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Butatrienes as Extended Alkenes: Barriers to Internal Rotation and Substitution Effects on the Stabilities of the Ground States and Transition States

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The barriers to internal rotation of methylated, ethynylated, and vinylated butatrienes and alkenes were calculated at the CASPT2/6-31G(d)//B3LYP/6-31G(d) level. Calculated butatriene rotational barriers are lower than those of analogous alkenes, but there is a larger variance in rotational barrier for alkenes than for butatrienes. The barriers to rotation were analyzed by isodesmic equations designed to estimate the substituent effects in the ground (GS) and transition (TS) states individually. The GSs of both series are stabilized to roughly the same extent. In contrast, the TSs of butatrienes are more stabilized overall than those of alkenes. Much of the stabilization in the TS of butatrienes comes from the internal triple bond and not from the substituent. Estimation of the substituent stabilization alone reveals the TSs of ethylenes to be more stabilized by substitution than butatrienes.

Introduction

It is known that substitution dramatically affects the magnitude of the internal rotational barrier of alkenes.[1] Experimental rotational barriers[1d,2] have been determined for many derivatives, while computation[1c,3] has supplemented these data and has helped to address the intricacies of both the thermal and photoinduced processes.[4] It is established that thermal rotation/isomerization proceeds through a perpendicular singlet diradical transition state (Scheme 1, top).[3a] The barrier ($\Delta G^{\ddagger}$) for dideuterioethylene is 65 kcal/mol,[2a] while substituted alkenes can have dramatically lower barriers. Substitution has an influence on both the transition state (TS) and the ground state (GS).[5] In the TS, the orthogonal radical centers can be strongly stabilized through conjugation[6] and hyperconjugation.[7] These effects also operate in the GS, but the interaction is now between the π-bonds and the substituent. Steric effects also influence both. The rotational barrier of 6-dimethylamino-6-methylfulvene (**1**) is only 16.4 kcal/mol[5] (Scheme 2), a 49 kcal/mol decrease compared to ethylene, which is achieved through a combination of representative effects: the cyclopentadienyl ring and the dimethylamino and methyl groups all provide stabilization in the TS and GS, and there is also steric destabilization of the GS. Steric effects may also influence the stability of the TS. For example, increasing steric bulk of substituents on the ortho positions of **2** causes a steady increase of the rotational barrier. This effect has been assigned to the interaction of the substituent, R, and the dimethylamino group in the TS, which are more proximal in this state than in the GS.[2h] Work on substituted alkenes has been motivated by the challenge to theoretical and synthetic chemists of designing systems in which the relative energies of the planar and perpendicular states are reversed from the examples described. Compound **3** is one such successful example that favors the perpendicular geometry due to strong stabilization of the diradical centers and strong steric destabilization between proximal chlorine atoms in the planar form.[2i,j] Materials chemists have taken advantage of all these effects to evolve substituted systems as functional devices that are switchable between geometrically defined chemical states, such as overcrowded alkenes (**4**).[8]

Butatriene is intriguing as a geometrically extended alkene. Both share the same planar GS and perpendicular TS for rotation (Scheme 1). Steric interactions in substituted butatrienes should be dramatically reduced in both the GS and TS compared to analogous alkenes; steric interactions are an essential point of control in the design of alkene-based molecular switches.[8] In contrast, stabilizing electronic interactions with the diradicaloid centers are increased in butatrienes, via the internal triple bond, compared to the ethylenes. Substitution of butatrienes has only been studied in a preliminary fashion.[9] No systematic study of substitution effects on the GS and TS of alkenes has been reported, although GS effects have been treated systematically;[3f] from these, TS effects can be indirectly estimated.

The previous computational study[9] of butatrienes at the B3LYP/6-31G(d) level[10] is extended here. The geometries of the GS and TS of mono-, 1,4-di-, and 1,1,4,4-tetra-substituted derivatives have been computed. The analogous alkene series is also calculated for comparison. Ethylene (**5**), as well as the methylated (**6**−**8**), ethynylated (**9**−**11**), and vinylated (**12**−**14**) derivatives were studied. The butatriene series includes butatriene (**15**) and methylated (**16**−**18**), ethynylated (**19**−**21**), and vinylated (**22**−**24**) derivatives. Rotational barriers were computed with single-point CASPT2 calculations[11] on the B3LYP/6-31G(d) geometries. Of interest are the specific substitution effects on the GS and TS and how these influence the observed rotational barrier. A new evaluation scheme has recently been proposed,[13a−c] conceptually similar to Pople's bond separation energy schemes,[12] and is used here to estimate the stabilization from substitution of radical centers (TS) as well as double and triple bonds (GS). This scheme differs from other evaluation methods, based on relative heats of hydrogenation[14] or BDEs,[15]

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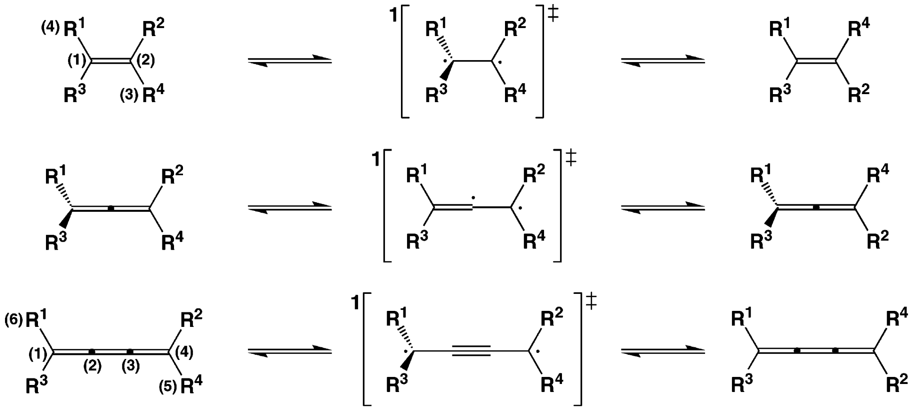
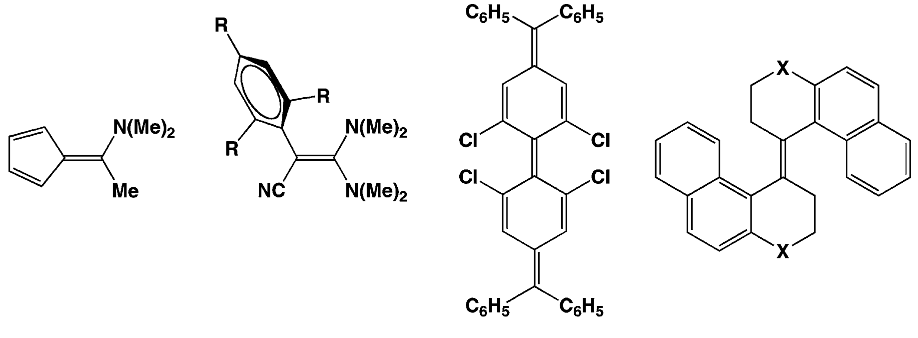
SCHEME 1: Rotation of Alkenes (top), Allenes (middle), and Butatrienes (bottom) through Diradical Transition States



SCHEME 2: Examples of Substituted Alkenes



because it employs reference states that provide a more universal evaluation of the effects of conjugation. These effects are integrated into a general model for rotation through diradical TSs.

