Conformational Thermodynamic and Kinetic Parameters of Methyl-Substituted 1,3-Butadienes

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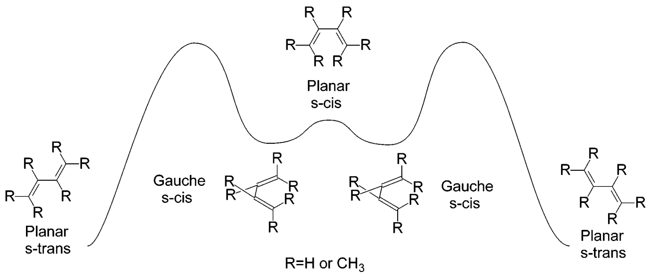

The s-trans/s-cis conformational equilibria of 10 methyl-substituted 1,3-butadienes [(*E*)- and (*Z*)-1,3-pentadiene; 2-methyl-1,3-butadiene; (*E*)-2-methyl-1,3-pentadiene; 2,3-dimethyl-1,3-butadiene; (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-2,4-hexadiene; 2,5-dimethyl-2,4-hexadiene; and (*E*,*E*)-2,4-dimethyl-2,4-hexadiene] were explored by trapping high-temperature conformational equilibria by cryogenic deposition. The vapor state enthalpy differences of these s-trans/s-cis conformers, $\Delta H_{\mathrm{t}\rightleftharpoons\mathrm{c}}$, were determined by varying the equilibrating temperature and integrating the resulting matrix isolated IR spectra. The results obtained are in good agreement with ab initio calculations at the G3 level. From these thermodynamic parameters, methyl group nonbonded interactions in conjugated 1,3-butadienes were delineated. Rates of decay of s-cis conformers to their s-trans rotamers were obtained in the solid-state by warming up trapped high-temperature equilibrated samples formed from neat depositions. These data were analyzed in terms of dispersive kinetics with matrix site effects in the solid-state modeled by a Gaussian distribution of activation energies. The activation barriers thus obtained were compared with G3 calculations of the enthalpies of activation.

Introduction

Acyclic 1,3-dienes represent the simplest conjugated system and as such have drawn considerable attention both theoretically[1] and experimentally[2] over the years. They are involved in both thermal and photochemical synthetically useful reactions. These reactions were also intimately involved in the development of our understanding of the control of reactions by molecular orbital symmetry.[3] Further, 1,3-dienes are models for the more extended conjugated components of the visual[4] and photosynthetic systems.[5]

The torsional energy profiles, i.e., the change in enthalpy occurring during rotation of the central single bond of the conjugated diene unit, have been of continuing interest.[6] Acyclic diene molecules may exist in s-cis or s-trans conformations, either of which may have planar or gauche geometries.[7] It is generally accepted that the planar s-trans conformation is the global minimum, separated from the s-cis rotamer by a barrier of some 6−7 kcal/mol (Figure 1).[8] There is still some controversy as to whether the s-cis form has a planar or gauche geometry.[9] In fact, it appears that the torsional potential function can be changed considerably by steric or electrostatic forces. Understanding how this function

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(1) (a) Shih, S.; Buenker, R. J.; Peyermihoff, S. D. *Chem. Phys. Lett.* **1972**, *16*, 244. (b) Skaarup, S.; Boggs, J. E.; Skancke, P. N. *Tetrahedron* **1976**, *32*, 1179. (c) Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890.

(2) (a) Berry, R. S. *J. Chem. Phys.* **1957**, *26*, 1660. (b) Perahia, D.; Pullman, A. *Chem. Phys. Lett.* **1973**, *19*, 73. (c) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294. (d) Rayez, J. C.; Dannenberg, J. *Chem. Phys. Lett.* **1976**, *41*, 492.

(3) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry;* Academic Press: New York, 1970.

(4) Oseroff, A. R.; Callender, R. H. *Biochemistry* **1974**, *13*, 4243.

(5) Srinivasan, R. *J. Am. Chem. Soc.* **1960**, *82*, 5063.

(6) (a) Murcko, M. A.; Castejon, H.; Wiberg, K. B. *J. Phys. Chem.* **1996**, *100*, 16162. (b) Guo, H.; Karplus, M. *J. Mol. Struct.* **1992**, *260*, 347.

(7) Aston, J. G.; Woolley, H. W.; Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67−79.

(8) Aten, C. F.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1968**, *90*, 2463.

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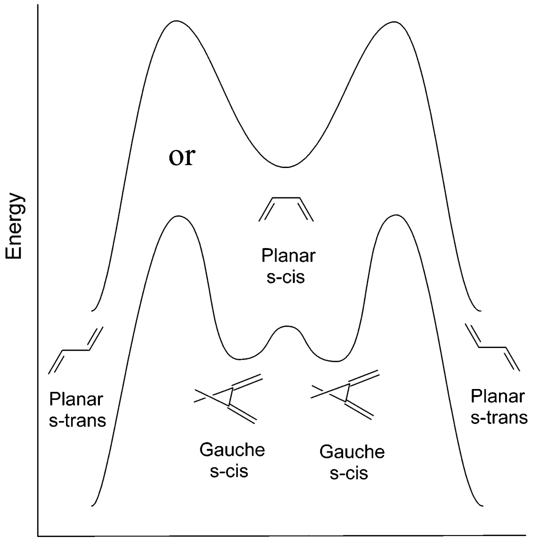

FIGURE 1. Structures and the two possible potential energy surfaces for the rotation about the central bond of acyclic 1,3-dienes.

is influenced by substituents is an obvious prerequisite toward understanding the torsional potential energy surfaces of the ground and the electronically excited states of the more extended conjugated carbon chains found in retinal[10] and other polyenes.[11]

