

by Ensinger.⁵¹ The data were analyzed on an IBM-PC computer, using a calibration program written by Tomasik⁴⁹ and Wilgis⁴⁴ and a nonlinear, doubly weighted least-squares program written by Buddenbaum,⁴⁶ with modifications by Vogel,⁵² Pinnick,⁵³ Bowersox and Tomasik,⁵⁴ and Wilgis.⁴⁴

Product Determination. Product studies by ²H NMR spectroscopy were performed in the following manner. A 1.0-mL sample of reaction mixture (approximately 0.1 M in deuterium) with a molar excess of 2,6-lutidine was prepared in a 1.0-mL volumetric flask. The solution was transferred to an NMR tube, sealed, and allowed to react for at least 10 half-lives. The ²H NMR spectra were recorded by using a Nicolet 360-MHz spectrometer at 55.4 MHz. The Fourier transform NMR spectra were taken by using between 500 and 1000 scans. Product ratios were determined by comparison of the weighed cutouts of the peaks.

Chemical shifts for products, which varied slightly with solvent, were as follows in 97T: bicyclo[3.1.0]hexane (*1-d*, δ 1.44; 2,2,6,6-*d*₄, δ 0.42, 1.95); cyclohexene (*1-d*, δ 6.0; 3-*d*, δ 2.22; 4,4-*d*₂, δ 1.70); 3-(trimethylsilyl)cyclohexene (2-*d*, δ 6.0; 6,6-*d*₂, δ 2.2); 4-(trimethylsilyl)cyclohexene (*1-d*, δ 6.0; 3,3-*d*₂, δ 2.2); *cis*-3-(trimethylsilyl)cyclohexanol (*1-d*, δ 3.78; 2,2,6,6-*d*₄, δ 1.34, 1.44, 2.32, 2.33); *trans*-3-(trimethylsilyl)cyclohexanol (*1-d*, δ 4.32; 2,2,6,6-*d*₄, δ 2.0, 1.6, 1.7); *cis*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether (*1-d*, δ 3.67; 2,2,6,6-*d*₄, δ 1.34, 1.44, 2.32, 2.33); *trans*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether (*1-d*, δ 4.2; 2,2,6,6-*d*₄, δ 2.0, 1.6, 1.7); 3-*tert*-butylcyclohexene-1-*d* and 4-*tert*-butylcyclohexene-2-*d* (δ 5.97); *cis*- and *trans*-3-*tert*-butylcyclohexanol and *cis*- and *trans*-3-*tert*-butylcyclohexyl trifluoroethyl ether (*1-d*, δ 4.10; 2,2,6,6-*d*₄, δ 2.10); 3-*tert*-butylcyclohexene-2,2,6,6-*d*₃ and 4-*tert*-butylcyclohexene-1,3,3-*d*₃ (δ 5.9 and 2.2).

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Coope for ¹H and ²H NMR spectra, Ford P. Wilgis for ¹³C NMR spectra and ¹⁸O analyses, Dr. Lester Taylor for the GC/MS analysis, and Teresa Wright-Kester for ¹³C NMR spectra.