Computational Methods

Geometries were optimized using the programs *Gaussian 98*[16] or *Gaussian 03*.[17] Stationary points were characterized by harmonic vibrational frequency analysis.[18] Molecular energies are calculated as the sum of the electronic energy, zero-point energy, and thermal correction obtained from these analytical frequencies (using the scaling factor for B3YP/6-31G(d)[19]) at 298 K.[20] Diradical species were optimized using unrestricted wave functions with the initial guess HOMO and LUMO orbitals mixed at each stage of optimization.[16,17] Electronic energies, geometries, and thermal corrections are given in the Supporting Information. All geometries were calculated at the B3LYP/6-31G(d) level.

Since experimental thermochemical data are sparse, especially for butatrienes, energetics were computed with a variety of methods. The computational study of radicals and diradicals requires multiconfiguration methods and adequate treatment of electron correlation. Large systematic errors are sometimes found for a particular method.[11] Spin contamination is a major concern when using unrestricted wave functions and can be quite severe for diradical systems.[21] Density functional theory (DFT) methods are known to have relatively minor spin contamination compared to the uHF and uMPn.[22] However, complete active space (CAS) methods are most appropriate for the treatment of diradicals. In the CAS formalism, a subset of molecular orbitals (the active space) is calculated with the multiconfiguration self-consistent field (SCF) method, which does not suffer from spin contamination. The active spaces used here contain all π-electrons and are built from the highest-energy molecular orbitals of π-bonding character and corresponding lowest-energy antibonding orbitals. Both singlet and triplet energies were computed. Single-point CASPT2/6-31G(d)//B3LYP/6-31G(d) energies with (6,6), (8,8), (10,10), and (14,14) active spaces were calculated as appropriate. These calculations were accomplished with the program MOLCAS.[23] The CASPT2 data agrees with the B3LYP/6-31G(d) level. There is a mean absolute deviation in rotational barriers between these methods of only 0.6 kcal/mol. To further corroborate the B3LYP/6-31G(d) and CASPT2/6-31G(d) data, the CBS-RAD method was employed. It was developed specifically by Radom to achieve highly accurate energies for radical species.[15c,24] Energies were obtained following the procedure in ref 24a. This method has been extensively tested on a range of molecules of varying constitution and size, but it has not, to our knowledge, been attempted on diradicals.[15c,24] The accuracy of this method is not maintained for diradicals; only sporadic agreement with the DFT and CAS values is achieved at this level. The CBS-RAD data often predict unreasonable rotational barriers that are not in agreement with experimental data. This level is not used or discussed further.

G3(MP2)[25] calculations were applied as an additional measure of ground-state stabilization energies. G3(MP2) is a variation of the G3[26] method which is less computer-intensive (MP2 instead of MP4 basis-set extension) but has a comparable mean absolute deviation for the G3 test set of 1.18 kcal/mol. Again, good agreement between this level and those of the DFT and CASPT2 levels is obtained. With respect to the CASPT2 numbers, G3(MP2) has a mean absolute deviation of 3.0 kcal/mol.

Tables for these levels are presented in the Supporting Information. All data used in the analyses to follow are CASPT2/6-31G(d)//B3LYP/6-31G(d) except where these were unobtainable, in which case B3LYP/6-31G(d) data substitute.

Results and Discussion

As mentioned, the internal rotation of dideuterioethylene ($\Delta G^{\ddagger} = 65$ kcal/mol)[2a] proceeds through a perpendicular diradical transition state. For our present purposes, we will consider this state to be nonstabilized, although both radicals are stabilized to some degree through hyperconjugation between adjacent CH_2 groups.[27] Upon substitution, this barrier may be lowered. For example, methyl substitution in 2-butene ($\Delta G^{\ddagger} = 62.8$ kcal/mol) has a small effect,[2b] while the rotational barrier of the central double bond in 1,3,5-hexatriene ($\Delta G^{\ddagger} = 42.2$ kcal/mol) is quite lower due to vinyl substitution.[2e,f] For the former, each radical center in the transition state can be considered akin to the ethyl radical. This assumes again that there is no interaction across the C(R)−C(R) single bond. Ethyl radical has a well-known radical stabilization energy ($\Delta H_{\mathrm{RSE}} = 3.6$ kcal/mol).[15c] Since there are two such radicals in the transition state, the rotational barrier is expected to be lowered by twice this value, which is defined as the transition state stabilization ($\Delta H_{\mathrm{TSS}} = 7.2$ kcal/mol). The triene, 1,3,5-hexatriene, possesses two allylic radicals in its transition state ($\Delta H_{\mathrm{RSE}} = 17.6$ kcal/mol)[15c] and therefore has a considerable transition-state stabilization ($\Delta H_{\mathrm{TSS}} = 35.2$ kcal/mol). However, both observed barriers are larger than the prediction based on the radical stabilization energies alone.

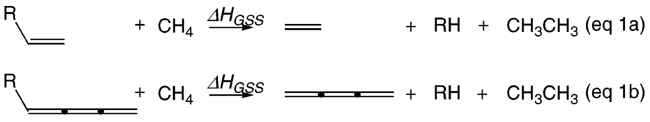
To understand the rotational barriers of these species, the energetic effect of the substituent on the GS must be considered. The methyl group hyperconjugative stabilization of a double bond ($\Delta H_{\mathrm{hCE}} = 2.7$ kcal/mol)[14] is considerable. The ground-state stabilization of 2-butene ($\Delta H_{\mathrm{GSS}} = 5.2$ kcal/mol) is twice the ΔH_{hCE} value. Thus, the rotational barrier of 2-butene is actually only 2 kcal/mol lower compared to ethylene, since effects in the TS and GS compensate for each other ($\Delta H_{\mathrm{TSS}} - \Delta H_{\mathrm{GSS}} = 7.2 - 5.2$ kcal/mol). This is nearly the decrease found experimentally. Likewise, 1,3,5-hexatriene is stabilized by two conjugative interactions with its central double bond. These interactions can be likened to those in 1,3-butadiene ($\Delta H_{\mathrm{CE}} = 3.4$ kcal/mol).[14] A rough estimate of the stabilization in the triene is twice this value ($\Delta H_{\mathrm{GSS}} = 6.8$ kcal/mol). The net effect is 28.4 kcal/mol ($\Delta H_{\mathrm{TSS}} - \Delta H_{\mathrm{GSS}} = 35.2 - 6.8$ kcal/mol); this is considerably overestimated in comparison to experiment, but closer than the estimate that considers transition state effects alone.

