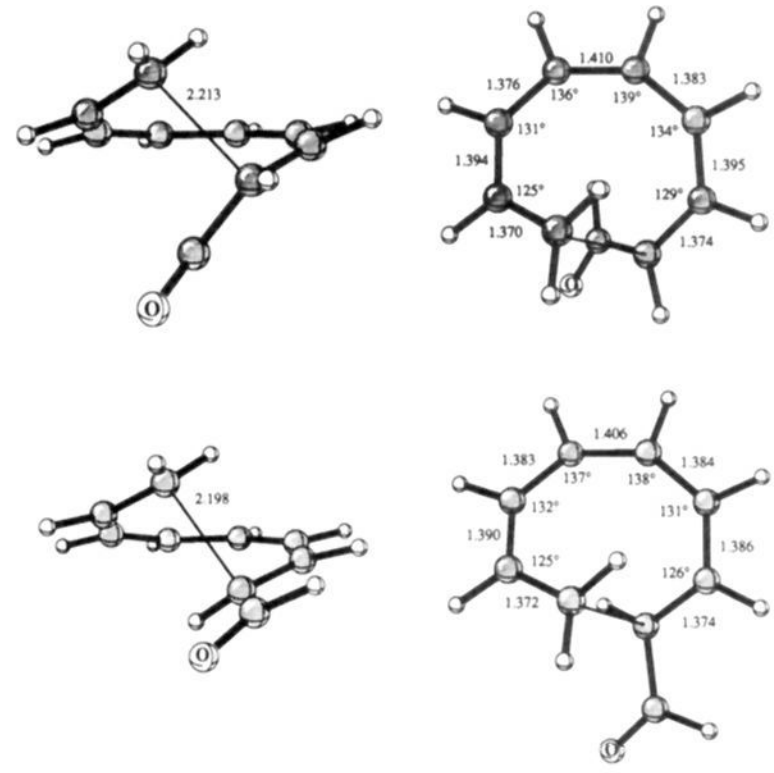

Figure 5. RHF/3-21G transition structures for the conrotatory electrocyclization of *cis*- and *trans*-1-formyl-1,3,5,7-octatetraene. Two views of each transition structure are shown.

the electrocyclic ring closure of three 1-substituted 1,3,5,7-octatetraenes have been calculated and are shown in Tables I and II. The activation energies for electrocyclizations of the *cis*-1-fluoro- and *cis*-1-methyl-1,3,5,7-octatetraenes are 0.3 and 0.6 kcal/mol larger than the activation energy for the electrocyclization of 1,3,5,7-octatetraene, while the activation energy for the electrocyclization of *cis*-1-formyl-1,3,5,7-octatetraene is 0.4 kcal/mol smaller (without ZPE corrections it is 0.3 kcal/mol larger). The steric crowding of the inside position is somewhat larger in the transition structure than in the tetraene. The trans isomers have 0.2–0.4 kcal/mol lower activation energies for cyclization than the parent compound. Each of these substituents stabilizes the transition structures slightly. The energies of reaction are influenced by the substituent interactions with the polyene. Thus, fluorine destabilizes the tetraene relative to the triene because it prefers a saturated position. Methyl has a small effect, while formyl stabilizes the tetraene to a significant extent through extended conjugation with the π-system.

The equilibrium between 1,3,5,7-octatetraenes, and 1,3,5-cyclooctatrienes generally favors the cyclooctatrienes. To assess torquoselectivity without corrections for ground-state substituent effects, it is easier to compare the ring openings of 7-substituted 1,3,5-cyclooctatrienes with those of 3-substituted cyclobutenes. The activation energies for inward and outward rotation of several 7-substituted cyclooctatrienes are given in Table III. The substituents range from a moderately strong π-electron donor (F) to a weak donor (CH_3) to a strong electron acceptor (CHO). The transition structures for these reactions are shown in Figures 3–5. The geometries of these transition structures are remarkably similar to each other and to the parent transition structure. The forming bond lengths range from 2.18 to 2.22 Å, while the partial double bond lengths alternate slightly, resembling the octatetraene more than cyclooctatriene values. The activation energies of the corresponding cyclobutene ring openings are given in Table V, while the raw data are given in Table IV. The computed activation energy differences between inward and outward rotations of substituted 3-cyclobutenes have been shown to have a nearly linear dependence on the empirical resonance parameter σ_R°.[1] A graph of the differences of inward and outward activation energies for the three substituted cases of cyclooctatriene and cyclobutene are plotted against σ_R° in Figure 6. There is a small preference for outward rotation of the substituent in 7-substituted 1,3,5-cyclooctatrienes regardless of its electron-donating or electron-accepting ability. The helical transition structure causes sub-