Registry No. 1, 99810-99-8; 1- α -*d*, 122722-74-1; 1- β -*d*₄, 122722-76-3; 2, 99811-00-4; 2- α -*d*, 122722-75-2; 2- β -*d*₄, 122722-77-4; 3, 122722-65-0; 3- β -*d*₄, 122722-78-5; 4, 122722-66-1; 4- β -*d*₄, 122722-79-6; 5, 966-02-9; 5- α -*d*, 1688-18-2; 5- β -*d*₄, 1099-68-9; 6, 966-01-8; 6- α -*d*, 968-89-8; 6- β -*d*₄, 1099-67-8; 3-(trimethylsilyl)cyclohexanone, 7531-60-4; *cis*-3-(trimethylsilyl)cyclohexanol, 7452-98-4; *trans*-3-(trimethylsilyl)cyclohexanol, 7452-99-5; 3-(trimethylsilyl)cyclohexanone-2,2,6,6-*d*₄, 122722-67-2; *cis*-3-(trimethylsilyl)cyclohexanol-2,2,6,6-*d*₄, 109702-24-1; *trans*-3-(trimethylsilyl)cyclohexanol-2,2,6,6-*d*₄, 109702-25-2; *cis*-3-(trimethylsilyl)cyclohexanol-1-*d*, 122722-68-3; *trans*-3-(trimethylsilyl)cyclohexanol-1-*d*, 122722-69-4; *cis*-3-*tert*-butylcyclohexanol, 10488-10-5; *trans*-3-*tert*-butylcyclohexanol, 16201-66-4; 3-*tert*-butylcyclohexanone, 936-99-2; *cis*-3-*tert*-butylcyclohexanol-2,2,6,6-*d*₄, 122722-70-7; *trans*-3-*tert*-butylcyclohexanol-2,2,6,6-*d*₄, 122722-71-8; *cis*-3-*tert*-butylcyclohexanol-1-*d*, 122722-72-9; *trans*-3-*tert*-butylcyclohexanol-1-*d*, 122722-73-0; bicyclo[3.1.0]hexane-1-*d*, 122722-80-9; bicyclo[3.1.0]hexane-2,2,6,6-*d*₄, 122722-81-0; cyclohexene-1-*d*, 42843-17-4; cyclohexene-3-*d*, 84108-31-6; cyclohexene-4,4-*d*₂, 122722-82-1; 3-(trimethylsilyl)cyclohexene-2-*d*, 122722-83-2; 3-(trimethylsilyl)cyclohexene-6,6-*d*₂, 122722-84-3; 4-(trimethylsilyl)cyclohexene-1-*d*, 122722-85-4; 4-(trimethylsilyl)cyclohexene-3,3-*d*₂, 122722-86-5; *cis*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-1-*d*, 122722-87-6; *cis*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-2,2,6,6-*d*₄, 122722-88-7; *trans*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-1-*d*, 122722-89-8; *trans*-3-(trimethylsilyl)cyclohexyl trifluoroethyl ether-2,2,6,6-*d*₄, 122722-90-1; 3-*tert*-butylcyclohexene-1-*d*, 102853-34-9; 4-*tert*-butylcyclohexene-2-*d*, 122722-91-2; *cis*-3-*tert*-butylcyclohexyl trifluoroethyl ether-1-*d*, 122722-92-3; *cis*-3-*tert*-butylcyclohexyl trifluoroethyl ether-2,2,6,6-*d*₄, 122722-93-4; *trans*-3-*tert*-butylcyclohexyl trifluoroethyl ether-1-*d*, 122722-94-5; *trans*-3-*tert*-butylcyclohexyl trifluoroethyl ether-2,2,6,6-*d*₄, 122722-95-6; 3-*tert*-butylcyclohexene-2,6,6-*d*₃, 122722-96-7; 4-*tert*-butylcyclohexene-1,3,3-*d*₃, 122722-97-8; bicyclohexane, 285-58-5; cyclohexene, 110-83-8; 3-(trimethylsilyl)cyclohexene, 40934-71-2; 4-(trimethylsilyl)cyclohexene, 40934-72-3; 3-*tert*-butylcyclohexene, 14072-87-8; 4-*tert*-butylcyclohexene, 2228-98-0; 3-*tert*-butylcyclohexanone-2,2,6,6-*d*₄, 122722-98-9.