Although there are a plethora of calculations examining the energy differences between the two conformations of 1,3-butadiene,[5,12,13] there are very few experimental explorations of the 1,3-diene potential energy surface and almost all of these are concerned with the parent compound, 1,3-butadiene. Early calorimetric work found a 2.5 kcal/mol s-trans/s-cis enthalpy difference.[7,14] Later re-examination of this work coupled with Raman spectroscopy derived a potential function with an s-cis form 2.66 kcal/mol above the s-trans form.[15] A study on the temperature dependence of NMR parameters of 1,3-butadiene found a best fit for ΔH° of 2.1 kcal/mol with an assumed ΔS° of R ln 2.[16] Using the UV spectrum obtained for the s-cis form from matrix-isolated photoequilibration of the two conformers, a variable high-temperature UV study gave a $\Delta H^\circ_{5\ 20}$ of 3.0 kcal/mol.[17] Another variable temperature UV study using principle-component analysis to deconvolute the spectra gave a ΔH° of 2.95 kcal/mol.[18] Some years later, this group used the same method but with a simulated temperature spectral broadening to give an s-cis/s-trans enthalpy difference of 2.926 kcal/mol.[19]

The low isomerization barrier and the magnitude of the s-cis/s-trans energy difference preclude easy determination of the enthalpic difference between the two rotamers, so very little is known about the effects of substituents on the s-trans/s-cis energy difference. In fact, isoprene is the only other acyclic 1,3-diene on which there is experimental information about the torsional potential. Early work gave values of 1.7 and 1.5 kcal/mol for the enthalpy difference between the two conformers of isoprene.[20] The temperature dependence of a 555 cm^{-1} shoulder in the Raman spectrum of a neat solution of isoprene gave a ΔH° of 1.1 kcal/mol. An electron diffraction study gave an energy difference of 1.76 kcal/mol.[21] A variable temperature UV study gave a $\Delta H^\circ_{5\ 10}$ of 1.78 kcal/mol, but an assumed ΔS value was used.[22] All ab initio calculations on the isoprene system have given enthalpy differences substantially greater than any of the experimental values.[23] The only other report of an experimental investigation of a 1,3-diene potential energy surface was a negative observation by Durig et al. These authors saw no evidence for the s-cis form in the vibrational spectrum of 2,3-dimethyl-1,3-butadiene and assigned a $\Delta H^\circ_{t \rightleftharpoons c}$ greater than 2.5 kcal/mol.[24]

There has been substantial controversy over the source of the barrier to rotation of the central bond of a conjugated diene unit with both electron delocalization[25,26] and a "natural" $sp^2{-}sp^2$ carbon torsion[27] being used to explain the increased barrier to rotation of the central diene single bond as compared with that of ethane. Potential functions obtained from fitting vibrational data gave a 3.97 kcal/mol barrier for 1,3-butadiene and a 3.2 kcal/mol barrier for isoprene.[28] There are, however, only two direct measurements of the s-cis/s-trans barrier of 1,3-dienes: 1,3-butadiene (3.9 kcal/mol)[9b] and isoprene (3.9 kcal/mol).[29] Both were obtained by monitoring the s-cis decay in neat matrixes from confor-

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(9) For discussions about the geometry of s-cis conformer, see: (a) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842. (b) Squillacote, M. E.; Sheriden, R. S.; Chapman, O. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. (c) Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 1056. (d) Arnold, B. R.; Balaji, V.; Downing, J. W.; Radziszewski, J. G.; Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1991**, *113*, 2910. (e) Wiberg, K. W.; Rosrnberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1509. (f) Kofranek, M.; Karpfen, A.; Lischka, H. *Chem. Phys. Lett.* **1992**, *189*, 281. (g) De Mare, G. R.; Panchenko, Y. N.; Auwera, J. V. *J. Phys. Chem. A* **1997**, *101*, 3998.

(10) Liu, R. S. H.; Hammond, G. S. *Photochem. Photobiol. Sci.* **2003**, *2*, 835.

(11) Mirkin, N. G.; Krimm, S. *J. Phys. Chem.* **1993**, *97*, 13887.

(12) (a) Breulet, J.; Lee, T. J.; Schaefer, III. *J. Am. Chem. Soc.* **1984**, *106*, 6250. (b) Bock, C. W.; George, P.; Trachtman, M. *Theor. Chim. Acta* **1984**, *64*, 293. (c) Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1985**, *68*, 57. (d) Alberts, I. L.; Schaefer, H. F *Chem. Phys. Lett.* **1989**, *161*, 375.

(13) (a) Rice, J. E.; Liu, B.; Lee, T. J. *Chem. Phys. Lett.* **1989**, *161*, 277. (b) Guo, H.; Karplus, M. *J. Chem. Phys.* **1991**, *94*, 3679.

(14) Compton, D. A. C.; George, W. O. *J. Chem. Soc., Perkin 2* **1976**, 1666.

(15) Bock, C. W.; Geoge, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin 2* **1979**, 26.

(16) Lipnick, R. L.; Garbisch, P. W., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6370.

(17) Mui, P. W.; Grunwald, E. *J. Am. Chem. Soc.* **1983**, *105*, 2530.

(18) Sun, Y. P.; Sears, D. F., Jr.; Satiel, J. *J. Am. Chem. Soc.* **1988**, *110*, 6277.

(19) Satiel, J.; Sears, D. F., Jr.; Turek, A. M. *J. Phys. Chem. A* **2001**, *105*, 7569.

(20) Kilpatrick, J. E.; Beckett, C. W.; Prozen, E. J.; Pitzer, K. S.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1949**, *42*, 225.

(21) Traetteberg, M. P.; Paulen, G.; Cyvin, S. J.; Panchenko, Y. N.; Mochalov, V. I. *J. Mol. Struct.* **1984**, *116*, 141.

(22) Mui, P. W.; Grunwald, E. J. *J. Phys. Chem.* **1984**, *88*, 6340.

(23) (a)Kavana-Saebo, K.; Saebo, S.; Boggs, J. E. *J. Mol. Struct.* **1984**, *106*, 259. (b) Bock, C. W.; Panchenco, Y. N.; Krasnoshoshchiokov, S. V.; Aroca, R. *J. Mol. Struct.* **1987**, *160*, 337. (c) Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. L. *J. Comput. Chem.* **1987**, *8*, 581. (d) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817.

(24) Durig, J. R.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 2879.