Table IV. Total Energies of Reactants, Transition Structures, and Products for the Electrocyclic Ring Opening of Cyclobutene and 3-Substituted Cyclobutenes[a]

structure	AM1	RHF/3-21G	ZPE	IMF	RHF/6-31G* [b]	MP2/6-31G* [b]
cyclobutene	0.072 82	−154.030 72[c,d]	58.4		−154.898 31[d]	−155.407 75[c,d]
3-fluorocyclobutene	−0.001 65	−252.349 60	53.5		−253.750 18	−254.426 33
3-methylcyclobutene	0.063 22	−192.853 18	77.4		−193.935 19	−194.577 33
3-formylcyclobutene	0.026 15	−266.117 51[e]	65.0		−267.622 01[e]	−268.429 14
butadiene	0.047 57	−154.059 46[c,d]	57.8		−154.919 61[d]	−155.420 71[c,d]
cis-1-fluorobutadiene	−0.033 29	−252.378 02	52.9		−253.766 93	−254.437 14
trans-1-fluorobutadiene	−0.032 62	−252.380 81	53.3		−253.767 85	−254.438 22
cis-1-methylbutadiene	0.033 24	−192.879 80	76.9		−193.956 25	−194.589 15
trans-1-methylbutadiene	0.031 41	−192.882 39	76.7		−193.959 08	−194.591 66
cis-1-formylbutadiene	−0.003 64	−266.150 00	65.1		−267.645 60	−268.444 74
trans-1-formylbutadiene	−0.005 53	−266.151 29	64.9		−267.650 94	−268.448 76
TS (parent)	0.129 13	−153.964 35[c,d]	56.8	899.4*i*	−154.824 59[d]	−155.349 42[c,d]
TS (fluoro in)	0.056 02	−252.265 54	51.7	901.8*i*	−253.656 25	−254.352 88
TS (fluoro out)	0.042 98	−252.293 08	52.1	777.7*i*	−253.683 31	−254.377 52
TS (methyl in)	0.119 61	−192.777 74	75.8	849.3*i*	−193.853 55	−194.512 91
TS (methyl out)	0.113 13	−192.788 04	75.5	813.5*i*	−193.863 04	−194.520 87
TS (formyl in)	0.074 55	−266.062 15[e]	63.9	728.5*i*	−267.561 52[e]	−268.385 14
TS (formyl out)	0.075 16	−266.055 02[e]	63.6	807.2*i*	−267.554 13[e]	−268.377 18

[a] Energies are in hartrees, zero-point energies in kcal/mol, and imaginary vibrational frequencies in cm^{-1}. [b] Single-point energy evaluation on the optimized RHF/3-21G geometries. [c] See ref 1a. [d] See ref 24. [e] See ref 1b.

Table V. Activation Energies and Relative Eneriges of the Transition Structures for Inward and Outward Rotation of the Substituent for the Ring Opening of 3-Substituted Cyclobutenes[a]

substituent	basis set	E_a(in)	E_a(out)	ΔE_a[b]
F	AM1	36.2	28.0	8.2
	3-21G	52.7	35.5	17.2
	6-31G*[c]	58.9	42.0	16.9
	MP2/6-31G*[c]	46.1	30.6	15.5
	MP2/6-31G*[c] + ZPE	44.3	29.2	15.1
CH_3	AM1	35.4	31.3	4.1
	3-21G	47.3	40.9	6.4
	6-31G*[c]	51.2	45.3	5.9
	MP2/6-31G*[c]	40.4	35.4	5.0
	MP2/6-31G*[c] + ZPE	38.8	33.5	5.3
CHO	AM1	30.4	30.8	−0.4
	3-21G	34.7	39.2	−4.5
	6-31G*[c]	38.0	42.6	−4.6
	MP2/6-31G*[c]	27.6	32.6	−5.0
	MP2/6-31G*[c] + ZPE	26.5	31.2	−4.7

[a] Energies in kcal/mol. [b] $\Delta E_a = E_{in} - E_{out}$. [c] SIngle-point energy evaluation on the optimized RHF/3-21G geometries.