An ab Initio Study of Vinylallene Conformations

Douglas Bond¹

Department of Chemistry, University of California, Riverside, Riverside, California 92523, and Department of Chemistry, Riverside Community College, 4800 Magnolia, Riverside, California 92506

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Ab initio optimizations and MP2/6-31G* single-point calculations are performed for the polyene compounds (*Z*)-1,3-pentadiene (5), 1,2,4-pentatriene (6), and (*Z*)-1,2,4-hexatriene (7). The *s*-*trans* conformer is found to predominate in all cases; however, the preference is less for the vinylallenes than for either butadiene or pentadiene. Compound 6 was found to be planar in both the *s*-*trans* and *s*-*cis* conformations; however, nonplanar twist structures for 5 and 7 were found at lower energy than the planar *s*-*cis*. As further evidence of steric crowding in the *s*-*cis* conformation, the methyl group of compounds 5 and 7 are found to stagger rather than eclipse the double bond in the *s*-*cis* conformation. The reduced methyl rotation barrier in the *s*-*trans* pentadiene and hexatriene is found to be a result of steric repulsions and reduced π interactions between the out of plane methyl hydrogens and the π bond. Geometries, orbital energies, and intramolecular interactions are examined with a view to understanding the enhanced reactivities of the vinylallenes. In these, few differences between the normal dienes and the vinylallenes are found.

Introduction

Vinylallenes have been shown to undergo [1,5]-sigmatropic rearrangements at temperatures lower than those commonly employed for conjugated dienes. For example,

(*Z*)-2-methyl-1,3-pentadiene (1) reacts at 225 °C (E_{act} = 32.8 kcal/mol),² while the corresponding shift occurs at 100 °C in the vinylallene 5-methyl-1,2,4-hexatriene (3) (E_{act} = 24.6 kcal/mol).³

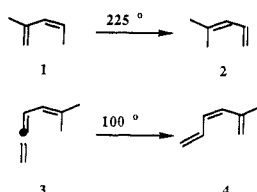
(1) Address correspondence to Riverside Community College.

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Table I. Selected Calculated (3-21G) and Experimental Bond Lengths (Å) and Angles (Deg) for the Dienes 5-7 (See 7d for Numbering of Carbon Skeleton)

compound	C ₁ =C ₂	C ₂ -C ₃	C ₃ =C ₄	C ₄ -C ₅	C ₁ =C ₆	C ₁₂₃	C ₂₃₄	C ₃₄₅
5								
s-cis eclipsed	1.322	1.477	1.325	1.507		131.15	132.54	130.56
s-cis staggered	1.323	1.473	1.325	1.511		129.37	129.95	127.59
s-trans eclipsed	1.321	1.467	1.324	1.509		123.29	126.97	127.61
s-trans staggered	1.321	1.466	1.323	1.517		123.65	125.39	125.65
s-cis twisted ^a	1.319	1.478	1.322	1.509		125.62	127.28	127.33
expt ^b	1.34	1.48	1.34	1.50		122.0	124.2	128.8
6								
s-cis	1.297	1.403	1.319		1.292	125.18	125.92	
s-trans	1.298	1.471	1.320		1.291	123.56	123.79	
expt ^c	1.313	1.462	1.338		1.310	124.3	124.1	
7								
s-cis eclipsed	1.298	1.478	1.323	1.506	1.293	129.67	130.82	128.77
s-cis staggered	1.300	1.474	1.323	1.506	1.293	128.65	128.99	126.71
s-trans eclipsed	1.299	1.472	1.323	1.509	1.291	122.89	126.53	127.64
s-trans staggered	1.299	1.471	1.323	1.517	1.291	123.28	128.99	126.71
s-cis twisted ^d	1.297	1.479	1.322	1.509	1.292	125.63	127.41	126.86

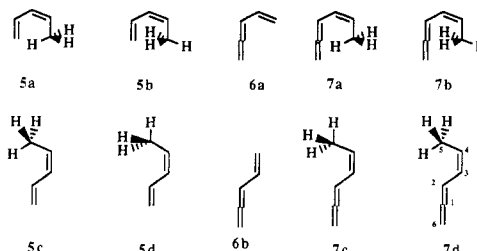
^aThe twist angle is 47°. ^bReference 24. These are often cited as being experimental values. In fact, as reported by Hsu and Flygare, they are assumed parameters. No definitive structural data have been reported for this system. ^cTraetteberg, M.; Bakken, P.; Hopf, K. *Acta Chem. Scand.* 1980, 34A, 461-462. The structure was determined by electron diffraction. ^dTwist angle is 39°.

