

Transition Structures of Thermally Allowed Disrotatory Electrocyclizations. The Prediction of Stereoselective Substituent Effects in Six-Electron Pericyclic Reactions

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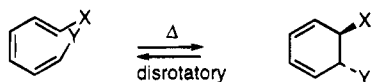
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The transition structures for the disrotatory electrocyclizations of a variety of 1-substituted 1,3,5-hexatrienes (F, CH₃, CN, CHO, NO, BH₂) have been located using ab initio molecular orbital calculations and the 3-21G basis set. Energy corrections for electron correlation were performed using second-order Møller–Plesset theory and the 6-31G* basis set. A comparison of the two disrotatory processes, involving either inward or outward rotation of the substituent, supports the theoretical model of torquoselectivity developed for the conrotatory processes of 3-substituted cyclobutenes. Electronic effects have a smaller influence on the preference for inward or outward rotation of the substituent in the hexatrienes, and steric effects have a larger influence than in the cyclobutene electrocyclizations.

Introduction

The interconversion of 1,3,5-hexatriene with 1,3-cyclohexadiene is the simplest example of a disrotatory six-electron electrocyclic reaction allowed by the Woodward–Hoffmann rules.¹

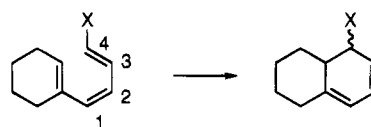


There have been many theoretical and experimental studies of the stereochemistry,² activation parameters,³ and structure–reactivity relationships⁴ for disrotatory pericyclic reactions. We were intrigued by the nature of the transition structures for such processes and by the question of whether the outward and inward rotational preferences of substituents, X and Y, would be the same as found with the conrotatory processes. The stereoselectivities and activation parameters of conrotatory pericyclic reactions have been predicted by theory⁵ and shown by experiment⁶ to be strongly influenced by the electronic properties of substituents attached to the forming and breaking bonds. We report here a study of these ques-

tions for hexatriene cyclizations using ab initio molecular orbital theory.

Background

The first gas-phase kinetic study of the 1,3,5-hexatriene ring closure was conducted by Lewis and Steiner.^{3a} They determined the activation energy for this electrocyclization to be 29.9 ± 0.5 kcal/mol and the activation entropy to be -5 eu. The electrocyclization to form 1,3-cyclohexadiene is exothermic by 15.2 kcal/mol. The influence of alkyl substitution at all three positions in different triene cyclizations have been reported by Marvell and co-workers.^{4d} The rates of cyclization were compared in

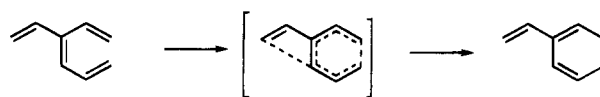


substituted (*Z*)-1-cyclohexenyl-1,3-pentadienes. A methyl group in the *cis* 4-position decreased the electrocyclization rate by about 100-fold, and a phenyl group by even a larger amount.^{4d} Schiess and co-workers have reported



that (*E,Z*)-1,2-distyrylcyclohexene reacts 20 times slower than the *E,E*-isomer.^{4f}

Alkyl and vinyl substituents at the 3-position of hexatriene lower the activation energy by 3–5 kcal/mol.⁴ The electrocyclization of 3-vinyl-1,3,5-hexatriene is the most rapid six-electron electrocyclic reaction of an acyclic system reported to date.^{4a,b} The enthalpy of activation is only 22 kcal/mol. This acceleration was attributed to



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anchimeric assistance provided by the vinyl group on the transition state.

The four-electron electrocyclic ring-opening of cyclobutene to butadiene is among the most thoroughly studied examples of pericyclic reactions.^{5,6} Our previous studies on the effects of substituents at the 3-position of cyclobutene upon inward and outward rotation of this electrocyclic ring opening led to a theoretical model based on electronic considerations.⁵ Such effects are predicted to occur in other $4n \pi$ electron electrocyclic processes, such as in the ring openings of 3-substituted cyclopropanes,⁷ 2-substituted oxiranes and aziridines,⁸ and the cyclizations of pentadienyl cations.^{9a} Related work on torquoselectivity in the Nazarov cyclization by Smith et al. has found an interesting directing effect of Si.^{9b} Previous models for the prediction of substituent effects on the rates of thermal pericyclic reactions have been qualitative and do not explicitly consider stereoselectivities.¹⁰⁻¹²

The interaction between the π -system (or p-orbital) of an inward or outward rotating substituent with the breaking CC bond of cyclobutene are shown below. The dashed line represents bonds to carbons 1 and 2 of 3-substituted cyclobutene. The drawings show the σ^* and σ orbitals of the breaking σ bond and a p orbital on a substituent at C-3.



Interaction of the σ^* and a substituent π orbital upon inward rotation.



Interaction of the σ^* and a substituent π orbital upon outward rotation.



Interaction of the σ and a substituent π orbital upon inward rotation.



Interaction of the σ and a substituent π orbital upon outward rotation.

The conrotatory process is ideally arranged to maximize the electronic difference between inward and outward rotation and to minimize the steric interactions involved in the transition structure. Upon outward rotation, the substituent overlaps only with the orbital on the attached carbon. Upon inward rotation, the substituent also overlaps with the orbital on the remote terminus of the breaking bond. When the substituent orbital is doubly occupied, outward rotation is favored. This minimizes the four-electron repulsion of the substituent orbital with the HOMO of the breaking bond and maximizes the two-electron stabilization of the substituent with the LUMO of the breaking bond. If the substituent orbital is vacant, then inward rotation is favored to maximize the two-electron stabilization arising from interaction of the substituent orbital with the HOMO of the breaking bond.