(25) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

(26) (a) Simpson, W. T. *J. Am. Chem. Soc.* **1953**, *75*, 597. (b) Simpson, W. T. *J. Am. Chem. Soc.* **1955**, *77*, 6164.

(27) (a) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1960**, *11*, 96. (b) Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890.

(28) Panchenko, Y. N.; Puppyshev, V. I.; Abramenkov, A. V.; Traetteberg, M.; Cyvin, S. J. *J. Mol. Struct.* **1985**, *130*, 355.

(29) Sheridan, R. S. Thesis, University of California, Los Angeles, CA, 1979.

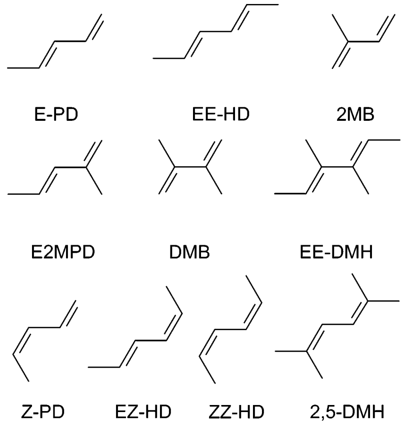

FIGURE 2. Ten methyl-substituted 1,3-dienes.

mational mixtures produced via a conformational trapping temperature jump technique. In both instances, a simple Arrhenius type unimolecular decay was assumed. Ab initio calculations of the barrier have always found values which are lower by about 1 kcal/mol than those observed in the solid matrixes.[6,12,23]

The effects of substituents on the structure of s-cis dienes, on the energy difference between the s-cis and the s-trans forms, and on the barrier separating the s-cis from the more stable s-trans conformer have not been experimentally investigated. Because even a small change in the conformational energy difference will have a profound change on the isomer ratio, it seemed appropriate to develop a picture of substituent effects on the 1,3-diene torsional potential. Given the importance of the methyl substituents in determining the pre- and post-irradiation conformations of the retinal moiety in the rhodopsin system,[30] we chose to examine methyl group substituent effects on the 1,3-diene potential energy surface by examining 10 different methyl-substituted dienes (Figure 2).

Results and Discussion

Our approach to investigating substituent effects on the 1,3-diene torsional surface is to measure the temperature dependence of the s-cis/s-trans ratio. Throughout this paper, we use a conformational trapping technique that involves establishing a high-temperature conformational equilibrium in a quartz tube oven and maintaining this equilibrium mixture until it impinges on a CsI window kept at about 20 K, where the high-temperature ratio of the conformers is trapped and measured (Figure 3).

A concern is that the ratios we measure do not truly reflect the oven-temperature equilibrium mixture. For the molecule to reach conformational equilibrium at oven temperature, the residence time of the molecule should be long compared with the time it needs to reach equilibrium. What is more, the mean free path of the molecule should be comparable to the dimensions of the oven so that all molecules can reach equilibrium at that temperature. The mean free path, λ, can be expressed as[31] $\lambda = 1/(\sqrt{2}\pi\sigma^2 n)$ where σ^2 is the molecular cross-sectional area and n is the number of molecules per cm^3. In a usual deposition experiment, a back pressure of 1.0 Torr was used with the pressure dropping to less than 10^{-6} Torr at the oven's end. At our maximum oven temperature of 830 °C and with the cross-sectional area of an N_2 molecule taken to be 3 Å^2, n can be determined to be 8.8×10^{15} molecules per cm^3. So, the λ is calculated to be 0.15 cm. The oven itself is a 10-cm long quartz tube with a 3-mm i.d. with the last 4 cm of the tube heated with a tight coil of 0.127-mm tantalum wire. The temperature is measured with a quartz capillary clad chromel−alumel thermocouple sited in the midportion of the heated section. In addition, there is a 1-mm thick tantalum oven electrical lead passing through the oven to the controlling variac.

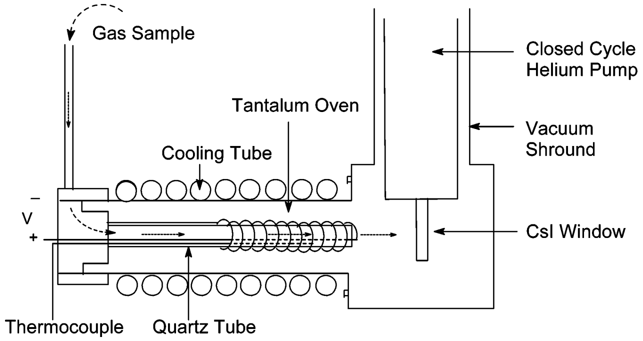

FIGURE 3. Schematic of the apparatus used for conformational trapping.

Because the mean free path of a molecule, λ, is about the same size as the radius of the oven, the movement of a gas molecule through the oven can be taken as intermediate between laminar and turbulent. The conductance of the tube, C, under these flow conditions can be expressed by the equation[32]

$$C = 2\pi a^3 \nu((0.1472a/\lambda) + ((1 + 2.507a/\lambda)/(1 + 3.095a/\lambda)))/3L$$

where a and L are the radius and length of the oven and ν, the speed of the molecule at the oven temperature, is given by the expression $\nu = (8kT/\pi m)^{1/2}$ with m being the molecular mass. For an oven temperature at 830 °C, the mean speed of a molecule is about $\nu = 7.6 \times 10^4$ cm/s and using $L = 4$ cm, $a = 0.15$ cm, and $\lambda = 0.15$ cm gives $C = 136$ cm^3/s. The average residence time, τ, of the molecule in the oven is related to the conductance by $\tau = \pi La^2/2C$,[32] which in this case predicts a residence time of 1.1×10^{-3} s.