Chart I

Subsequent work has shown that with appropriate substitution, these vinylallenes are capable of rearranging at room temperature,⁴ can afford significant π facial stereoselectivity,⁵ and are versatile synthetic intermediates providing entry into a variety of retinoids, vitamin D analogues, and drimanens.⁶

Several explanations invoking the allenic function have been advanced to explain the facility of the rearrangement.² (1) An sp^2 hybrid orbital is used to form the new C-H bond (as opposed to the sp^3 employed in pentadiene). In a symmetrical transition state, this could afford 3-5 kcal/mol of additional stabilization, since the vinylic C-H bond is known to be stronger by 6-10 kcal/mol.⁷ (2) Alternatively, if the transition state has any productlike character, it would benefit from the greater thermodynamic stability of the product. (3) Finally, there is a possibility that the hydrogen is transferred to the non-conjugated (terminal) rather than the conjugated π bond of the allene.⁸ The relative energetics of this mechanism are difficult to assess.

Although the most stable conformer of conjugated dienes is the s-trans, the [1,5]-sigmatropic rearrangement and the Diels-Alder reaction both require an s-cis or near s-cis conformation for reaction. Since the steric interactions found in the s-cis conformation of 1,3-pentadiene, (5a or 5c) should be greater than those found in the vinylallene (7a or 7c), we reasoned that this could also be partly responsible for the difference in activation energy. Little experimental work is available on the conformational en-

Chart II

ergy differences of these compounds; therefore, a study of several related polyene systems: 1,3-butadiene, (Z)-1,3-pentadiene (5a-d), 1,2,4-pentatriene (6a,b), and (Z)-1,2,4-hexatriene (7a-d), using ab initio molecular orbital methods,⁹ was undertaken to provide meaningful data. Considerable work has been done on the butadiene conformations,¹⁰ and we used our calculations on this system as a benchmark to establish the accuracy of the subsequent work. Several calculations of the pentadiene system have been undertaken recently,¹¹ but no treatment of all four conformers of the Z isomer has appeared. The pentatrienes 6a and 6b have recently been optimized at the 6-31G* level by Pasto with results comparable to those reported here.¹² No work with the hexatrienes 7a-d has been reported.

Methods

The ab initio calculations reported here were carried out with the GAUSSIAN 80 UCSF¹³ and GAUSSIAN 86 programs¹⁴

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(12) We are grateful to Professor Pasto for providing preprints of his work.

Table II. Calculated and Relative Energies for Butadiene and the Dienes 5-7

compound	AM1		3-21G//3-21G		N_{imag}^e	MP2/6-31G*//3-21G		expt ^b
	energy ^a	rel ^b	energy ^c	rel ^d		energy ^c	rel ^d	
1,3-butadiene								
s-cis	30.62	0.77	-154.05394	3.27	1	-155.41500	3.39 ^f	2.51 ^{g-i}
s-trans	29.85	0.00	-154.05946	0.00	0	-155.42070	0.00	0.00
5								
s-cis eclipsed	24.32	3.47	-192.86967	6.48	2	-194.57963	6.10	
s-cis staggered	22.58	1.72	-192.87238	4.54	1	-194.58256	4.02	
s-trans eclipsed	20.86	0.01	-192.87980	0.00	0	-194.58916	0.00	0.00
s-trans staggered	20.85	0.00	-192.87881	0.82	1	-194.58800	0.93	0.74 ^j
s-cis twisted			-192.87534	2.80	0	-194.58508	2.60	
6								
s-cis	61.07	0.59	-191.67272	2.55	0	-193.36456	2.83	
s-trans	60.48	0.00	-191.67655	0.00	0	-193.36883	0.00	
7								
s-cis eclipsed	52.80	2.34	-230.49115	3.80	1	-232.53216	3.21	
s-cis staggered	52.72	1.26	-230.49161	3.49	1	-232.53280	2.79	
s-trans eclipsed	51.47	0.01	-230.49701	0.00	0	-232.53708	0.00	
s-trans staggered	51.46	0.00	-230.49612	0.75	1	-232.53604	0.84	
s-cis twisted			-230.49283	2.62	0	-232.53378	2.17	