The stereochemical predictions for many substituted cyclobutenes have been recently verified by experiment.⁶

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The application of this theory to disrotatory processes is discussed in subsequent sections.

Theoretical Methods

Ab initio molecular orbital calculations were carried out with the GAUSSIAN 88 and 90 programs¹³ on the IBM ES9000 supercomputer at the Office of Academic Computing at UCLA or on Silicon Graphics computers. The reactants, transition structures, and products reported in this study were fully optimized. Structures and energies of the stationary points on the potential energy surface for the disrotatory electrocyclization of 1,3,5-hexatriene were obtained using restricted Hartree-Fock theory with the STO-3G, 3-21G, and 6-31G* basis sets.^{14,15} For the 1-substituted 1,3,5-hexatrienes, all stationary points were optimized with the 3-21G basis set. Electron correlation energy corrections were made using second-order Møller-Plesset Theory.¹⁶ The AM1 semiempirical program was also used in this study.¹⁷ Nonbonded energies were computed using Allinger's molecular mechanics program (MM2).¹⁸ The geometries of the RHF/3-21G transition structures were used to compute the initial steric energies. The terminal carbon atoms of the breaking CC bond were of atom type 1 (sp^3 hybridization), and the remaining carbon atoms were of type 2 (sp^2 hybridization).

Results and Discussion

Cyclohexadiene \leftrightarrow Hexatriene. The stationary points on the potential energy surface for the disrotatory electrocyclization of *cis*-1,3,5-hexatriene have been located using the 6-31G* basis set. During the course of this work, Baldwin et al. reported the transition structure and secondary kinetic isotope effects for the disrotatory electrocyclization of *cis*-1,3,5-hexatriene at the same level of theory.^{3b} The product, 1,3-cyclohexadiene, was fully optimized using C_2 symmetry. The computed geometries are in excellent agreement with both electron diffraction and microwave structures, as shown in Figure 1.¹⁹ The RHF/6-31G* bond lengths are, on the average, within 0.014 Å of the experimental bond lengths and the bond angles are within 1° of the experimental values.

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Table 1. Total Energies (au) and Zero Point (ZPE) of the Reactant, Transition Structure, and Product for the Electrocyclization of *cis*-1,3,5-Hexatriene

theory	1,3-cyclohexadiene (C_2)	TS ^a (C_s)	<i>cis</i> -1,3,5-hexatriene	
			C_{2v}	C_2
AM1 (ΔH_f)	0.02771	0.11761	0.07003	0.07605
RHF/STO-3G	-229.04385	-228.88806	-228.96510	-228.95457
RHF/3-21G	-230.54323	-230.44931	-230.51584	-230.50330
RHF/3-21G	82.9	80.7	80.8	80.3
ZPE				
RHF/6-31G*	-231.83190	-231.73188	-231.80509	-231.79198
RHF/6-31G*	85.7	83.4	84.3	84.1
ZPE				
RHF/6-31G* ^b	-231.83161	-231.73173	-231.80500	-231.79176
MP2/3-21G ^b	-231.07944	-231.00683	-231.04978	-231.04020
MP2/6-31G* ^b	-232.59075	-232.51498	-232.55662	-232.54439
MP2/6-31G* ^c	-232.62068	-232.54456	-232.58630	-232.57375

^a One imaginary frequency computed: disrotatory TS ($908.5i \text{ cm}^{-1}$). ^b Single point energy determination using the optimized 3-21G structure. ^c Single point energy determination using the optimized 6-31G* structure.



Torsional angle $165.4 = 14.1^\circ, 18.3^\circ, 17.5^\circ, 17.0^\circ, 18.0^\circ$

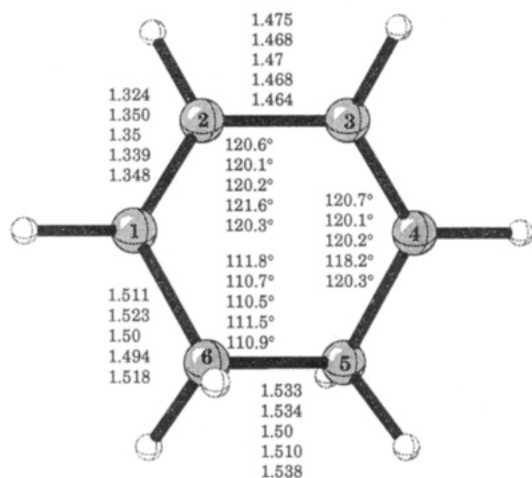


Figure 1. The RHF/6-31G* ground state of cyclohexadiene (C_2). All values are reported in angstroms and deg. The top value is the computed RHF/6-31G* number, and following in order are the electron diffraction (ref 19a), microwave (ref 19e), microwave (ref 19b), and electron diffraction (ref 19d) numbers.