This theoretical value for the average resident time can be compared to a residence time determined from experimental conditions. In a typical experiment, 0.025 mol of a 1000:1 nitrogen/diene mixture was deposited over 5 h. This corresponds to 8.6×10^{17}molecules per second emitted from the oven. The heated portion of the oven is 4 cm long with a 0.15-cm radius and, using an average

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[30] (a) Sugihara, M.; Entel, P.; Buss, V. *Phase Transitions* **2002**, *75*, 11. (b) Han, M.; Groesbeek, M.; Sakmar, T. P.; Smith, S. O. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 13442. (c) Jäger, S.; Lewis, J. W.; Zvyaga, T. A.; Szundi, I.; Sakmar, T. P.; Kliger, D. S. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 8557. (d) Wald, G. *Science* **1968**, *163*, 230.

[31] Castellan, G. W. *Physical Chemistry*; Addison-Wesley: Reading, MA, 1971.

[32] Dushman, S.; Lafferty, J. M. *Scientific Foundation of Vacuum Techniques*; Wiley: New York, 1962.

pressure, contains 2.5 × 10^{15} molecules. Thus, the measured average residence time of a molecule in the oven is 2.8 × 10^{-3} s, which is very close to the value obtained from the above calculation. If 10 half-lives are allowed for complete equilibration, then the time for equilibration even at the lowest oven temperature used (25 °C) over a typical s-trans to s-cis diene barrier of 6 kcal/mol is 8 × 10^{-6} s; so the diene conformeric equilibrium will be completely established in the oven. Supporting this conclusion is the fact that at oven temperatures above 600 °C, isomerizations of the double bonds of the dienes occurred. As these isomerizations are known to have barriers of ~45 kcal/mol,[33] observation of the double bond isomerizations confirms that complete equilibration of the single bond rotamers must occur.

The high vacuum maintained at the exit of the quartz oven ensures that during the 2.5-cm transition by the molecules from the oven to the cold CsI window no collisions can occur with molecules at ambient temperatures. When the molecules of the high-energy conformer hit the cold CsI surface, they must lose all transitional energy and the vibrational energy in excess of the zero-point energy to the surroundings quickly before re-equilibration can occur. At 800 °C (our highest possible oven temperature), the normal modes[34] of s-cis butadiene will have 20 kcal/mol of excess vibrational energy. Using RRKM theory,[35] we can calculate a rate constant for the isomerization of this vibrationally excited s-cis 1,3-butadiene over a 4 kcal/mol barrier to be 1.66 × $10^{11}\mathrm{s}^{-1}$. In this study, the oven temperatures used were below 560 °C, so the excess vibrational energy and thus the rate constants of s-cis decay in our experiments will be substantially less than this value. With typical vibrational−vibrational energy transfer,[36] on the order of 10^{12} s^{-1}, vibrational energy will be lost to the matrix much faster than the decay of the high-energy conformers of the 1,3-dienes and the rotamer ratios observed at low temperatures in the matrix will mirror the ratios present in the high-temperature equilibrium mixture established in the oven.

Enthalpy Differences of s-Cis and s-Trans Dienes

Figure 4 shows the infrared spectra of (*E*)-pentadiene (*E*-PD) matrix isolated 1:1000 in N_2 deposited from various oven temperatures. Several bands (see Supporting Information) increase with increasing oven temperature and are assigned to the s-cis rotamer. This assignment was confirmed when these bands also appeared in high-temperature depositions of neat *E*-PD and decayed when the sample was warmed above 60 K. For depositions from oven temperatures below 555 °C, no double-bond isomerization occurred, as evidenced by subsequent high-field NMR of a deposited sample sublimed from the CsI window by warming the window to room temperature and subsequently trapped in liquid nitrogen. These spectra showed only *E*-PD with no (*Z*)-1,3-pentadiene (*Z*-PD) present.

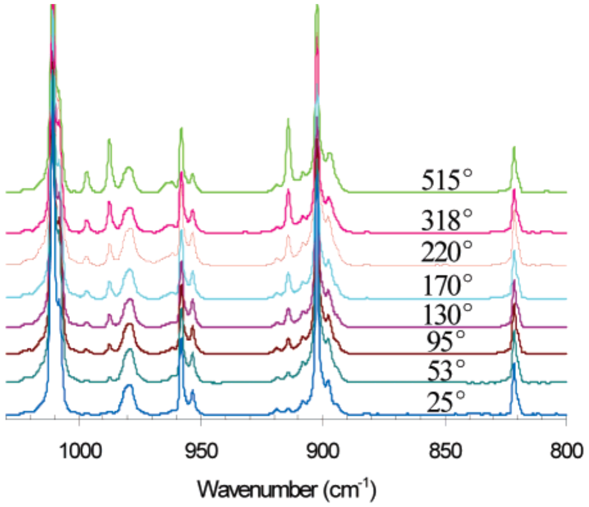

FIGURE 4. IR spectra of matrix-isolated *E*-PD deposited from indicated oven temperatures.

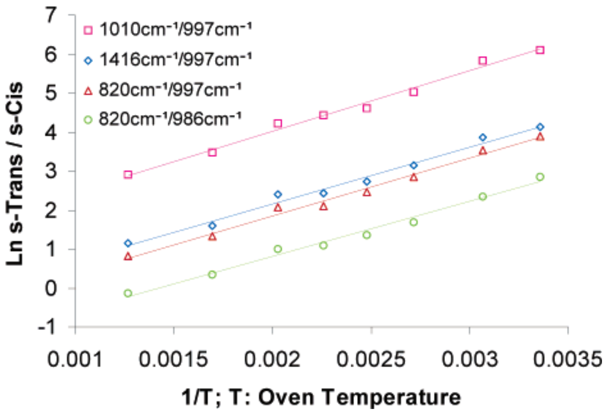

FIGURE 5. van't Hoff plots of relative integrated intensities of four pairs of s-trans and s-cis *E*-PD bands vs the reciprocal oven temperature.

The s-cis *E*-PD bands at 997 and 986 cm^{-1} were well separated from the s-trans bands which allowed accurate determination of their intensities. Figure 5 shows van't Hoff plots for these bands plotted as ratios with two different s-trans bands. The four enthalpies obtained agree within 0.3 kcal/mol, and their average gives a $\Delta H^{\circ}_{t\rightleftharpoons c}$ of 2.94 kcal/mol (Table 1). The linearity of these plots confirms that the conformational trapping technique used here does successfully trap the oven-temperature equilibrium mixture. The enthalpy difference between s-trans and s-cis rotamers of the nine other 1,3-dienes studied were obtained in the same manner and are listed in Table 1.