^a Heat of formation in kcal/mol. ^b Kilocalories/mole. ^c Hartrees. ^d Kilocalories/mole corrected for differences in zero point energies. ^e Number of imaginary frequencies. ^f Other computational studies have obtained comparable results: ref 9c reports a value of 3.26 kcal/mol from a partial optimization; full optimization gives 3.45 kcal/mol using a double ζ basis set (ref 9d). ^g Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans 2* **1976**, 1666-1671. ^h Spectroscopic methods give similar results: 2.50 kcal/mol (Carreira, L. A. *J. Chem. Phys.* **1975**, *62*, 3851-3854) and 2.66 kcal/mol (Bock, C. W.; George, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 26-34); a smaller value, 2.105 kcal/mol, is obtained by NMR (Lipnick, R. L.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6370-6375). ⁱ The relative energies shown here are based on a planar s-cis and planar s-trans. There is evidence for a gauche isomer at lower energy than the s-cis: see ref 10c,d,g and Pincelli, U.; Cadioli, B.; Levy, B. *Chem. Phys. Lett.* **1972**, *13*, 249-252. ^j Reference 24.

employing their standard methods and basis sets. Geometry optimizations were performed with the AM1 method¹⁵ and 3-21G basis set and were followed by 3-21G frequencies and single-point calculations at the MP2/6-31G*//3-21G level.

The intramolecular interactions and orbital energies were analyzed using the HF/3-21G wave functions with the natural bond orbital set of methods,¹⁶ using the program G82NBO.¹⁷ The steps of the method involve natural population analysis (NPA),^{16b} the formation of localized natural bond orbitals (NBO),^{16a} and finally, the formation of natural localized molecular orbitals (NLMOs)^{16c} by allowing the natural bond orbitals to delocalize to full occupancy.

Results

A. Geometries. The bond lengths and bond angles shown in Table I show a close correspondence with experimental values where these are known. In general, the bond angles open somewhat in going from the s-trans to the s-cis. These effects are magnified when the eclipsing group is a methyl, indicating increased steric interactions. The geometries from our AM1 calculations are not shown, but in general, the bond angles were found to be approximately 2° larger in both conformations than those obtained from ab initio methods.

B. Energies. The calculated and relative energies are shown in Table II. Our calculated values for the difference between the s-trans and s-cis conformations of butadiene

are comparable to those obtained by other groups.¹⁰ The energy difference tends to overestimate the experimental value by 1 kcal, and this is not unusual.¹⁸

The relative energies of the butadiene conformers by AM1 is smaller than that from ab initio calculations and deviates considerably from the experiment. These results are consistent with previous reports showing that AM1 (and its precursors) is not capable of accurately predicting the relative energies of the conformers of conjugated compounds.^{19,20} They stand in contrast to a more recent paper which reports good agreement in substituted benzene rotamers which are formally similar to our systems.²¹

As expected, the eclipsed s-trans pentadiene (5c) is the most stable conformer. Further, analysis at the 3-21G level shows all frequencies to be positive, confirming the presence of a stable structure. The methyl rotamer 5d has a single imaginary frequency corresponding to methyl rotation. The energy difference of 0.93 kcal/mol is smaller than that observed for methyl rotation in propene,²² but larger than the experimental value of 0.74 kcal/mol.²⁵

As expected, the energies of the two s-cis conformations are much higher in energy than the comparable s-cis conformer of butadiene. No experimental value is available here to compare the 4.02 kcal/mol energy difference, but a value of 2.58 kcal/mol has been reported from molecular mechanics.²³

The relative energies for pentadiene also reveal an unexpected result. It is well known that methyl groups prefer to eclipse double bonds.^{22,24} While this is true for the s-trans pentadiene, it is not so for the s-cis conformer, which is 2.08 kcal/mol more stable in the staggered conformation than in the eclipsed. This is a direct result of