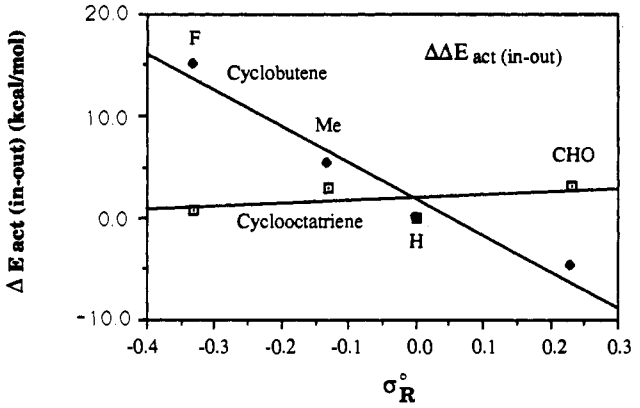

Figure 6. Plot of ΔE_a versus σ_R° for the electrocyclic ring openings of 7-substituted 1,3,5-cyclooctatrienes and 3-substituted cyclobutenes.

stituents on the inside or outside to experience essentially the same relationship to the breaking CC bond, since there is no twisting of the breaking bond. Consequently, the electronic nature of the substituent does not play an important role in directing the rotational preference. Steric effects do cause a small preference for all substituents to rotate outward, ranging from 0.8 kcal/mol for fluorine to 3.1 kcal/mol for a formyl group at the MP2/6-31G*//RHF/3-21G + ZPE level. The differences are slightly larger at the RHF levels studied, which may give more reliable numbers for these systems. This will be discussed below.

In the parent reaction (Figure 1), the two outside hydrogens are 2.69 Å from each other while an inside hydrogen is 2.42 Å from the carbon atom adjacent to the other carbon termini. Calculated secondary deuterium isotope effects for the parent electrocyclization yield a smaller k_H/k_D (0.93 for inside hydrogen, 0.98 for the outside hydrogen) for the inside hydrogen.[3] This corresponds to a tighter bending constant for the inside hydrogen, which results from more steric crowding.

The preference for an alkyl group to be outside in the transition structure of cyclization is in agreement with the experimental results of Huisgen et al.[8] $\Delta H^\ddagger$ values for cyclization of three decatetraenes have been measured experimentally. They are 15.1, 17.8, and 21.8 kcal/mol for the electrocyclizations of *tcct*-, *tccc*-, and *cccc*-5,7,9-decatetraene.[7] The tcct isomer, which cyclizes the fastest, has two methyl groups rotating out. The tccc isomer cyclizes second fastest and has one methyl group rotating out and one rotating in. The slowest cyclizing isomer, cccc, has two methyl groups rotating in. The change from a methyl out to a methyl in increases the activation energy by 2.7 and 4.0 kcal/mol (tcct → ccct, and ccct → cccc, respectively). Rotation of a second methyl group inward produces an additional Me–Me steric interaction. A change of only 0.9 kcal/mol is predicted at the MP2/6-31G* level. However, RHF calculations provide much better predictions. With the 3-21G basis set, a 2.7-kcal/mol difference is predicted, while with the 6-31G* basis set, a 2.9-kcal/mol difference is predicted. Both RHF results are in good accord with the 2.7-kcal/mol difference observed for the conversion of tcct and ccct.

Acknowledgment. We are grateful to the National Science Foundation for financial support of the research. This work was supported in part by a grant of computer time made possible under a joint study with the IBM Corporation on the IBM 3090/600J Supercomputer at the UCLA Office of Academic Computing.