Calculated Rotomeric Enthalpy Differences

Composite theoretical models have greatly improved the accuracy of ab initio calculations with heats of formation accurate to below 1 kcal/mol.[37,38] Because energy differences between conformers should be even

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[33] Stephenson, L. M.; Gemmer, R. V.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8620.

[34] Mui, P.; Grunwald, E. *J. Am. Chem. Soc.* **1982**, *104*, 6562.

[35] Bunker, D. L. *Theory of Chemical Reaction Rates*; McGraw-Hill: New York, 1969.

[36] Calaway, W.; Ewing, G. *J. Chem. Phys.* **1975**, *63*, 2842.

[37] Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

[38] Baboul, A. G.; Curtiss, L. A.; Redfern, P. C. *J. Chem. Phys.* **1999**, *110*, 7650.

TABLE 1. Experimental and Calculated s-Cis and s-Trans Enthalpy Differences and Calculated s-Cis Dihedral Angles of Ten Methyl-Substituted 1,3-Dienes

		calcd				calcd	
diene	exptl $\Delta H_{t\rightleftharpoons c}$[a]	$\Delta H_{t\rightleftharpoons c}$[a]	dihed ang[b]	diene	exptl $\Delta H_{t\rightleftharpoons c}$[a]	$\Delta H_{t\rightleftharpoons c}$[a]	dihed ang[b]
E-PD	2.94	2.98	37.6	*EE*-DMH	1.05	0.84	
EE-HD	2.89	2.99	37.6	*Z*-PD	2.98	2.93	43.3
2-MB	2.46	2.73	41.7	*EZ*-HD	2.89	2.93	43.5
E,2-MPD	2.37	2.65	41.3	*ZZ*-HD	0.98[c]	1.66	55.8
DMB	1.98	2.02	47.1	2,5-DMH	*d*	1.55	57.3

[a] In kcal/mol. [b] In degrees. [c] Derived from a van't Hoff plot of a series of neat depositions which showed incomplete trapping at 14 K. [d] High-energy form could not be trapped even at 14 K.

TABLE 2. Method and Basis Set Dependence of the Dihedral Angle in Degrees of s-Cis 1,3-Butadiene

method	6-31G (DP)	6-311G (2D2P)	6-311G (3DFP)	6-311+G (3DFP)
HF	39.04	41.74	41.04	41.66
B3LYP	30.36	33.33	32.95	33.50
MP2	37.63	37.84	37.65	38.22
CCSD	37.69	38.78	38.59	39.12

more accurately calculated, we felt that comparing computational results to our experimental s-cis/s-trans enthalpy differences would support the accuracy of our experimental values. There are several composite models available, but two of the most popular are the G3[37] and G3B3[38] theories which differ mainly in the methods used to calculate geometries and vibrational modes. The G3B3 theory uses a B3LYP density functional approach to calculate both geometries and zero-point energy, and the G3 theory uses a Moeller−Plesset 2 level computation to ascertain molecular geometry and a Hartree−Fock level calculation for determining frequencies. Table 2 lists the results of a series of geometry optimizations for s-cis 1,3-butadiene using different methods and basis sets. Note that at all basis sets the density functional geometry optimizations give a significantly smaller dihedral angle about the central diene bond than both the higher and lower level geometry optimizations, so we chose the G3 model to avoid the uncertainty given by the G3B3 geometries. The results of these calculations for the torsional potential energy surface of *E*-PD are presented in Figure 6.

The calculated enthalpy difference between s-cis and s-trans *E*-PD (2.98 kcal/mol) was found to reproduce the experimental data, 2.94 kcal/mol, in a very satisfactory fashion. The calculated enthalpy difference includes zero-point energy corrections but corresponds to an energy difference at 0 K. We calculated the heat capacities of the two rotamers and found that the temperature dependence of $\Delta H^\circ_{t\rightleftharpoons c}$ is quite low because the vibrational spectra of the s-cis and s-trans isomers are very similar. We calculate the temperature correction to $\Delta H^\circ_{t\rightleftharpoons c}$ to be less than 0.015 kcal/mol at 500 °C. The 0 K s-cis/s-trans enthalpy differences calculated at the G3 level for *E*-PD and the other nine acyclic 1,3-dienes are listed in Table 1. In addition, we calculate the G3B3 energies which are presented in the Supporting Information and which, despite the difference in the calculated s-cis geometries, closely match the G3 results.

Calculations at the G3 level reproduce the experimental $\Delta H_{t\rightleftharpoons c}$ quite well except for (*Z*,*Z*)-2,4 hexadiene (*ZZ*-HD). As shown below, the barrier separating the s-cis from the s-trans conformer for this compound is very low, and we believe this barrier is too low to ensure complete conformational trapping. In fact, we see no trapping at all of the minor form of the similar compound 2,5-dimethyl-2,4-hexadiene (2,5-DMH). Excluding *ZZ*-HD, the average difference between the calculated and experimental values of $\Delta H_{t\rightleftharpoons c}$ is only 0.13 kcal/mol. The largest deviations between the calculated and experimental values of the s-cis/s-trans enthalpy differences were found in the dienes with a single internal methyl group, 2-methyl-1,3-butadiene (2-MB) and 2-methyl-1,3-pentadiene (2-MPD), which showed deviations of 0.27 and 0.28 kcal/mol, respectively.

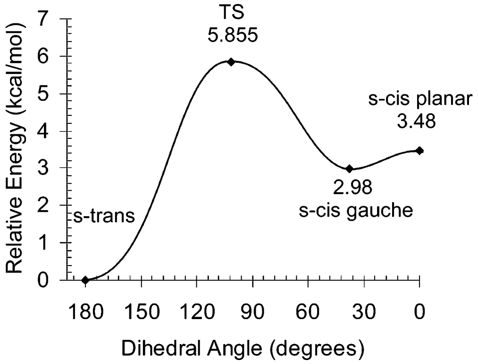

FIGURE 6. Calculated potential energy profile of *E*-PD at the G3 level.