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Table III. Calculated and Relative Energies for the Conformations of (*E*)-1,3-Pentadiene

compound	3-21G//3-21G		expt ^{b,c}
	energy ^a	rel ^b	
s-trans staggered	-192.87965	1.72	1.80
s-trans eclipsed	-192.88239	0.00	0.00
s-cis staggered	-192.87397	5.28	
s-cis eclipsed	-192.87682	3.50	

^aHartrees. ^bKilocalories/mole not corrected for differences in zero point energies. ^cReference 24.

the steric interactions between the planar methyl hydrogen and the hydrogens of C₁. This "abnormal" preferred conformation of s-cis pentadiene has the advantage of placing the methyl group in the correct position for the [1,5]-sigmatropic shift (this assumes a C_s as opposed to C_{2v} transition state). The overall energy difference between the two conformers of 4.02 kcal/mol (at the MP2/6-31G* level) is sufficient to add significantly to the overall activation energy for either a Diels-Alder reaction or a sigmatropic shift.

Both of these structures have imaginary frequencies corresponding to rotation of the methyl group and twisting of the conjugated π system. We removed all symmetry constraints from the two molecules and reoptimized, finding a single nonplanar structure from either which has no imaginary frequencies. This structure is 2.60 kcal/mol higher in energy than 5c and has a dihedral angle of ~50° at the C₂C₃ bond.

Again, AM1 gives values considerably less than our ab initio results. Further, AM1 fails to predict the increased stability of the s-trans eclipsed vs s-trans staggered. Experimentally, the eclipsed is 0.74 kcal/mol more stable than the staggered,²⁵ a result that is close to the ab initio (0.93 kcal/mol). AM1 does, however, correctly predict that the s-cis staggered conformation is more stable than the s-cis eclipsed and predicts an energy difference comparable to the ab initio result.

How much greater is the energy difference of the (*Z*)- than the (*E*)-pentadiene? Although our interest has been primarily the *Z* conjugated dienes, we performed 3-21G optimizations of the (*E*)-1,3-pentadiene to see if the results would match as closely. The energies are reported in Table III. In both the s-trans and s-cis, the methyl prefers the normal eclipsed conformation, providing further evidence that the deviation of the staggered s-cis (5b) is a result of steric effects. The energy difference between the eclipsed s-cis and s-trans (*E*)-pentadiene conformers is comparable to that of butadiene, a result that is not unexpected.

The conformational energy difference of 2.83 kcal/mol observed for the 1,2,4-pentatriene is smaller than that for butadiene or pentadiene, suggesting that reduced steric interactions make the s-cis conformation more accessible. Neither of these structures has an imaginary frequency. A similar result (2.79 kcal/mol) is observed for the (*Z*)-1,2,4-hexatriene. Barriers to methyl rotation for the s-trans hexatriene 7b are comparable to those in 5b (the conformational energy difference is 0.84 kcal/mol vs 0.93 kcal/mol, respectively); however, further evidence for reduced steric interactions in the s-cis vinylallenes is obtained by comparing the methyl rotation energies for 7c (0.42 kcal/mol) vs 5c (1.98 kcal/mol).

Compound 7c has all positive frequencies, while the remaining three each have one imaginary frequency. In the case of 7d, this corresponds to methyl rotation. The s-cis rotamers 7a,b show both methyl rotation and diene twisting in analogy to the pentadiene system. The twisted structure is 2.1 kcal/mol higher in energy than 7c and has a twist angle of 37°, slightly less than that observed for pentadiene.