Two possible conformations of *cis*-1,3,5-hexatriene were investigated. The C_{2v} and C_2 *cis*-1,3,5-hexatriene species were fully optimized and are shown in Figure 2. Only the planar C_{2v} conformer has been detected by electron diffraction, IR, and Raman studies.²⁰ Nonplanar C_2 *cis*-1,3,5-hexatriene is 7.9 kcal/mol higher in energy than the C_{2v} conformer (Table 1). A measure of the degree of out-of-plane deformation in the C_2 local minimum is given by the torsional angle, $C_1C_2C_3C_4 = 49.7^\circ$ (Figure 2). This is larger than the calculated torsional angle in *gauche* 1,3-butadiene. Recent high level calculations predict a

Table 2. Activation Energy and Energy of Reaction (kcal/mol) for the Electrocyclization of *cis*-1,3,5-Hexatriene

theory	E_a (closure)	ΔE (reaction)
AM1	29.9	-26.6
RHF/STO-3G	48.3	-49.4
RHF/3-21G	41.7	-17.2
RHF/6-31G*	45.9	-16.8
MP2/3-21G//RHF/3-21G	27.0	18.6
MP2/6-31G**//RHF/3-21G	26.1	-21.4
MP2/6-31G**//RHF/3-21G + ZPE ^a	26.0	-19.3
MP2/6-31G**//RHF/6-31G*	26.2	-21.6
MP2/6-31G**//RHF/6-31G* + ZPE ^b	25.3	-20.2
Experimental (ΔH^\ddagger , ΔH reaction)	29.0 ³	-15.22 ^{21,22}

^a Zero point energy correction obtained from RHF/3-21G vibrational frequency. ^b Zero point energy correction obtained from RHF/6-31G* vibrational frequency.

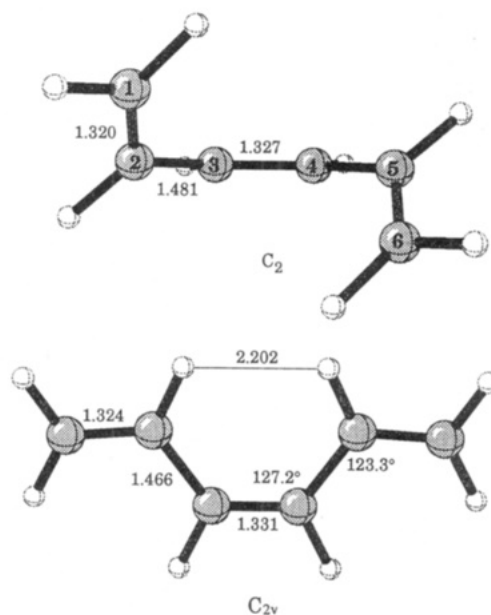


Figure 2. The RHF/6-31G* optimized structures of *cis*-1,3,5-hexatriene.

CCCC torsional angle of $38\text{--}39^\circ$ in *gauche* 1,3-butadiene.²¹ The larger torsional angle in *cis*-1,3,5-hexatriene is the result of a larger steric interaction between the *cis* hydrogens on the carbon termini.

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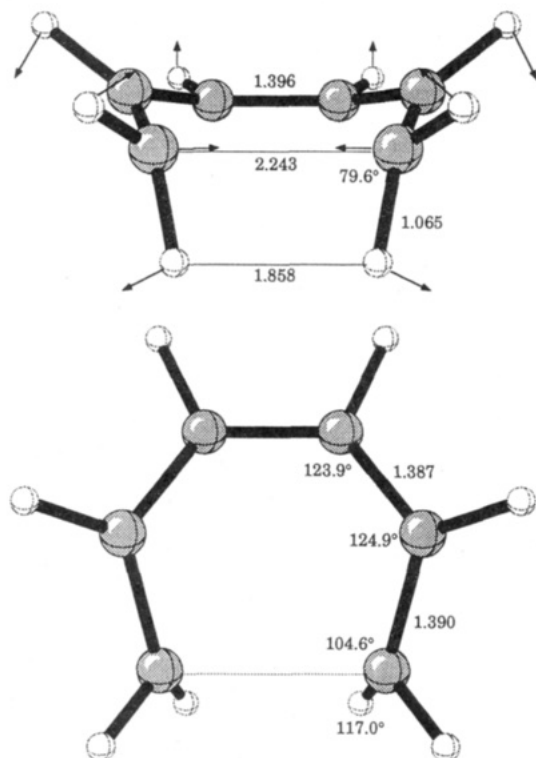


Figure 3. The RHF/6-31G* disrotatory transition structure of *cis*-1,3,5-hexatriene to form *cis,cis*-1,3-cyclohexadiene.

The disrotatory electrocyclization of *cis*-1,3,5-hexatriene has been found experimentally to have an activation enthalpy of 29 kcal/mol.³ The computed activation barrier at the highest level of theory employed is 25.3 kcal/mol (Tables 1 and 2), in reasonable agreement with experiment. The computed activation entropy is -4.5 eu, in good agreement with the experimental values of -5 eu. The energy of reaction is computed to be 20.2 kcal/mol, compared to the experimental value of 15 kcal/mol.²² The disrotatory transition structure (C_s) is shown in Figure 3.^{3b} Two interesting features are the boatlike conformation of the forming six-membered ring and the close interaction distance (1.858 Å) of the two inward hydrogens of the terminal carbons. This interaction causes serious steric interference to cyclization, as confirmed from MM2 calculations. The predicted steric interaction between the inward hydrogens is repulsive by 3.7 kcal/mol using normal MM2 parameters for hydrogen at this distance. It might be expected that either the forming CC bond for this disrotatory electrocyclization would be longer than other pericyclic reactions in order to relieve some of the strain caused by the repulsive interaction between the inward hydrogens, or that the activation energy for this process would be larger than typical activation energies for pericyclic reactions. This is not the case. As mentioned previously, both the computed and experimental activation barriers are less than or equal to the typical activation barrier for pericyclic reactions, 32 ± 3 kcal/mol.²³ The length of the forming CC bond is 2.243 Å, also typical of pericyclic reactions (2.1–2.3 Å).²³

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Substituted Cyclohexadienes and Hexatrienes.