The experimental rotational barrier of the parent dideuterioallene system is not available. It differs from ethylene in that the unsubstituted transition state is formally stabilized. Allenes possess one vinylic and one allylic radical in the TS (Scheme 1, middle). The allyl radical is stabilized as above,[15c] while the vinyl radical is somewhat destabilized ($\Delta H_{\mathrm{RSE}} = -5.7$ kcal/mol).[15d] The net effect is stabilizing ($\Delta H_{\mathrm{TSS}} = 11.9$ kcal/mol) and should result in a decreased rotational barrier relative to that of ethylene (the TSs of ethylene and of allene require the breaking of one net double bond). The rotational barrier for methylated 1,3-dimethylallene ($\Delta G^{\ddagger} = 46.2$ kcal/mol) supports this assertion.[28a]

The TS for butatriene is composed of two propargylic radicals, both stabilized ($\Delta H_{\mathrm{RSE}} = 14.5$ kcal/mol)[15c] (Scheme 1, bottom); the combined stabilization ($\Delta H_{\mathrm{TSS}} = 29.0$ kcal/mol) predicts a considerably lower barrier of 36.0 kcal/mol compared to ethylene (the TS of ethylene and of butatriene require the breaking of one net double bond). The experimental barrier for 1,4-dimethylbutatriene ($\Delta G^{\ddagger} = 31.8$ kcal/mol)[28k] is a good approximate value for the barrier of butatriene itself. Substitution, as for ethylene, results in additional lowering of the rotational barrier. For example, the measured tetraalkynyl butatriene free-energy rotational barrier is 20 kcal/mol;[9] this is close to the value for amide bond rotation.[29] The 1,4-dialkynylbutatriene has an experimental free-energy barrier of 25 kcal/mol.[9] An approximate stabilization in the transition state for tetraalkynylbutatriene is six times the ΔH_{TSS} value of propargyl radical (above), and for the dialkynyl derivative, it is four times this value. Obviously, there must also be considerable stabilization in the ground state based on the observed barriers. Measured rotational barriers for 1,4-dimethyl-1,4-diphenylbutatriene ($\Delta G^{\ddagger} = 13$ kcal/mol)[28i] and 1,4-di-*tert*-butyl-1,4-diphenylbutatriene ($\Delta G^{\ddagger} = 26.9$ kcal/mol)[28j] are also quite low.

The conventional estimates of ground-state stabilization used above are derived by comparison of relative heats of hydrogenation as follows. The following experimental data are taken from NIST.[30] The hydrogenation of propene is 2.7 kcal/mol less exothermic than ethylene. This difference is assigned to the stabilization from the methyl substituent. From relative heats of hydrogenation estimates, a vinyl substituent stabilizes a double bond by 3.8 kcal/mol (1,3-butadiene vs 2 × 1-butene) and an ethynyl substituent stabilized a double bond by 1 kcal/mol (buta-1-en-3-yne vs 1-butene and 1-butyne). This scheme has been used since the early 1930s and gives mostly qualitatively correct answers,[14] but it has been shown, more recently, that it underestimates the extent of stabilization.[13] The problem lies with the choice of reference state. The original formulation of this scheme considered 1-butene and 1,3-butadiene because, upon complete hydrogenation, both conveniently lead to the same product, butane; thus, there is a simple point of comparison. However, the hyperconjugation in 1-butene, which is considerable, is ignored. An energetic comparison between 1,3-butadiene and 1-butene measures the relative effects of conjugation in the former and hyperconjugation in the latter. Because these effects are both stabilizing, the final measured difference in energy is an underestimation of conjugative stabilization. Comparisons between compounds stabilized by hyperconjugation, such as 1-butene and 1-propene, are also problematical. The hydrogenation of these alkenes leads to butane and propane, respectively. These alkanes are stabilized by different degrees of what has been termed protobranching, which arises from 1,3-nonbonded interactions between hydrogen atoms and is clearly manifested in the relative stabilities of branched and linear hydrocarbons. A complete discussion is presented elsewhere.[13b] The same concepts apply to the comparative heats of hydrogenation of substituted butatrienes and butatriene.

Evaluation schemes that avoid the issues in using hydrogenation energies are available. The ground state stabilization (ΔH_{GSS}) is estimated via isodesmic transformations[11] where the stabilization is taken as the heat of reaction of eq 1a (alkenes) and eq 1b (butatrienes).

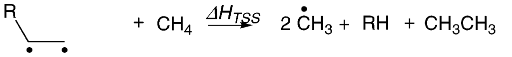


These compare substituted alkenes and butatrienes to isolated ethylene and butatriene and the appropriate severed substituent (RH). Ethane and methane are included to balance the number of C−C and C−H bonds on either side of the equation. Appropriate coefficients are chosen to achieve this balance and are easily derived. The interaction between the substituent and the ethylene or butatriene includes one or more of the following: the stabilization arising from π-conjugation, hyperconjugation, nonbonded interactions, and hybridization in the σ framework. All these effects fall within the definition of conjugative stabilization.[13a] The use of such schemes has been the subject of recent lively discussion.[13,31]

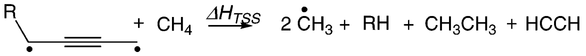
Estimates of the transition state stabilization described previously relied on the radical stabilization energy (RSE), which is conventionally defined as the BDE[15c] of a C−H bond of interest relative to the BDE of methane as a standard reference state. The conventional method employs RC−H compounds as reference states for the radical product RC. The energies of the reactants and products are both influenced by substitution with R; the heat of reaction is a measure of the relative ability of the substituent to stabilize each.[32] Again, the magnitude of the heat of reaction is reduced because the substituent effects are compensating.

Alternative estimates of radical stabilization energies that avoid this issue are constructed without the conjugate reference (RC−H). For example, allyl radical can be compared to methyl radical, ethylene, and ethane, whereas propargyl radical can be compared to acetylene, methyl radical, and ethane. The conjugates, propene and propyne, respectively, are absent. The new RSEs are 22.3 and 21.9 kcal/mol, respectively,[13c] compared to the conventional RSEs of 16.7 and 14.5 kcal/mol.[15c] The RSE trends predicted using nonconventional estimates were shown to agree with HMO[33a,b] and PMO[33c,d] theories, while conventional estimates do so inconsistently.[13c]

Transition state stabilization (ΔH_{TSS}) (the radical stabilization energy of the transition state) is defined as the heat of reaction of eq 2a (alkenes) and eq 2b (butatrienes).



(eq 2a)

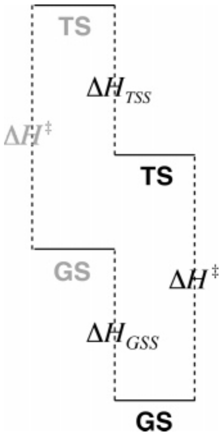


(eq 2b)

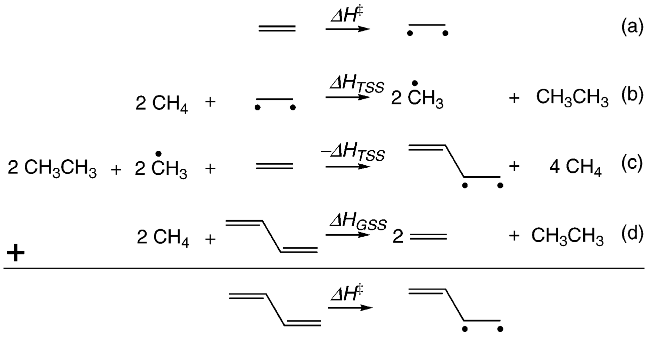
These equations have the same structure as the RSE equations described above. This transformation is also similar to eq 1, but here, a diradical is compared to two methyl radicals and RH. Again, ethane and methane are used with appropriate coefficients in order to balance CC and CH bonds.