C. Orbital Energies and Interactions. Table IV summarizes the orbital energies of the four conjugated diene systems. The calculated HOMO energies tend to be lower than experiment, but within 2.5%. Agreement is even better for the one LUMO for which the experimental energy is available; however, the ab initio results for the

Table IV. Molecular Orbital Energies (6-31G*) of Conjugated Dienes 5-7 (eV)

compd	orbital	s-cis ^a		s-trans ^b		expt ^c
		<i>E</i>	symmetry	<i>E</i>	symmetry	
5	HOMO-2	-12.77	A'	-12.81	A'	-11.7
	HOMO-1	-11.53	A''	-11.65	A'	-11.1
	HOMO	-8.53	A''	-8.47	A''	-8.67
	LUMO	3.53	A''	3.61	A''	3.57
6	HOMO-2	-12.19	A''	-12.21	A''	-11.4
	HOMO-1	-10.29	A'	-10.30	A'	-10.04
	HOMO	-8.53	A''	-8.76	A''	-8.88
	LUMO	3.33	A''	3.54	A''	
7	HOMO-2	-11.58	A''	-11.87	A''	
	HOMO-1	-10.07	A'	-10.26	A'	
	HOMO	-8.46	A'	-8.49	A''	
	LUMO	3.59	A''	3.77	A''	

^aEnergies are for the staggered conformation. ^bEnergy is for the more stable eclipsed conformation. ^cBieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P.; *Helv. Chim. Acta* 1977, 60, 2213-2233.

Table V. Energies (kcal/mol) from the 3-21G Wave Function for Hyperconjugative Interactions to and from the Methyl Out-of-Plane Hydrogens in Dienes 5 and 8

donor orbital	acceptor orbital	(Z)-1,3-pentadiene				(E)-1,3-pentadiene			
		eclipsed		staggered		eclipsed		staggered	
		s-cis	s-trans	s-cis	s-trans	s-cis	s-trans	s-cis	s-trans
C ₃ C ₄ π	C ₅ H ₁₂ σ*	2.88	3.03	2.63	2.64	3.37	3.39	2.47	2.52
C ₄ H ₈ σ	C ₅ H ₁₂ σ*			0.89	0.85			0.81	0.80
C ₅ H ₁₂ σ	C ₃ C ₄ π*	4.86	4.57	4.14	3.84	4.49	4.43	3.71	3.69
C ₅ H ₁₂ σ	C ₃ C ₄ σ*	1.97	1.74			1.47	1.50		
C ₅ H ₁₂ σ	C ₄ H ₈ σ*			1.34	1.36			1.40	1.46
C ₄ H ₈ σ	C ₅ H ₁₁ σ*	2.75	2.48			2.21	2.18		
C ₄ H ₁₁ σ	C ₃ C ₄ σ*			3.91	3.65			3.42	3.48
C ₅ H ₁₁ σ	C ₄ H ₈ σ*	3.06	3.26			3.53	3.65		

lower energy occupied orbitals are not as good. The HOMO-LUMO separation is virtually identical in compounds **5** and **7**.

Are there intramolecular attractions which provide insight into the conformational preferences or offer clues to potential reactivity? By orthogonalizing the ab initio wave functions, the NBO method¹⁶ allows the molecular orbitals to be localized and the interaction energies between localized orbitals and antibonds to be determined. As expected, there is a significant interaction between the conjugated π bonds; however, there are no interactions between the allene π bonds and none between the methyl hydrogens and either of the allene π bonds in **7b** that would suggest the beginnings of a reaction in the ground state.

Based on gas-phase attachment energies, Staley et al.²⁶ have suggested that there is a through-space interaction between the out-of-plane methyl hydrogens and the $C_{12}\pi^*$ causing conformation **5d** to be preferred over **5c**. This interaction could explain the increased population of **5c** and the decreased rotational barrier of the methyl group in this conformation.²⁴

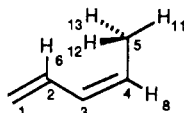


Table V shows all interactions above the threshold (0.50 kcal/mol) between the methyl hydrogens or their antibonds and any other orbitals except those that are conformation independent (i.e. those between the $C_5H_{12}\sigma$ and the $C_4C_5\sigma^*$ or $C_5H_{11}\sigma^*$ and between the $CH_{12}\sigma^*$ and $C_4C_5\sigma$ or $C_5H_{11}\sigma$). No interactions of the type suggested by Staley between the out-of-plane hydrogens and the $C_1C_2\pi^*$ were found, and, indeed, the distance between the atoms is probably too large (more than 3 Å) for such an interaction to be significant.