Solid-State Decay of s-Cis 1,3-Dienes

A sublimation temperature for N_2 of ~30 K prevents examination of the s-cis to s-trans decay using matrix isolated samples. Many of the IR bands of the s-cis rotamers were, however, observable in neat depositions, i.e., variable temperature depositions through the quartz tube oven of samples of pure diene. A portion of the infrared spectrum of *E*-PD deposited as a neat sample from both room and high temperatures is compared to a matrix isolated sample in Figure 7. Although, as expected, the bands of the neat depositions are broader than those of the matrix isolated sample, many of the s-cis bands are readily apparent in the high-temperature neat depositions. When the CsI plate was warmed to 60 K, these bands rapidly disappeared and nonoverlapped bands corresponding to s-trans *E*-PD, such as 1416, 1010, and 820 cm^{-1}, increased until the remaining spectrum was essentially identical to that of a sample deposited from room temperature.

Figure 8 shows the decay process at 53 K of the 986-cm^{-1} band of the s-cis *E*-PD isomer which was produced from a 542 °C deposition. These decays were monitored

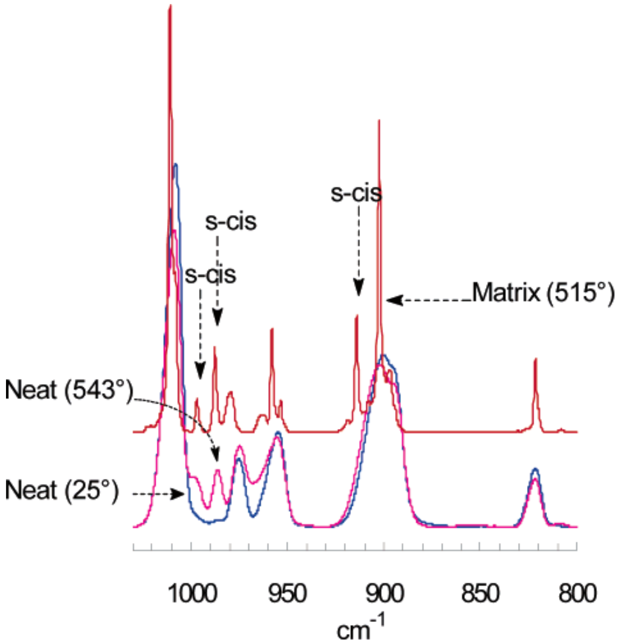

FIGURE 7. Comparison of IR spectra of neat- and matrix-isolated depositions of *E*-PD (a) neat from 25 °C, (b) neat from 515 °C, (c) matrix isolation from 515 °C.

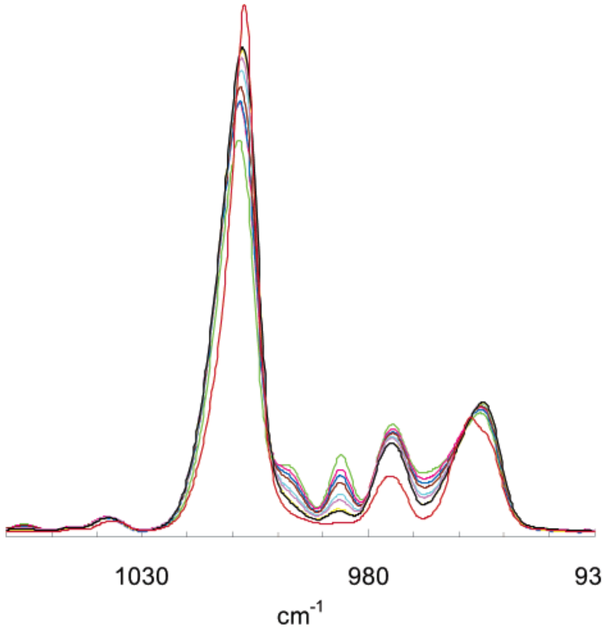

FIGURE 8. Decay of s-cis *E*-PD at 53 K produced from a 536 °C neat deposition.

for at least two half-lives and, as the data in Figure 9 show, the decay is not a simple first-order process as had been previously assumed.

This result is not unusual for kinetics occurring in a nonfluid medium. Molecules in a rigid matrix may experience different microenvironments, and these different sites will have inherently different first-order kinetics. It has been found that such kinetic data can be treated by using a time-dependent rate coefficient,[39,40] $k(t) = Bt^{\alpha-1}$, where $0 < \alpha \leq 1$ is a measure of site effects. The lower the magnitude of α, the greater the site effects are on the decay process. When $\alpha = 1$, there is no effect and the process is first order. The α parameter is referred to as a dispersion parameter or a heterogeneity index. Substituting the expression above for $k(t)$ into the first-order rate law followed by integration gives $\ln I/I_o = -(B/\alpha)t^{\alpha} = -(k_o/t)^{\alpha}$ where I_o and I are the initial and the time-dependent integrations of the s-cis rotamer, B is a constant, and k_o represents the most probable rate constant.[41] Figure 9 shows the fit of our data for the decay of the s-cis *E*-PD 986-cm^{-1} band to this equation which gives $\alpha = 0.32$ and $k_o = 7.34 \times 10^{-4}$ s^{-1}.

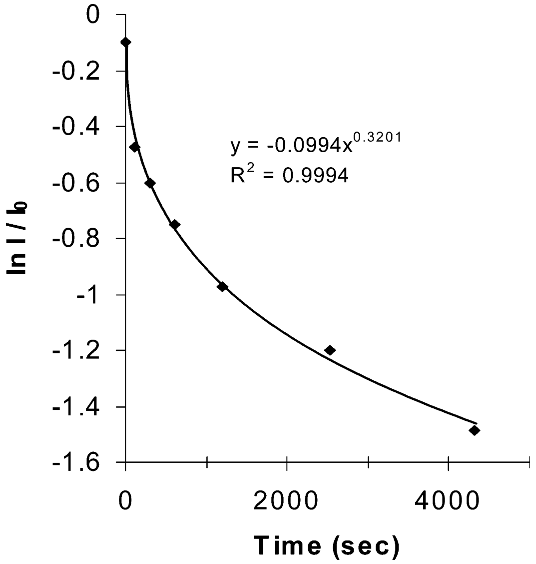

FIGURE 9. First-order plot of the decay of the 986-cm^{-1} band of s-cis *E*-PD at 53.1 K.