Thus, although experimental estimates of substitution effects are available for many of the compounds in this study, these are gathered from a variety of sources; they employ various experimental techniques and evaluation methods. Moreover, many of the well-known energies have recently been called into question[13] on the basis of conceptual flaws in the methods of their evaluation. Clearly a better approach to the study of substitution effects is computational and systematic. A specific advantage to the equations used in this study is their internally consistency expressed in the generalized energetic relationship between the GS and TS of internal rotation shown below in a thermodynamic cycle (Scheme 3). The $\Delta H^{\ddagger}$ value on the right in Scheme 3 is the computational or experimental rotational barrier. On the left, the $\Delta H^{\ddagger}$ quantity (in grey) is the hypothetical barrier between two hypothetical unstabilized states, GS and TS (in grey), where the stabilization, ΔH_{GSS} and ΔH_{TSS}, respectively, has simply been subtracted. The hypothetical stabilization free barrier ($\Delta H^{\ddagger}$) for ethylene is 74.3 kcal/mol. This is the sum of the directly calculated $\Delta H^{\ddagger}$ plus the stabilization in the TS (ΔH_{TSS}) for ethylene (data presented below). There is no ΔH_{GSS} for ethylene or butatriene by definition (eqs 1a and 1b). For butatrienes, the nonstabilized barrier ($\Delta H^{\ddagger}$) is 83.0 kcal/mol. Again, this is the sum of $\Delta H^{\ddagger}$ plus the stabilization in the TS (ΔH_{TSS}) for butatriene. These values are discussed in further detail below. The rotational barrier of any substituted derivative can be calculated from the ΔH_{GSS} and ΔH_{TSS} data. The ΔH_{TSS} of a given derivative is subtracted from the appropriate hypothetical barrier of ethylene or butatriene, and the ΔH_{GSS} value for this derivative is added. This is equivalent to adding the appropriate isodesmic equations, as shown using 1,3-butadiene as example (Scheme 4). The sum of eqs (a) and (b) in Scheme 4 is the hypothetical barrier ($\Delta H^{\ddagger}$) for ethylene. Equation (c), which gives the ΔH_{TSS} value for the 1,3-butadiene TS, is reversed with respect to eq 2a, since this value is being subtracted. Equation (d) is the ΔH_{GSS} quantity for 1,3-butadiene. As shown, the sum of (a) through (d) cancels out all the reference species, leaving only the energetic comparison of the GS and TS of 1,3-butadiene. Analogous treatments of **5**−**24** result in the same cancellation. The transition- and ground-state stabilization evaluations are internally consistent and are thus directly comparable.

SCHEME 3: Model for the Stabilization of GS and TS of Substituted Alkenes and Butatrienes



SCHEME 4



Structural Analysis. Calculated B3LYP/6-31G(d) bond lengths and angles of butatriene GSs are close to experimental values (MAD = 0.007).[9] Excellent agreement between experimental and calculated values is also obtained for alkenes (MAD = 0.006). Table 1 presents the data for the analogous butatriene and alkene series. Experimental data are provided in parentheses.[34a]

In general, the GS structures of alkenes and butatrienes are planar and the TS structures are perpendicular according to the 4−1−2−3 and 6−1−4−5 dihedral angles, respectively (the atom numbering scheme is defined in Scheme 1). Notable exceptions are the GS of tetravinylated **14** and dimethylated **7-TS**, which have dihedral angles of 171° and 98°, respectively. These deviations may arise from steric effects, which are analyzed below.

Structural analysis of the bond lengths confirms the structures of Scheme 1. The calculated 1−2 bond length for ethylene (**5**)

TABLE 1: Optimized B3LYP/6-31G(d) Structural Parameters (Å and deg) for Molecules 5−24 and Their Respective Perpendicular Transition States 5-TS−24-TS[a]

Alkenes

compound	bond lengths		bonds angles	dihedral angles
	1−2	2−3	1−2−3	4−1−2−3
ethylene (**5**)	1.331		121.9	0.0
	(1.3297)			
ethylene TS (**5-TS**)	1.449		122.0	90.0
propene (**6**)	1.333	1.502	125.2	0.0
	(1.3330)	(1.4957)		
propene TS (**6-TS**)	1.454	1.502	122.4	87.7
trans-2-butene (**7**)	1.335	1.502	125.3	180.0
	(1.347)	(1.508)		
trans-2-butene TS (**7-TS**)	1.459	1.502	122.5	98.0
2,3-dimethyl-*trans*-2-butene (**8**)	1.350	1.514	124.4	0.0
	(1.353)	(1.511)		
2,3-dimethyl-*trans*-2-butene TS (**8-TS**)	1.474	1.505	119.6	89.1
buta-3-yn-1-ene (**9**)	1.341	1.425	124.5	0.0
	(1.344)	(1.434)		
buta-3-yn-1-ene TS (**9-TS**)	1.465	1.380	123.4	90.2
hexa-1,5-diyn-3-ene (**10**)	1.354	1.418	123.7	180.0
hexa-1,5-diyn-3-ene TS (**10-TS**)	1.481	1.376	122.9	90.7
3,4-diethynyl-hexa-1,5-diyn-3-ene (**11**)	1.383	1.424	121.5	0.0
3,4-diethynyl-hexa-1,5-diyn-3-ene TS (**11-TS**)	1.509	1.396	119.1	90.0
1,3-butadiene (**12**)	1.341	1.458	124.3	180.0
	(1.345)	(1465)		
1,3-butadiene TS (**12-TS**)	1.461	1.397	124.8	93.1
hexatriene (**13**)	1.352	1.450	124.3	180.0
	(1.368)	(1.458)		
hexatriene TS (**13-TS**)	1.472	1.395	124.5	92.1
3,4-divinyl-1,3,5-hexatriene (**14**)	1.380	1.473[b]	122.3[b]	170.6[b]
3,4-divinyl-1,3,5-hexatriene TS (**14-TS**)	1.494	1.427	120.3	86.6

Butatrienes

compounds	1−2	2−3	3−4	4−5	3−4−5	6−1−4−5
buta-1,2,3-triene (**15**)	1.318	1.271			121.7	0.0
	(1.309)	(1.284)				
buta-1,2,3-triene TS (**15-TS**)	1.360	1.261			121.5	90.0
penta-1,2,3-triene (**16**)	1.318	1.271	1.321	1.505	125.0	0.1
	(1.309)[35b]	(1.284)[35b]	(1.309)[35b]	(1.516)[35b]		
penta-1,2,3-triene TS (**16-TS**)	1.361	1.260	1.365	1.505	124.3	90.1
hexa-2,3,4-triene (**17**)	1.321	1.271		1.506	125.0	179.9
hexa-2,3,4-triene TS (**17-TS**)	1.365	1.259		1.505	124.4	90.1
2,5-dimethyl-hexa-2,3,4-triene (**18**)	1.325	1.269		1.511	121.7	0.0
	(1.330)[35c]	(1.271)[35c]		(1.511)[35c]		
2,5-dimethyl-hexa-2,3,4-triene TS (**18-TS**)	1.371	1.258		1.509	121.4	90.0
hexa-5-yn-1,2,3-triene (**19**)	1.320	1.266	1.331	1.419	124.2	0.0
hexa-5-yn-1,2,3-triene TS (**19-TS**)	1.362	1.251	1.383	1.396	123.6	90.1
octa-1,7-diyn-3,4,5-triene (**20**)	1.335	1.260		1.416	124.1	180.0
octa-1,7-diyn-3,4,5-triene TS (**20-TS**)	1.386	1.241		1.395	123.5	90.2
3,6-diethynyl-octa-1,7-diyn-3,4,5-triene (**21**)	1.352	1.251		1.426	120.7	0.0
	(1.353)[9]	(1.248)[9]				
3,6-diethynyl-octa-1,7-diyn-3,4,5-triene TS (**21-TS**)	1.405	1.231		1.410	120.0	90.0
hexa-1,2,3,5-tetraene (**22**)	1.321	1.267	1.330	1.453	124.4	0.0
hexa-1,2,3,5-tetraene TS (**22-TS**)	1.363	1.250	1.385	1.419	124.4	90.3
octa-1,3,4,5,7-pentaene (**23**)	1.335	1.262		1.451	124.3	180.0
octa-1,3,4,5,7-pentaene TS (**23-TS**)	1.388	1.240		1.418	124.3	90.4
3,6-divinyl-octa-1,3,4,5,7-pentaene (**24**)	1.351	1.253		1.470	119.6a	176.5
3,6-divinyl-octa-1,3,4,5,7-pentaene TS (**24-TS**)	1.413	1.226		1.439	120.2	90.1