The interactions between the out-of-plane hydrogens and the $C_3C_4\pi$ bond are greater when the methyl eclipses the double bond than when it staggers the double bond. This data confirms the hypothesis of Hehre²⁷ and the calculations of Houk²⁴ that these interactions are the cause of the eclipsing effect. We found that these interactions were similar in both the s-trans and s-cis conformations; hence, the preference of the s-cis methyl for the staggered conformation is most likely due to steric effects.

We have previously noted the differences between the methyl rotation barrier in the *E* and *Z* isomers. The MP2/6-31G* energies for **5c-d** are close to experiment.²⁴ However, the values are considerably lower than those reported for propene²¹ and the (*E*)-1,3-pentadiene.²⁴ The ab initio results for the latter are presented in Table III and confirm the literature values, even at this modest level of theory.²⁸ Furthermore, this lowered rotation barrier in the *Z* isomer is also observed in (*Z*)-1,2,4-hexatriene. The σ interactions (Table V) are relatively constant throughout the conformations of the two compounds; however, the changes in π effects observed when the methyl is rotated are much smaller in the *Z* isomer than in the *E* by as much as 0.5 kcal or more. This coupled with a repulsion between H_6 and H_{11} in the eclipsed conformation, which is not found in any of the other conformers,

accounts for the lowered rotation barrier of the methyl in the *Z* isomer.

Concluding Remarks

The importance of conformation in the Diels-Alder reaction is emphasized in two recent reports. The first is qualitative. Studies of both diastereomers of pentadiene show that the *3E* isomer is capable of serving as both a dienophile and diene. In contrast, under similar conditions, the *Z* isomer acts only as a dienophile.²⁹

In a quantitative study, Ruecker et al.³⁰ showed that the rate of reaction of (*3E*)-pentadiene with tetracyanoethylene was 4.57×10^4 times faster than the corresponding reaction with the (*3Z*)-pentadiene. These authors reported rate data for several dienes with tetracyanoethylene. Based on their results they contend that there are three factors influencing the rate of the Diels-Alder reaction: (1) HOMO-LUMO energy separation, (2) distance between the 1,4 centers, and (3) the s-cis/s-trans equilibrium.

On two of these counts, pentadiene and hexatriene are similar. As noted above, the HOMO-LUMO separation in the two substances is similar and the distance between the 1,4 centers is comparable (3.16 Å in pentadiene vs 3.12 Å in hexatriene). In the case of the Diels-Alder reaction, the twist structures of pentadiene and hexatriene are not likely to be amenable to reaction, and the planar s-cis will be required. Therefore, the easier access to the s-cis conformation in the hexatriene suggests enhanced reactivity. Kinetic studies reported by Reich et al.³¹ support this. Unfortunately, only rate constants were reported, and it is impossible to determine what portion of the activation energy is a result of the conformational energy difference.

In the case of sigmatropic rearrangements, the twist structure positions the hydrogen for migration as effectively as the planar (the distances from the migrating hydrogen to the receptor carbon is between 2.6 and 2.7 Å in both the planar and twist). Since the difference in energy between the pentadiene and hexatriene twist structures is minimal, we conclude that conformation plays a minimal role in the enhanced rates of vinylallene [1,5]-sigmatropic rearrangements. An understanding of this phenomenon requires a more detailed understanding of the transition state. Further computational experiments are in progress to elucidate the causes of the enhanced reactivity of vinylallenes and the facial selectivity observed in the literature.

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Registry No. **5**, 1574-41-0; **6**, 10563-01-6; **7**, 31516-68-4; butadiene, 106-99-0.

Supplementary Material Available: Absolute energies and geometries of all species calculated here in GAUSSIAN 86 Archive Format (4 pages). Ordering information is given on any current masthead page.

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