This treatment of the multiple site problem corresponds to a Gaussian distribution of free energies of activation with the most probable $\Delta G_o^{\ddagger}$ related to the most probable rate constant, k_o, in the usual manner. A standard deviation for this distribution is related to α and can be expressed by $\sigma = (\pi/\sqrt{6})[(1 - \alpha)RT/\alpha]$.[41] For the decay of s-cis *E*-PD pictured in Figures 8 and 9, we find a $\Delta G_o^{\ddagger}$ of 3.69 kcal/mol with a 0.29 kcal/mol standard deviation in the distribution of the site specific free energies of activation. In the same fashion, the decay rates of a number of s-cis *E*-PD bands were monitored at multiple temperatures and fit to the expression for multiple site first-order decays. The data in Table 3 summarize these results for s-cis *E*-PD.

As expected, the most probable free energies of activation found are significantly higher than the barrier calculated at the G3 level (2.87 kcal/mol). Most sites in the neat matrix created during the depositions will hinder rotation and increase the barrier. A few sites will, however, be large enough to have little impact on the barrier, and decays in these sites would approximate decays in the gas phase. Sites with activation energies three standard deviations away from the most probable

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(39) Gebicki, J.; Plonka, A.; Krantz, A. *J. Chem. Soc., Perkin 2* **1990**, 2051.

(40) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240.

(41) (a) Plonka, A.; Paszkiewicz, A. *Chem. Phys.* **1996**, 212. (b) Plonka, A.; Berlin, Y. A.; Chekunaev, N. L. *Chem. Phys. Lett.* **1989**, *158*, 380.

TABLE 3. Most Probable Free Energies of Activation and Standard Deviations for the Decays of s-Cis *E*-PD Bands at Indicated Temperatures

decay temp (K)	bands (cm^{-1})	$\Delta G_0^{\ddagger}$ (kcal/mol)	σ (kcal/mol)
52.0	986	3.68	0.27
	1614	3.65	0.35
53.1	986	3.69	0.29
	575	3.70	0.32
54.1	986	3.75	0.26
	1614	3.81	0.24

TABLE 4. Experimental ($\Delta G_0^{\ddagger}$) and Calculated ($\Delta H^{\ddagger}$) Kinetic Parameters for the s-Cis → s-Trans Decay of the Methyl-Substituted 1,3-Butadienes

	exptl		calcd
diene	$\Delta G_0^{\ddagger a}$	$\Delta G_0^{\ddagger} - 3\sigma^a$	$\Delta H^{\ddagger}a$
E-PD	3.71	2.84	2.87
EE-HD	3.95	3.23	2.82
2-MB	3.67	3.19	2.58
E,2-MPD	3.76	2.80	2.61
DMB	3.27	2.73	1.64
EE-DMH	4.3		1.55
Z-PD	2.71	1.75	1.74
EZ-HD	2.66	2.06	1.73
ZZ-HD	2.22	1.68	1.72
2,5-DMH	*b*	*b*	1.56

[a] In kcal/mol. [b] s-cis form cannot be trapped.

activation energy, representing only 0.13% of the total sites, seem to best approximate this gas phase site. For the decays of s-cis *E*-PD, the average of all the $\Delta G_0^{\ddagger} - 3\sigma$ values is 2.84 kcal/mol which gives good agreement with the calculated value.

The calculated (G3 level) and experimental s-cis to s-trans energy barriers for the 10 methyl-substituted 1,3-butadienes are listed in Table 4. There is a fairly good correlation between the experimental $\Delta G_0^{\ddagger} - 3\sigma$ values and the calculated $\Delta H^{\ddagger}$ values with two notable exceptions. Except for that of the untrappable 2,5-DMH, the calculated barriers for the decay of s-cis 2,3-dimethyl-1,3-butadiene (DMB) and *(E,E)*-3,4-dimethyl-2,4-hexadiene (*EE*-DMH) are the smallest of all the calculated barriers. Yet, the trapping of these two s-cis conformers is efficient, certainly more so than that of s-cis *ZZ*-HD which was not completely trapped even at window temperatures of 14 K but which is calculated to have a higher barrier! The experimental and calculated values for the s-cis/s-trans energy differences of DMB and *EE*-DMH agree well (Table 1). Thus, it appears that the calculated transition state energies are too low. The $\Delta G_0^{\ddagger} - 3\sigma$ value for DMB is over 1 kcal/mol larger than the calculated barrier. Unfortunately, the dispersion of sites was very large in the *EE*-DMH depositions and depended on the decay temperature, so obtaining an accurate approximation for the gas-phase barrier was not possible in this system. It is interesting to note that the calculated barrier for 2-MB is also much smaller than that observed, which may indicate that the methyl groups on the 2 and 3 positions of the diene unit cause problems in accurately calculating the transition state energy. The accuracy of the zero-point energy contributions to the total energies of the conformers might be suspect considering the low-frequency torsional motions of the methyl groups, but treating the methyl groups as hindered rotors for both 2-MB and DMB did not change the zero-point energy corrections significantly for either the conformational energy difference or the barrier.

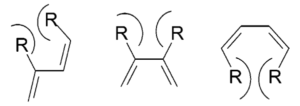


FIGURE 10. Steric interactions in the 1,3-diene framework.