[a] Experimental data are given in parentheses and are taken from ref 34a unless otherwise indicated. The atom-numbering is defined in Scheme 1. [b] Average value.

is 1.331 Å. Substitution elongates the 1−2 bond of the GS. The extent of the effect is dictated by the amount and type of substitution. Tetrasubstituted systems are most elongated, followed by di- and mono-substituted compounds. Methyl substitution is least effective. The bond length in propene (**6**) is 1.333 Å, a 0.002 Å increase compared to ethylene (**5**). Ethynyl and vinyl groups elongate the 1−2 bond to a far greater extent. The effect of these groups is nearly the same. The 1−2 bond lengths of compounds **9** and **12** are both 1.341 Å, 0.01 Å larger than the parent. The effects in the GS are matched almost exactly in the TS. The TS structure of ethylene (**5-TS**) resembles that expected for a diradical with an elongated 1−2 bond length of 1.449 Å compared to the GS. Upon substitution, this central bond elongates according to the amount and type of substitution. The 1−2 bond lengths of **6-TS**, **9-TS**, and **12-TS** are 1.454, 1.465, and 1.461 Å, respectively. Since the effects on the GS and TS are identical, the change upon rotation from the planar to perpendicular form is fairly constant. This change comparing **5** and **5-TS** is 0.118 Å. The central 1−2 bond of **14-TS** is 0.114 Å longer than in **14**. The average change over **5**−**14** is 0.122 Å.

The central double bond in butatriene (**15**) (2−3) is more acetylenic in character than the 1−2 bond in ethylene. The 1−2 bond length is 1.271 Å, 0.06 Å shorter than ethylene. The adjacent bonds (1−2) of **15** are somewhat shorter than ethylenic with bond lengths of 1.318 Å. Substitution of the GS results in elongation of the 1−2 bond and contraction of the 2−3 bond. The 1−2 bond lengths of methyl (**16**), ethynyl (**19**), and vinyl (**22**) butatriene derivatives are 1.318, 1.320, and 1.321 Å, respectively. The butatriene transition state (**15-TS**) has a 1−2 bond length of 1.360 Å, extended by 0.042 Å compared to **15**. The 1−2 bond lengths of methyl (**16-TS**), ethynyl (**19-TS**), and vinyl (**22-TS**) butatriene derivatives are 1.361, 1.362, and 1.363 Å, respectively.

The structural effects of substitution on butatrienes are muted relative to alkenes. For example, the 1−2 bond in butatriene elongates by 0.034 Å upon tetravinyl substitution (**24**), while tetravinylethylene has an elongation of 0.049 Å.

There is a smaller change in bond length upon rotation of butatrienes than alkenes. The largest change in the alkene series for the 1−2 bond is for **10** versus **10-TS** of 0.127 Å. The difference between **24-TS** and **24** is only 0.062. On average, the change for the butatriene series (**15**−**24**) is only 0.048 Å. Thus, the GSs of butatrienes are closer in structure and energy to their respective TSs than the ethylene GSs are to their respective TSs.

When steric effects are present in the GS, the rotational barrier is lowered, but when they influence the stability of the TS, the barrier will be raised. Substituent effects on ethanes and 2-butyne have been recently compared. The extended distance between endgroups in 2-butyne reduces steric interactions between them.[35]

Analysis of the dihedral angles in the TS and GS shows some deviation from perfectly planar and perpendicular structures in both series. The dihedral angle (4−1−2−3) of **7-TS** is 98° versus 90° for this angle (6−1−4−5) in **17-TS**. The GS of **14** is somewhat twisted with an average dihedral angle of 171° (4−1−2−3). This twisting is diminished, but not absent, in **24**, which has a dihedral angle of 177°. The significance of such small deviations is questionable considering that the monosubstituted propene TS (**6-TS**) is also not perfectly perpendicular. It has a dihedral angle (4−1−2−3) of 87.7°. Nonetheless, the dihedral angles of the butatriene series are all near 90° for the TSs, whereas those of the alkene series can deviate by a few degrees as for **7-TS**, **10-TS**, **12-TS**, **13-TS**, and **14-TS**, possibly indicating some steric interaction.

Singlet−Triplet Vertical Transitions. A pure diradical, where the radicals occupy orthogonal orbitals, will have a singlet−triplet gap near zero.[36] Vertical singlet−triplet energy gaps ($\Delta H_{\mathrm{ST}}^{\mathrm{VERT}}$) were calculated[23] for both the GS and TS in both series (Table 2).

These energies corroborate the conclusions from geometric analysis and establish the singlet electronic state as the lowest in energy for all compounds studied. The CASPT2 level predicts ground states with large singlet−triplet vertical transition energies favoring strongly the singlet state for both alkenes and butatrienes. Alkene singlet−triplet gaps are much larger than for butatrienes. The magnitude of the gap decreases significantly upon substitution for both. The transition states also favor the singlet electronic structure. The vertical transition energies are small, characteristic of diradical systems, and approach zero upon substitution. They are smaller for alkenes than for butatrienes. These results are consistent with more diffuse radical centers in butatriene TSs than alkene TSs.

Rotational Barriers. CASPT2 rotational barriers for the alkene series are given in Table 2 and plotted in Figure 1a. When CASPT2 data are unavailable, B3LYP data were used (in italics). The data in Figure 1a are arranged by order of decreasing rotational barrier ($\Delta H^{\ddagger}$) from left to right. The values range from 59.9 (**6**) to 18.8 kcal/mol (**14**) covering over 41.1 kcal/mol! Enynes with one (**9**), two (**10**), and four (**11**) ethynyl groups have transition state barriers that are 7.5, 14.8, and 28.5 kcal/mol lower than **5** ($\Delta H^{\ddagger} = 59.6$), respectively. These are approximately additive with respect to the number of substituents. The barriers of polyenes **12**−**14** are reduced to a greater extent by 9.6, 19.2, 40.8 kcal/mol, respectively. In contrast, the rotational barriers of methylated derivatives **6**−**7** are 0.3 kcal/mol larger than for ethylene; here, ground-state effects are larger than transition-state effects. The barrier of the tetramethyl derivative (**8**) is lower by 5.1 kcal/mol.