Substitution at the 5-position of 1,3-cyclohexadiene can be either pseudoaxial or equatorial. The axial conformers are more stable by 0.3, 0.1, and 1.2 kcal/mol for methyl, formyl, and nitroso groups, respectively, at the MP2/6-



31G*/RHF/3-21G + ZPE level of theory. Fluorine is slightly more stable in the equatorial conformer (0.4 kcal/mol). Cyano shows no preference.

Substitution at the 1-position of 1,3,5-hexatriene can be either *cis* or *trans*. The boryl, cyano, formyl, methyl, and nitroso groups prefer the *trans* configuration by 2.9, 0.2, 3.3, 1.8, and 1.5 kcal/mol, respectively. The fluoro substituent is more stable in the *cis* configuration by 0.4 kcal/mol. This is likely the result of a stabilizing interaction between the fluoro group and the vinyl hydrogen at the 3-position, which are separated by 2.418 Å. This type of H–F interaction is found to occur in the disrotatory transition structure and is discussed in more detail later.

In the following discussion, we compare the transition structures with substituents in the inside or outside position. These transition structures are shown in Figures 4 and 5. The transition structures for inward and outward rotations of 1-substituted 1,3,5-hexatrienes display two trends. The perturbation of the transition structure by the substituent is minimal for outward rotation, while inward rotation causes significant geometric distortions. The parent system has an angle between the inward hydrogen and forming CC bond of 79.6° (Figure 3). The angles at the remote terminus (inner hydrogen–C_{forming bond}–C_{forming bond}) showed very small deviations: -1.0° , -0.5° , -0.2° , -0.3° , -1.0° , and -0.4° as compared to the parent for the series F, Me, CN, CHO, NO, and BH₂, respectively. Very little deviation from the parent system was observed for the substituted angle (substituent–C_{forming bond}–C_{forming bond}). These differences are 0.8°, -0.7° , -0.3° , 0.1°, 0.7°, and -0.4° , for the same series of substituents, respectively. The inward rotating substituents cause a substantial increase of geometric deformation for both the remote and substituted angles. The remote angle differences are -7.4° , -3.1° , -1.0° , 1.4°, -1.0° , and 10.0° as compared to the parent for the series F, Me, CN, CHO, NO, and BH₂, respectively. The substituted angles had larger deviations of 6.7°, 12.2°, 8.9°, 6.8°, 4.8°, and -11.8° , for the same series of substituents, respectively. The large geometric deformations caused by inward rotation of the substituent are the result of the steric repulsions between the substituent and the inward hydrogen, except with BH₂, which interacts in a stabilizing fashion with a nearby CH bond.

As observed with pericyclic reactions in general, the length of a breaking or forming CC single bond is typically 2.1–2.3 Å.²³ The transition structures with an inward rotating substituent have a larger variance of bond length as compared to the transition structures with an outward rotating substituent. The computed forming CC bond lengths at the RHF/3-21G level are 2.210, 2.275, 2.298, 2.287, 2.269, and 2.348 Å for inward rotation for the series, F, Me, CN, CHO, NO, BH₂, while for outward

Table 3. The Total Energies (ΔH_f for AM1) of the Reactants, Transition Structures, and Products for the Electrocyclizations of 1-Substituted 1,3,5-Hexatrienes. Energies are in Hartrees, Zero-Point Energies are in kcal/mol, and Imaginary Vibrational Frequencies are in cm^{-1}

structure		AM1	RHF/3-21G	ZPE	IMF	RHF/6-31G ^a	MP2/6-31G ^a
1-fluoro-1,3,5-hexatriene	cis	-0.01030	-328.83771	76.3	-	-330.65345	-331.57455
	trans	-0.01094	-328.83472	75.9	-	-330.65258	-331.57338
1-methyl-1,3,5-hexatriene	cis	0.05573	-269.33602	99.8	-	-270.84149	-271.72514
	trans	0.05379	-269.33890	99.7	-	-270.84456	-271.72789
1-cyano-1,3,5-hexatriene	cis	0.11573	-321.73701	80.8	-	-323.54242	-324.56864
	trans	0.11495	-321.73728	80.7	-	-323.54302	-324.56873
1-formyl-1,3,5-hexatriene	cis	0.01895	-342.60642	88.1	-	-344.53073	-345.58087
	trans	0.01685	-342.60694	87.6	-	-344.53657	-345.58528
1-nitroso-1,3,5-hexatriene	cis	0.07991	-358.41781	79.1	-	-360.44733	-361.53820
	trans	0.07759	-358.41813	78.9	-	-360.44977	-361.54031
1-boryl-1,3,5-hexatriene	cis	0.08906	-255.62838	88.3	-	-257.06153	-257.88405
	trans	0.08567	-255.63291	88.2	-	-257.06612	-257.88848
5-fluoro-1,3-cyclohexadiene	ax	-	-328.86235	77.9	-	-330.68299	-331.60960
	eq	-0.04254	-328.86519	77.8	-	-330.68354	-331.60945
5-methyl-1,3-cyclohexadiene	ax	0.02123	-269.36493	101.9	-	-270.86622	-271.75973
	eq	0.02022	-269.36389	101.7	-	-270.86679	-271.75930
5-cyano-1,3-cyclohexadiene	ax	0.08250	-321.76046	82.6	-	-323.56275	-324.59695
	eq	0.08175	-321.76019	82.4	-	-323.56368	-324.59702
5-formyl-1,3-cyclohexadiene	ax	-0.01642	-342.62739	89.2	-	-344.55233	-345.61053
	eq	-0.01670	-342.62838	89.1	-	-344.55328	-345.61118
5-nitroso-1,3-cyclohexadiene	ax	0.04753	-358.44007	80.6	-	-360.46702	-361.566
	eq	0.04739	-358.43941	80.4	-	-360.46689	-361.56500
5-boryl-1,3-cyclohexadiene	ax	0.05627	-255.64623	89.6	-	-257.07647	-257.91059
	eq	0.05616	-	-	-	-	-
TS fluoro	in	0.04760	-328.76593	79.3	888.3i	-330.57358	-331.52934
TS fluoro	out	0.03543	-328.77272	79.4	807.6i	-330.58394	-331.53682
TS methyl	in	0.11380	-269.26244	103.6	846.6i	-270.76003	-271.67949
TS methyl	out	0.10403	-269.27042	103.6	844.5i	-270.76908	-271.68578
TS cyano	in	0.17274	-321.66191	84.2	812.9i	-323.46129	-324.52251
TS cyano	out	0.16306	-321.67065	84.5	830.9i	-323.46987	-324.52842
TS formyl	in	0.07411	-342.53160	87.2	781.8i	-344.45837	-342.54350
TS formyl	out	0.06500	-342.54031	87.5	818.2i	-344.46198	-342.54345
TS nitroso	in	0.12609	-358.34795	82.6	774.0i	-360.37137	-361.49955
TS nitroso	out	0.12384	-358.35097	82.7	745.2	-360.36249	-361.49690
TS boryl	in	-	-255.57044	91.9	645.9i	-256.99756	-257.86161
TS boryl	out	0.13594	-255.56545	92.0	778.7i	-256.99159	-257.84701

^a Single point energy evaluation on a RHF/3-21G geometry.

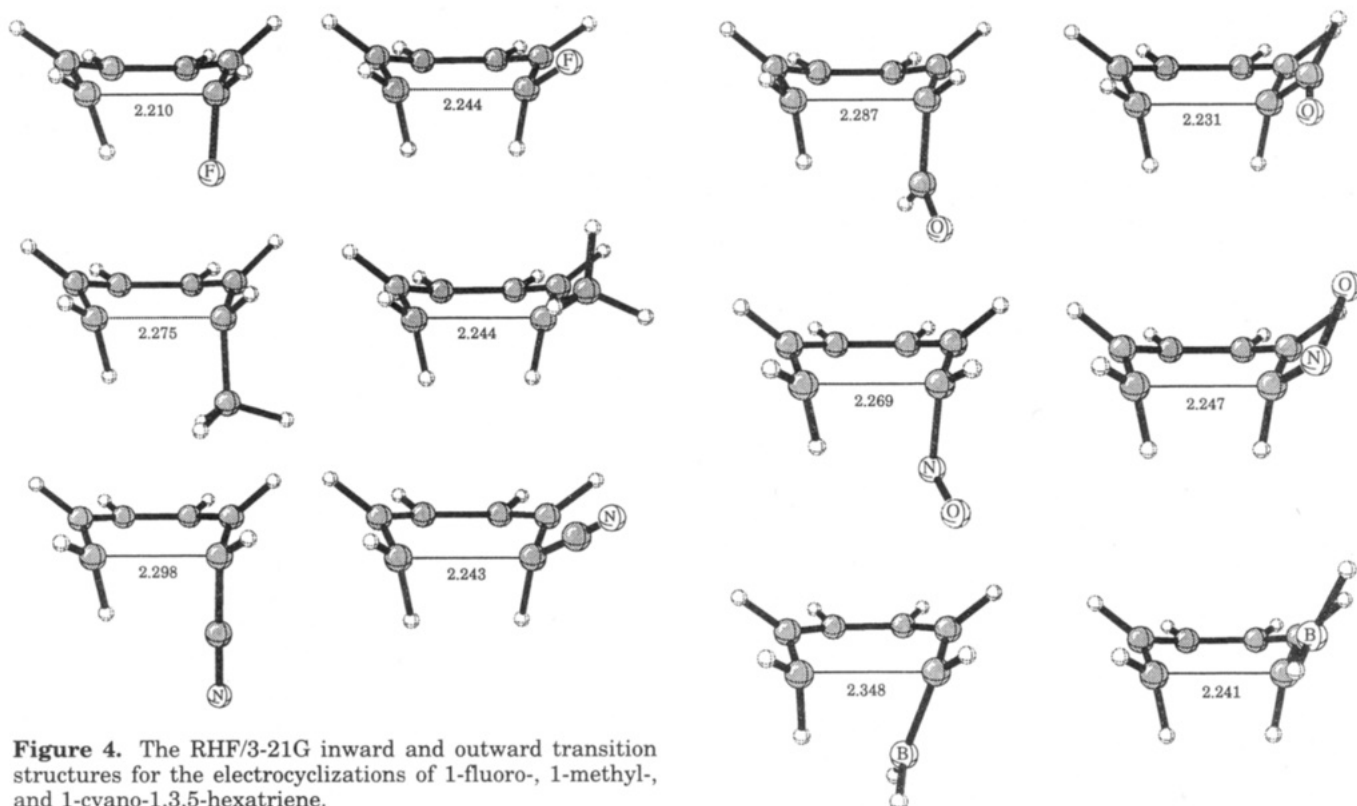


Figure 4. The RHF/3-21G inward and outward transition structures for the electrocyclizations of 1-fluoro-, 1-methyl-, and 1-cyano-1,3,5-hexatriene.

rotation these forming CC bond lengths are 2.244, 2.244, 2.243, 2.231, 2.247, and 2.241 Å. The computed forming bonds for inward rotation tend to be longer than those

Figure 5. The RHF/3-21G inward and outward transition structures for the electrocyclizations of 1-formyl-, 1-nitroso-, and 1-boryl-1,3,5-hexatriene.