The rotational barrier for 1,2,3-butatriene (**15**) has not been determined experimentally, but is predicted here ($\Delta H^{\ddagger} = 28.0$ kcal/mol). The effects of substitution for the butatriene series are presented in Figure 1b. The range of values is much smaller than that for the alkene series, 19.4 kcal/mol. Ethynyl substitution with one (**19**), two (**20**), or four (**21**) groups leads to lowered rotational barriers that are 3.2, 6.9, and 12.1 kcal/mol less than butatriene. The vinyl series **22**−**24** are 4.0, 8.1, and 18.8 kcal/mol lower. These follow a roughly additive trend. All methyl-substituted compounds (**16**−**18**) have larger rotational barriers, but the increase is small; even the permethylated (**18**) derivative has a barrier only 0.6 kcal/mol larger than the barrier for butatriene.

From Figure 1, it is clear that the rotational barriers are lower for butatrienes than alkenes. However, this difference diminishes as the barriers decrease. The rotational barriers of ethylene **5** and butatriene **15** are separated by 31.6 kcal/mol, whereas **24** and **14** are separated by only 9.6 kcal/mol. This is due to the greater decrease in barrier for the alkene series compared to the butatrienes and is related to the results from structural analysis that show the geometric effects are muted for the latter.

Ground State Stabilization (ΔH_{GSS}). The ΔH_{GSS} energy for alkenes is defined via the isodesmic eq 1a. The values are presented in Table 2. These are also presented graphically in Figure 1a. The ΔH_{GSS} of propene (**6**) is 6.5 kcal/mol. This is twice as large as the conventional estimate that is based on heats of hydrogenation. The stabilization that results from multiple substitution is approximately additive; 2-butene (**7**) and tetramethylethylene (**8**) are stabilized by two times ($\Delta H_{\mathrm{GSS}} = 13.0$ kcal/mol) and four times ($\Delta H_{\mathrm{GSS}} = 22.9$ kcal/mol) the amount in **6**, respectively. Enyne **9** ($\Delta H_{\mathrm{GSS}} = 15.1$ kcal/mol) is stabilized nearly the same amount as that calculated for 1,3-butadiene (**12**) ($\Delta H_{\mathrm{GSS}} = 15.3$ kcal/mol). Estimates from heats of hydrogenation give a value of only 3.8 kcal/mol for the conjugative stabilization in 1,3-butadiene.[30] The value derived from eq 1a is close to the more recent estimates.[13a,b] Multiple ethynyl or vinyl substituents also increase this stabilization in an additive manner. The stabilizations of disubstituted **10** ($\Delta H_{\mathrm{GSS}} = 30.8$ kcal/mol) and **13** ($\Delta H_{\mathrm{GSS}} = 31.6$ kcal/mol) are about half those values for **11** ($\Delta H_{\mathrm{GSS}} = 66.9$ kcal/mol) and **14** ($\Delta H_{\mathrm{GSS}} = 54.5$ kcal/mol), respectively.

The ΔH_{GSS} values for butatrienes (eq 1b) can be found in Table 2 and Figure 1b. The stabilizations in **16** ($\Delta H_{\mathrm{GSS}} = 6.7$ kcal/mol), **19** ($\Delta H_{\mathrm{GSS}} = 14.5$ kcal/mol), and **22** ($\Delta H_{\mathrm{GSS}} = 16.3$ kcal/mol) are about one-half and one-fourth of their respective disubstituted (**17** ($\Delta H_{\mathrm{GSS}} = 13.2$ kcal/mol), **20** ($\Delta H_{\mathrm{GSS}} = 35.1$ kcal/mol), and **23** ($\Delta H_{\mathrm{GSS}} = 33.1$ kcal/mol)) and tetrasubstituted (**18** ($\Delta H_{\mathrm{GSS}} = 28.9$ kcal/mol), **21** ($\Delta H_{\mathrm{GSS}} = 64.3$ kcal/mol), and **24** ($\Delta H_{\mathrm{GSS}} = 58.2$ kcal/mol) derivatives.

The GS stabilization of the butatriene series is generally larger than for the analogous alkene. The differences can be large, as for **18** and **24**, which are 6.0 and 3.7 kcal/mol more stabilized

TABLE 2: CASPT2/6-31G(d)//B3LYP/6-31G(d) Rotational Barriers and Stabilization Energies[a]

compound	ΔH_{ST}^{VERT}	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}_{exp}$	ΔH_{GSS}	ΔH_{TSS}
Alkenes					
ethylene (**5**)	104.5			0.0	
ethylene TS (**5-TS**)	0.9	59.6	65[2a]		14.7
propene (**6**)	104.4			6.5	
propene TS (**6-TS**)	0.9	59.9			20.9
trans-2-butene (**7**)	104.0			13.0	
trans-2-butene TS (**7-TS**)	0.9	59.9	62.8[2b]		27.4
2,3-dimethyl-*trans*-2-butene (**8**)	100.7			22.9	
2,3-dimethyl-*trans*-2-butene TS (**8-TS**)	0.7	54.5			42.7
buta-3-yn-1-ene (**9**)	83.9			15.1	
buta-3-yn-1-ene TS (**9-TS**)	0.9	52.1			37.3
hexa-1,5-diyn-3-ene (**10**)	67.9			30.8	
hexa-1,5-diyn-3-ene TS (**10-TS**)	0.9	44.8			60.3
3,4-diethynyl-hexa-1,5-diyn-3-ene (**11**)	*46.0*			*66.9*	
3,4-diethynyl-hexa-1,5-diyn-3-ene TS (**11-TS**)	*0.1*	*31.1*			*106.2*
1,3-butadiene (**12**)	74.5			15.3	
1,3-butadiene TS (**12-TS**)	0.8	50.0			39.6
hexatriene (**13**)	58.6			31.6	
hexatriene TS (**13-TS**)	0.7	40.4	42.2[2c]		65.6
3,4-divinyl-1,3,5-hexatriene (**14**)	53.3			54.5	
3,4-divinyl-1,3,5-hexatriene TS (**14-TS**)	0.8	18.8			109.9
Butatrienes					
buta-1,2,3-triene (**15**)	62.8			0.0	
buta-1,2,3-triene TS (**15-TS**)	4.1	28.0			55.0
penta-1,2,3-triene (**16**)	62.3			6.7	
penta-1,2,3-triene TS (**16-TS**)	4.0	28.3			61.4
hexa-2,3,4-triene (**17**)	61.9			13.2	
hexa-2,3,4-triene TS (**17-TS**)	3.9	28.3	31.8[28k]		67.9
2,5-dimethyl-hexa-2,3,4-triene (**18**)	60.5			28.9	
2,5-dimethyl-hexa-2,3,4-triene TS (**18-TS**)	3.7	28.6			83.3
hexa-5-yn-1,2,3-triene (**19**)	53.0			14.5	
hexa-5-yn-1,2,3-triene TS (**19-TS**)	3.4	24.8			72.7
octa-1,7-diyn-3,4,5-triene (**20**)	*42.7*			*35.1*	
octa-1,7-diyn-3,4,5-triene TS (**20-TS**)	*1.4*	*21.1*	25[9][b]		*101.1*
3,6-diethynyl-octa-1,7-diyn-3,4,5-triene (**21**)	28.9			*64.3*	
3,6-diethynyl-octa-1,7-diyn-3,4,5-triene TS (**21-TS**)	0.5	15.9	20.2[9][b]		135.4
hexa-1,2,3,5-tetraene (**22**)	50.3			16.3	
hexa-1,2,3,5-tetraene TS (**22-TS**)	3.2	24.0			75.3
octa-1,3,4,5,7-pentaene (**23**)	41.3			33.1	
octa-1,3,4,5,7-pentaene TS (**23-TS**)	2.3	19.9			96.1
3,6-divinyl-octa-1,3,4,5,7-pentaene (**24**)	31.0			58.2	
3,6-divinyl-octa-1,3,4,5,7-pentaene TS (**24-TS**)	0.8	9.2			136.0

[a] Singlet−triplet vertical transition energies (ΔH_{ST}^{VERT}). Calculated ($\Delta H^{\ddagger}$) and experimental rotational barriers ($\Delta G^{\ddagger}_{exp}$) of ethylenes (5−14) and butatrienes (15−24). Ground-state (ΔH_{GSS}) and transition-state (ΔH_{TSS}) stabilization calculated from eqs 1 and 2, respectively. All data are in kcal/mol at 298 K using scaled thermal corrections from the (B3LYP/6-31G(d) zero-point energy and thermal correction scaling factors are used). Data in italics are B3LYP/6-31G(d)//B3LYP/6-31G(d). [b] Approximated values estimated from related derivatives.

than **8** and **14**, respectively. The exceptions are **19** and **21**, which are slightly less stabilized in the GS than **9** and **11**, respectively. The MAD between these series is 2.2 kcal/mol.

Transition State Stabilization (ΔH_{TSS}). The heat of reaction of eq 2 is defined as the stabilization energy of the transition state (ΔH_{TSS}). Numerical results are given in Table 2 and are graphically presented in Figure 1a,b for alkenes and butatrienes, respectively. The transition state of ethylene (**5-TS)** is formally stabilized by 14.7 kcal/mol according to eq 2. This stabilization originates from the two hyperconjugative interactions between the π-CH_2 orbital of one CH_2 group and the singly occupied p orbital of the other, and vice versa, as shown in Scheme 5.[37] The distance between these interacting orbitals is similar to the distance in propene between the π and π-CH_2 orbitals.[34a] Thus, it is reasonable to expect some stabilization resulting from the interaction of these orbitals on the order of the hyperconjugative interaction in propene. This stabilization is termed the inherent transition state stabilization (ΔH_{iTSS}) because it derives from the parent system and not from substitution.

Substitution stabilizes the transition states of **6-TS−14-TS** in addition to hyperconjugative stabilization. Subtraction of the inherent stabilization in **5-TS** from the calculated ΔH_{TSS} values estimates the stabilization stemming from substitution (ΔH_{sTSS}), i.e., $\Delta H_{TSS} = \Delta H_{iTSS} + \Delta H_{sTSS}$.[38] Thus, the ΔH_{sTSS} of **6-TS** is 6.2 kcal/mol ($\Delta H_{TSS} - \Delta H_{iTSS} = 20.9-14.7$). Likewise, the ΔH_{sTSS} values of **9-TS** and **12-TS** are 22.6 and 24.9 kcal/mol, respectively. Transition state effects are also nearly additive. This stabilization values in **7-TS** ($\Delta H_{sTSS} = 12.7$ kcal/mol), **10-TS** ($\Delta H_{sTSS} = 45.6$ kcal/mol), and **13-TS** ($\Delta H_{sTSS} = 50.9$ kcal/mol) are twice as much as in the monosubstituted derivatives, and those in **8-TS** ($\Delta H_{sTSS} = 28.0$ kcal/mol), **11-TS** ($\Delta H_{sTSS} = 91.5$ kcal/mol), and **14-TS** ($\Delta H_{sTSS} = 95.2$ kcal/mol) are roughly four times these values.

The butatriene transition state (**15-TS**) is stabilized by 55.0 kcal/mol (ΔH_{iTSS}). Hyperconjugative effects similar to those presented in Scheme 5 act on the stability of this TS in conjunction with the conjugative interaction between the radical p orbital and the π-bonds of the internal triple bond. The stabilization derived from substitution (ΔH_{sTSS}) for the butatriene series is the calculated ΔH_{TSS} value minus the inherent stabilization of 55.0 kcal/mol. Thus, compounds **16-TS**, **19-TS**, and **22-TS** are stabilized by 6.4, 17.7, and 20.3 kcal/mol, respectively. Disubstituted compounds (**17-TS** ($\Delta H_{sTSS} = 12.9$ kcal/mol), **20-TS** ($\Delta H_{sTSS} = 46.1$ kcal/mol), and **23-TS** (ΔH_{sTSS}

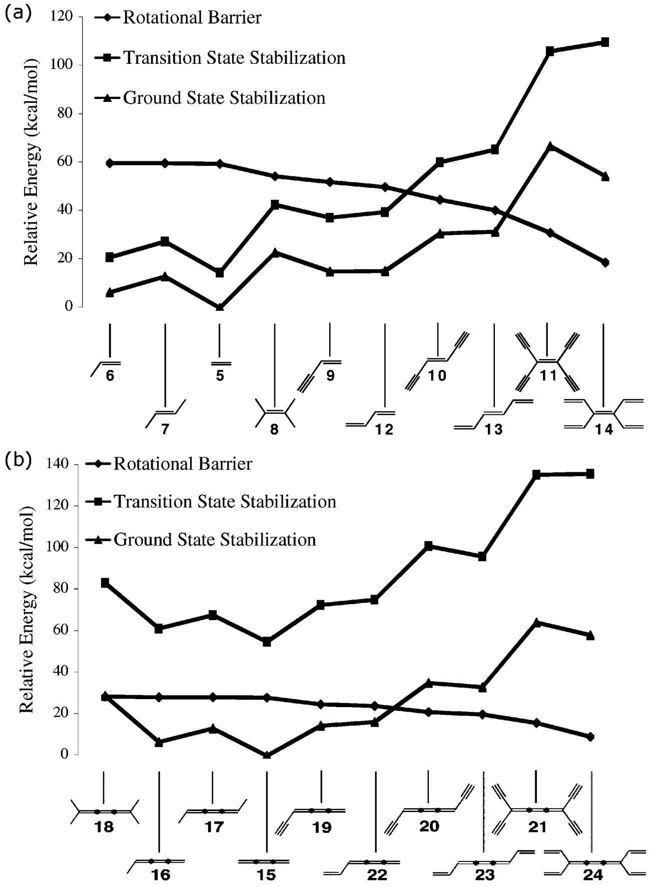
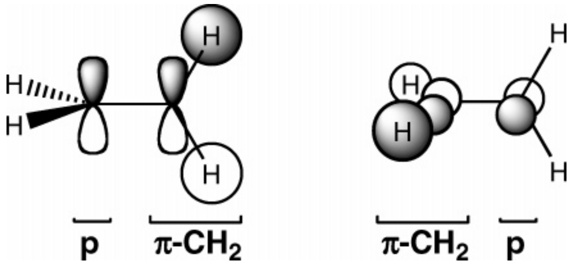


Figure 1. (a) Rotational barriers for alkenes (**5**−**14**) (diamonds) with ΔH_{TSS} (squares) and ΔH_{GSS} (triangles) energies (left). (b) Rotational barriers for butatrienes (**15**−**24**) (diamonds) with ΔH_{TSS} (squares) and ΔH_{GSS} (triangles) energies (right).