Table 4. The Relative Energies (kcal/mol) of the Reactants, Transition Structures, and Products for the Electrocyclizations of 1-Substituted 1,3,5-Hexatriene

structure	AM1	RHF/3-21G	RHF/6-31G* ^a	MP2/6-31G* ^a	MP2/6-31G* ^a + ZPE ^b
1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS	29.9	41.7	46.0	26.1	26.0
1,3-cyclohexadiene	-26.6	-17.2	-16.7	-21.4	-19.3
1-cis-1-fluoro-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (FLUORO IN)	36.3	45.0	50.1	28.4	31.4
5-fluoro-1,3-cyclohexadiene	-20.2	-17.2	-18.9	-22.0	-20.4
1-trans-1-fluoro-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (FLUORO OUT)	29.1	38.9	43.1	22.9	26.4
5-fluoro-1,3-cyclohexadiene	-19.8	-19.1	-19.4	-22.7	-20.7
1-cis-1-methyl-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (METHYL IN)	36.4	46.2	51.1	28.6	32.4
5-methyl-1,3-cyclohexadiene	-22.3	-18.1	-15.9	-21.7	-19.6
1-trans-1-methyl-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (METHYL OUT)	31.5	43.0	47.4	26.4	30.3
5-methyl-1,3-cyclohexadiene	-21.1	-16.3	-13.9	-20.0	-17.8
1-cis-1-cyano-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (CYANO IN)	35.8	47.1	50.9	28.9	32.3
5-cyano-1,3-cyclohexadiene	-2.3	-14.7	-13.3	-17.8	-16.2
1-trans-1-cyano-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (CYANO OUT)	30.2	41.8	45.9	25.3	29.1
5-cyano-1,3-cyclohexadiene	-20.8	-14.5	-13.0	-17.8	-16.1
1-cis-1-formyl-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (FORMYL IN)	34.6	46.9	45.4	23.4	22.5
5-formyl-1,3-cyclohexadiene	-22.2	-13.8	-14.2	-19.0	-18.0
1-trans-1-formyl-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (FORMYL OUT)	30.2	41.8	46.8	26.2	26.1
5-formyl-1,3-cyclohexadiene	-20.9	-13.5	-10.5	-16.3	-14.8
1-cis-1-nitroso-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (NITROSO IN)	29.0	43.8	47.7	24.3	27.8
5-nitroso-1,3-cyclohexadiene	-20.3	-14.0	-12.4	-18.0	-16.5
1-trans-1-nitroso-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (NITROSO OUT)	29.0	42.1	54.8	27.2	31.0
5-nitroso-1,3-cyclohexadiene	-18.9	-13.8	-10.8	-16.7	-15.0
1-cis-1-boryl-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (BORYL IN)		36.4	40.1	14.1	17.7
5-boryl-1,3-cyclohexadiene	-20.6	-11.2	-9.4	-16.7	-15.4
1-trans-1-boryl-1,3,5-hexatriene	0.0	0.0	0.0	0.0	0.0
TS (BORYL OUT)	31.5	42.3	46.8	26.0	29.8
5-boryl-1,3-cyclohexadiene	-18.4	-8.4	-6.5	-13.9	-12.5

^a Single point energy evaluation on the optimized RHF/3-21G geometries. ^b Zero point energy corrections obtained from RHF/3-21G vibrational frequencies.

for outward rotation. This distortion relieves steric repulsion between the inward rotating substituent and the inward hydrogen on the remote terminus.

There is one anomaly concerning the length of a forming CC bond; it exists for inward rotation of the fluorine substituent. The forming CC bond length is 2.210 Å, which is 0.03 Å shorter than that of the parent transition structure. An electrostatic attraction between the inward hydrogen and fluorine may lead to the shortening of the forming CC bond, the decrease of the angle between the inward hydrogen and the forming CC bond, as well as the decrease of the distance between the inward hydrogen and the fluorine (1.835 Å) compared to the distance between the inner hydrogens in the parent transition structure (1.858 Å). This is reflected in the model MM2 calculations which indicate that the 1,4 H-F interaction is stabilizing by 7.0 kcal/mol.

The total and relative energies of the reactants, transition structures, and the products for the electrocyclic ring closures of six 1-substituted 1,3,5-hexatrienes have been calculated and are shown in Tables 3 and 4. The activation energies for the electrocyclizations of four of the 1-cis-1-substituted 1,3,5-hexatrienes are 1.8–6.4 kcal/mol larger than the activation for cyclization of 1,3,5-hexatriene, as expected due to the steric crowding and the π -donating nature of the substituents in the transition structure. The activation energies for the electrocyclic ring closure of 1-cis-1-formyl- and 1-cis-1-boryl-1,3,5-

hexatriene are 3.5 and 8.3 kcal/mol lower than for the parent system. Electronic effects overcome steric effects in these cases. Formyl, nitroso, and boryl groups are strong resonance electron-acceptors. The vacant orbitals interact in a stabilizing fashion with the remote termini of the trienes in the transition states.