SCHEME 5: Orbitals involved in hyperconjugation across the central single bond of the TS of ethylene



= 41.1 kcal/mol)), and tetrasubstituted derivatives (**18-TS** (ΔH_{sTSS} = 28.3 kcal/mol), **21-TS** (ΔH_{sTSS} = 80.4 kcal/mol), and **24-TS** (ΔH_{sTSS} = 81.0 kcal/mol)) are also about two and four times these values, respectively.

The effects of methyl substitution are larger for butatrienes than alkenes by 0.2, 0.2, and 0.3 kcal/mol for **16-TS**, **17-TS**, and **18-TS**, respectively. The opposite is true for ethynyl and vinyl substitution. Ethynyl-substituted **9-TS** and **11-TS** are 4.9 and 11.1 kcal/mol more stabilized than **19-TS** and **21-TS**. The stabilization in **10-TS** and **20-TS** is nearly the same. Polyenes **12-TS**−**14-TS** are 4.6, 9.8, and 14.2 kcal/mol more stabilized than their butatriene analogues (**22-TS**−**24-TS)**, respectively. The MAD with respect to ΔH_{sTSS} between these series is 5.1 kcal/mol, larger than the MAD for the ΔH_{GSS} values.

Analysis of Rotational Barriers from ΔH_{GSS} and ΔH_{TSS}. The difference, $\Delta H_{\mathrm{GSS}} - \Delta H_{\mathrm{sTSS}}$, for a given derivative is identical to the difference in the calculated rotational barriers, $\Delta H^{\ddagger}(\mathbf{X}) - \Delta H^{\ddagger}(\mathbf{5}$ or $\mathbf{15}) = \Delta\Delta H^{\ddagger}$, where $\mathbf{X} = \mathbf{5}-\mathbf{24}$. For example, this difference for compound **6** is 0.3 kcal/mol ($\Delta H_{\mathrm{GSS}} - \Delta H_{\mathrm{sTSS}}$ = 6.5 kcal/mol − 6.2 kcal/mol), exactly the same as that calculated directly ($\Delta H^{\ddagger}(\mathbf{6}) - \Delta H^{\ddagger}(\mathbf{5})$). This is possible because of the internal consistency in the rotational model of Scheme 3. Where it fails to be exact, the fault lies in the mixing of CASPT2 and B3LYP/6-31G(d) data (**11**, **20**, **21**, and **24**); the numbers differ by a few kilocalories per mole in either direction, because there is no longer beneficial error cancellation.

The origin of the observed rotational barrier trends can now be clearly determined by analysis of the $\Delta H_{\mathrm{GSS}} - \Delta H_{\mathrm{sTSS}}$ data. For instance, the greatly reduced barriers for vinylated alkenes are the result of the dominance of the ΔH_{sTSS} quantity over that of ΔH_{GSS}. The stabilization of the monovinylated **12-TS** (ΔH_{sTSS} = 24.9 kcal/mol) is larger than the stabilization in **12** (ΔH_{GSS} = 15.3 kcal/mol). Compare the ΔH_{sTSS} and ΔH_{GSS} of 95.2 and 51.5 kcal/mol for **14-TS** and **14**, respectively; the difference is about four times the difference between **12-TS** and **12**. This trend is maintained for the ethynylated (**9**−**11**) compounds as well. As predicted, the GS stabilization is larger for **6** (ΔH_{GSS} = 6.5 kcal/mol) and **7** (ΔH_{GSS} = 13.0 kcal/mol) compared to **6-TS** (ΔH_{sTSS} = 6.2 kcal/mol) and **7-TS** (ΔH_{sTSS} = 12.7 kcal/mol) but smaller for **8** (ΔH_{GSS} = 22.9 kcal/mol) compared to **8-TS** (ΔH_{sTSS} = 28.0 kcal/mol); a methyl group stabilizes a double bond more than a radical center. The effect in **8** may be steric in nature.

The difference in stabilization for **24-TS** (ΔH_{sTSS} = 81.0 kcal/mol) and **24** (ΔH_{GSS} = 58.2 kcal/mol) is smaller than for the analogous alkene. This is true for the comparison of vinyl- and ethynyl-substituted **19**−**23** as well. The stabilizations are nearly identical in the TS and GS of methylated **16**−**18**. The larger ground state stabilization and the smaller transition state stabilization of the butatriene series compared to the ethylenes leads to a smaller net effect on the rotational barriers of butatrienes.

Conclusions

The structures of the ground and transition states for rotations about the double bonds of butatrienes and alkenes have been analyzed at the B3LYP/6-31G(d) level. The effects of methyl substitution on the bond lengths are small compared to those of ethynyl and vinyl groups, which show similar behavior to each other. This is in agreement with work dealing with the comparative stabilization abilities of double and triple bonds.[13b,c] The GS of butatrienes are geometrically closer to their respective TSs than are the GS of alkenes to their TSs. In general, the alkene double bond is more influenced by substitution than the butatriene cumulenic bonds, and the effects are magnified in the TS. These structural effects are in accord with the calculated energetic effects at the CASSCF/6-31G(d)//B3LYP/6-31G(d) level. The rotational barriers of butatrienes are lower than alkenes due to the strong inherent stabilization from the central acetylenic bond in the TS. This also lowers the effect of substitution compared to alkenes. The individual effects in the GS and TS have been assessed using isodesmic equations. The stabilization of the GS is larger for butatrienes than alkenes, but in the TS, substitution affords more stabilization for alkenes than butatrienes, in general. These combined effects lead to a much smaller substitution effect on the observed rotational barriers of butatrienes than of alkenes.

While alkenes have been thoroughly investigated, the experimental investigation of substituted butatrienes is just beginning.[39] The rotational barrier can be controlled by proper choice of substituents, and this could lead to interesting new molecules with tunable rotational properties for application in the material sciences. Large arrays of all-carbon networks built from alkynylbutatrienes[40] may have interesting dynamic conformational behavior at ambient temperatures. Estimates for higher-order unsubstituted and substituted even cumulenes are in progress.

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Supporting Information Available: Optimized Cartesian coordinates, electronic energies, and thermal corrections (298 K) at the B3LYP/6-31G(d) level for all molecules studied. Single-point energies for these systems at the CASPT2, CBS-RAD, and G3(MP2) levels are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) The radical centers in the ethylene TS are commonly consider nonstabilized. The rotational barrier is often cited as confirmation of the bond enthalpy of a double bond, since it is assumed that the only difference between the ground and transition states for ethylene is the breakage of the π-system responsible for double bonding. The nonadiabatic BDE of ethylene into two $^3CH_2$ fragments is 173 kcal/mol. Subtracting the value for the rotational barrier in ethylene (65 kcal/mol) leaves a σ-bonding energy of 108 kcal/mol. This value is larger than the bond strength in ethane of 90 kcal/mol, as to be expected on the basis of hybridization arguments. However, a better estimate of the π-bonding in ethylene corrects for the significant hyperconjugative stabilization presented above. The hyperconjugative stabilization is added to the rotational barrier ($65 + 14.7$ kcal/mol $= 79.7$ kcal/mol), and this is subtracted from the BDE of ethylene yielding a σ-bonding energy of 93.3 kcal/mol, only slightly larger than the bond energy in ethane.

(38) This is a simplistic method, since it assumes that the hyperconjugative contribution in the transition state to rotation of ethylene does not change for the substituted species. A few reasons to expect some change are differences in C−C vs C−H hyperconjugative stabilization and changes in bond lengths and angles.

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