For outward rotation, the donors F and Me have higher activation energies for either ring opening or closure than the parent system. By contrast, these groups tend to stabilize the conrotatory ring openings or cyclizations in the cyclobutene-butadiene system.⁵ All groups except formyl destabilize the inward transition state for cyclization, while all electron-withdrawing groups, except nitroso, stabilize the transition states for ring opening of the cyclohexadienes.

The energies of reaction for the substituents studied follow a simple trend. Electron-withdrawing groups stabilize the triene relative to the diene by 1.3–6.8 kcal/mol through conjugation with the π -system of the triene, lowering the exothermicity of the cyclization. With the exception of fluorine, trans substituents always stabilize the triene better than cis substituents due to smaller steric crowding in the trans isomer. Cis and trans fluoro and cis methyl groups prefer a saturated position by 0.3–1.4 kcal/mol. A trans methyl group stabilizes the triene more than the diene.

Comparisons of Cyclohexadiene and Cyclobutene Torquoselectivity. The equilibrium between the 1-sub-

Table 5. Activation Energies and Relative Energies of the Transition Structures for Inward and Outward Rotation of the Substituent for the Ring Opening of 5-Substituted 1,3-Cyclohexadienes. $\Delta E_a = E_{in} - E_{out}$. Energies in kcal/mol

substituent	basis set	E_a (in)	E_a (out)	ΔE_a
F	AM1	56.5	48.9	7.6
	3-21G	62.2	58.0	4.2
	6-31G* ^a	68.0	62.5	5.5
	MP2/6-31G* ^a	50.4	45.6	4.8
	MP2/6-31G* ^a + ZPE ^b	51.8	47.1	4.7
CH ₃	AM1	58.7	52.6	6.1
	3-21G	64.3	59.3	5.0
	6-31G* ^a	67.0	61.3	5.7
	MP2/6-31G* ^a	50.3	46.4	3.9
	MP2/6-31G* ^a + ZPE ^b	52.0	48.1	3.9
CN	AM1	57.1	51.0	6.1
	3-21G	61.8	56.3	5.5
	6-31G* ^a	64.2	58.9	5.3
	MP2/6-31G* ^a	46.7	43.1	3.6
	MP2/6-31G* ^a + ZPE ^b	48.5	45.2	3.3
CHO	AM1	56.8	51.1	5.7
	3-21G	60.7	55.3	5.4
	6-31G* ^a	59.6	57.3	2.3
	MP2/6-31G* ^a	42.4	42.5	-0.1
	MP2/6-31G* ^a + ZPE ^b	40.5	40.9	-0.4
NO	AM1	49.3	47.9	1.4
	3-21G	57.8	55.9	1.9
	6-31G* ^a	60.1	65.6	-5.5
	MP2/6-31G* ^a	42.3	43.9	-1.6
	MP2/6-31G* ^a + ZPE ^b	44.3	46.0	-1.7
BH ₂	AM1	—	49.9	—
	3-21G	47.6	50.7	-3.1
	6-31G* ^a	49.5	53.3	-3.8
	MP2/6-31G* ^a	30.8	39.9	-9.1
	MP2/6-31G* ^a + ZPE ^b	33.1	42.3	-9.2

^a Single point energy evaluation on the optimized RHF/3-21G geometries. ^b Zero point energy correction obtained from RHF/3-21G vibrational frequencies.

stituted 1,3,5-hexatrienes and the 5-substituted 1,3-cyclohexadienes lies on the side of the diene. However, to assess torquoselectivity without corrections for ground state substituent effects, it is easier to compare the electrocyclic ring openings of 5-substituted 1,3-cyclohexadienes with those of 3-substituted cyclobutenes. The activation energies for the disrotatory ring opening of 5-substituted 1,3-cyclohexadienes are shown in Table 5, while the activation energies for the corresponding 3-substituted cyclobutenes are shown in Table 6. The difference between activation energies for inward and outward rotation in cyclobutene ring-openings are linearly related to the substituent constant, σ_R^5 . The energy differences between the inward and outward transition structures for the disrotatory electrocyclic ring-openings of 5-substituted 1,3-cyclohexadienes are plotted versus σ_R in Figure 6. A significant reduction in the activation energy differences is computed for the 1,3-cyclohexadienes. A preference for outward rotation is computed for electron-donors (fluoro and methyl), while a preference for inward rotation is found for the electron acceptors (formyl, nitroso, and boryl). The cyano group has essentially no preference, due to the relatively high lying σ^* orbital and small size. The dependence of stereoselection on the electronic characteristics of substituents still exists in the disrotatory processes, but to a smaller degree.

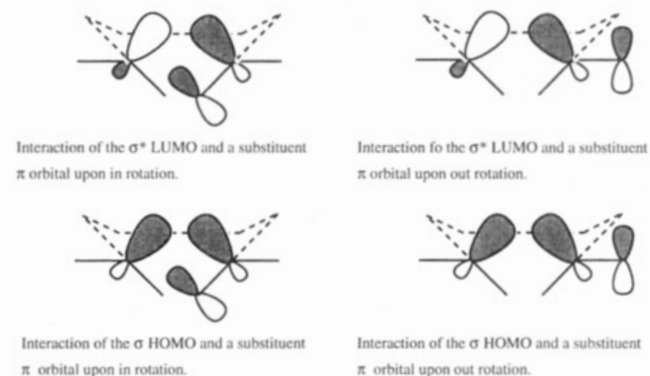
In a disrotatory process, the predicted electronic effect found in the conrotatory reaction is diminished. For example, consider the interaction between either the HOMO or LUMO of the forming bond and a p- or π -orbital of a substituent, as shown below. Here, as with

Table 6. Activation Energies and Relative Energies of the Transition Structures for Inward and Outward Rotation of the Substituent for the Ring Opening of 3-Substituted Cyclobutenes. $\Delta E_a = E_{in} - E_{out}$. Energies in kcal/mol

substituent	basis set	E_a (in)	E_a (out)	ΔE_a
F	AM1	36.2	28.0	8.2
	3-21G	52.7	35.5	17.2
	6-31G* ^a	58.9	42.0	16.9
	MP2/6-31G* ^a	46.1	30.6	15.5
	MP2/6-31G* ^a + ZPE ^b	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* ^a	51.2	45.3	5.9
	MP2/6-31G* ^a	40.4	35.4	5.0
	MP2/6-31G* ^a + ZPE ^b	38.8	33.5	5.3
CN	AM1	33.2	30.7	2.5
	3-21G	43.9	39.3	4.6
	6-31G* ^a	47.2	42.9	4.3
	MP2/6-31G* ^a	36.8	32.6	4.2
	MP2/6-31G* ^a + ZPE ^b	35.2	31.0	4.2
CHO	AM1	30.4	30.8	-0.4
	3-21G	34.7	39.2	-4.5
	6-31G* ^a	38.0	42.6	-4.6
	MP2/6-31G* ^a	27.6	32.6	-5.0
	MP2/6-31G* ^a + ZPE ^b	26.5	31.2	-4.7
NO	AM1	31.2	30.1	-1.1
	3-21G	34.5	37.1	-2.6
	6-31G* ^a	39.1	41.7	-2.6
	MP2/6-31G* ^a	26.4	31.3	-4.9
	MP2/6-31G* ^a + ZPE ^b	25.1	29.8	-4.7
BH ₂	AM1	17.4	29.2	-11.8
	3-21G	17.1	32.2	-15.1
	6-31G* ^a	20.8	39.0	-19.8
	MP2/6-31G* ^a	11.0	30.8	-19.8
	MP2/6-31G* ^a + ZPE ^b	10.8	29.5	-18.7

^a Single point energy evaluation on the optimized RHF/3-21G geometries. ^b Zero point energy correction obtained from RHF/3-21G vibrational frequencies.

the conrotatory case, a net stabilization occurs upon outward rotation of either electron-acceptors or electron-



donors. This arises from two-electron interactions shown at the right: a donor π orbital interaction with σ^* LUMO, or an acceptor substituent vacant orbitals mixes with the σ HOMO. Stabilization upon inward rotation is predicted for an electron-acceptor substituent with a low-lying vacant orbital. The amount of overlap between substituent and σ HOMO orbitals of the inward transition structure is reduced compared to that in the conrotatory process. This reduces the amount of stabilization of an inward-rotating electron-acceptor and the amount of destabilization of an inward-rotating electron-donor. The influence of electronic control upon selectivity is decreased.

While steric effects are not important in determining the stereoselectivities of conrotatory cyclobutene ring

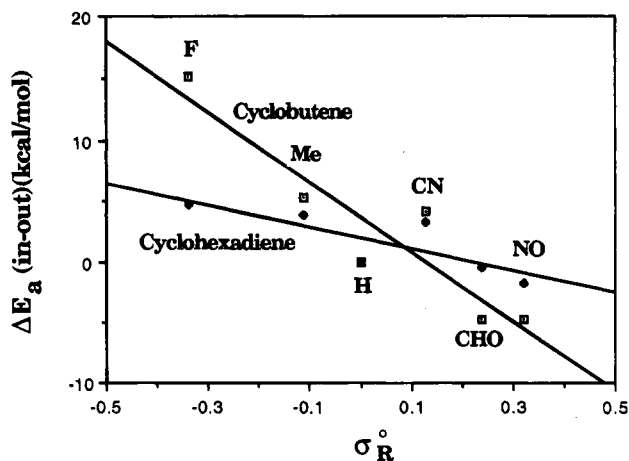


Figure 6. Plot of ΔE_a versus σ_R for the electrocyclic ring openings of 5-substituted 1,3-cyclohexadienes and 3-substituted cyclobutenes.

openings, the disrotatory motion leads to larger steric effects, since the two inward hydrogens of the terminal carbon atoms are separated by less than the sum of the van der Waals radii. Substitution of any type of func-

tional group for an inward hydrogen will cause larger steric interactions at the transition structure. There is less electronic control of stereoselectivity and more steric control. This combination of effects is manifested in the overall reduction in the activation energy differences for all substituents studied. For example, inward rotation is favored for the ring opening of 3-borylcyclobutene by 18.7 kcal/mol at the MP2/6-31G**//RHF/3-21G + ZPE level of theory, but inward rotation in 5-borylcyclohexadiene is favored by only 9.2 kcal/mol. Outward rotation is favored by 15.1 kcal/mol for 3-fluorocyclobutene, but only by 4.7 for 5-fluorocyclohexadiene. The electronic effects of torquoselectivity are a function of the extent of overlap of the substituents with the breaking bond. This is larger for cyclobutene openings than in cyclohexadiene formation.

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