Steric Interactions in Methyl-Substituted 1,3-Dienes

The transition states for the rotation of the central single bond of the dienes studied all have a central dihedral angle of about 100° which minimizes steric and electronic interactions across the diene framework. Indeed, in absolute energy terms, the calculated transition state for the *Z*-PD rotation is less than 0.19 kcal/mol higher than that of *E*-PD. Similarly, the calculated absolute transition state energies for the central bond rotations of *EZ*- and *ZZ*-HD are less than 0.1 and 0.2 kcal/mol, respectively, higher than that of the *EE*-HD isomer. That the rotational transition states of the dienes containing cis methyl groups are slightly higher than those of the corresponding trans isomers suggests that some residual 1,3 steric interaction of these methyls with the third carbon of the diene unit still remains. However, these differences are slight, and we can use the absence of large steric interactions in the rotational transition states to compare the absolute energy changes of the individual s-cis and s-trans conformers of pairs of geometric isomers and so understand the steric interactions which affect the s-cis and s-trans energies.

Figure 10 details the steric interactions that can occur in the diene framework. The first of these raises the energy of s-trans rotamers and the second two introduce strain into s-cis rotamers. All three can be mitigated by twisting about the central bond. The parent compound, 1,3-butadiene, and *E*-PD and *EE*-HD all lack any of these steric interactions except for the terminal H−H interaction of their s-cis isomers. Not unexpectedly, therefore, the $\Delta H_{t\rightleftharpoons c}$ is nearly invariant with these three dienes. Our experimental values of 2.94 and 2.89 kcal/mol for the rotomeric energy difference of *E*-PD and *EE*-HD, respectively, agree quite well with that found for 1,3-butadiene, 2.92 kcal/mol, as well as with the values we calculated. In fact, the close correspondence between the three diene experimental values as well as with the calculated energy differences supports the efficacy of the conformational trapping technique.

An interesting case occurs when we examine the geometric isomers of these compounds. Even with the presence of a *Z*-substituted methyl group, the $\Delta H_{t\rightleftharpoons c}$ for *Z*-PD (2.98 kcal/mol) and *EZ*-HD (2.89 kcal/mol) are not different from those of their *E* and *EE* isomers. Yet, the barriers separating the s-cis from the s-trans isomer are affected by the *(Z)*-methyl substitution and are significantly lower for these compounds. The $\Delta G_0^{\ddagger} - 3\sigma$'s for *Z*-PD and *EZ*-HD are 1.75 and 2.06 kcal/mol as compared with 2.84 and 3.23 kcal/mol for *E*-PD and *EE*-HD. Two steric interactions are in play here (Figure 11). A 1,4 CH_3−H interaction raises the energy of the s-cis isomers of *Z*-PD and *EZ*-HD and lowers the s-cis to s-trans

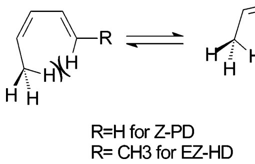


FIGURE 11. Offsetting steric interactions in *Z*-PD and *EZ*-HD.

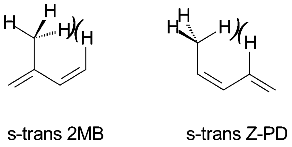

s-trans 2MB s-trans Z-PD

FIGURE 12. Steric interactions in s-trans 2-MB and *Z*-PD.

barrier, but a 1,3 CH_3-H interaction in the s-trans conformer raises the conformer an apparently identical amount, leaving the overall s-cis/s-trans energy difference the same. The absence of a "cross-diene" steric interaction as revealed by the similar absolute energies of the transition state energies for the *E*-PD/*Z*-PD and *EE*-HD/*EZ*-HD pairs indicates that the steric interactions in the s-cis and s-trans conformers raise their energies by roughly the amount that the s-cis to s-trans barrier is lowered, i.e., slightly more than 1 kcal/mol.

The presence of a methyl group on one of the central carbons of the diene unit changes the steric environment substantially. The 1,3 $H-CH_3$ interaction in s-trans 2-MB has been used to explain the very small (1.1−1.8 kcal/mol) s-trans/s-cis enthalpy difference found in several investigations.[14,20−22] We find that the $\Delta H_{t\rightleftharpoons c}$ for 2-MB is 2.41 kcal/mol, which is significantly larger than previous experimental values but is still smaller than the "unperturbed" enthalpy differences of *E*-PD and *EE*-HD. This experimental value is slightly smaller than the 2.73 kcal/mol value obtained from our G3 calculations. The s-cis to s-trans barrier observed in 2-MB is not substantially different than those of *E*-PD and *EE*-HD (3.19 kcal/mol vs 2.84 and 3.23 kcal/mol), so, as seems reasonable, there are no new large steric interactions in the s-cis 2-MB rotamer and the decrease in the energy difference between the rotamers is, as determined previously, due to the 1,3 $H-CH_3$ steric interaction present in the s-trans isomer. The magnitude of this interaction is, however, considerably less than has been previously believed. It raises the s-trans energy only ~0.5 kcal/mol, not the 1−1.5 kcal/mol as surmised formerly. It is interesting to compare this 1,3 $H-CH_3$ steric interaction in s-trans 2-MB with the 1,3 CH_3-H interaction present in s-trans *Z*-PD and *EZ*-HD. In the latter two cases, the interaction raises the s-trans energy by more than 1 kcal/mol (twice the magnitude of the interaction in 2-MB). A closer look shows that these interactions are subtly different. To avoid an antibonding $\pi_{CH3}-\pi^*$ interaction, methyl groups attached to double bonds adopt a geometry with one of the hydrogens eclipsed to the attached double bond.[42] As shown in Figure 12, the 1,3 steric interaction in s-trans *Z*-PD occurs between two hydrogens that are in the same plane, whereas that in s-trans 2-MB occurs between staggered hydrogens and is therefore less.

The s-cis/s-trans enthalpy difference of DMB is reduced by about 1.0 kcal/mol compared with that of the parent compound, 1,3-butadiene,[19] and *E*-PD and *EE*-HD (**Table 1**). This reduction is accompanied by some decrease in the s-cis to s-trans barrier. This result indicates that the two inner methyl groups raise the steric energy more in the s-trans than in the s-cis rotamer, which is a surprise because the steric interaction that stands out at first glance is the 2,3 CH_3-CH_3 interaction of the s-cis form. Although this interaction certainly raises the energy of the s-cis form as indicated by the lower s-cis to s-trans barrier compared with those of *E*-PD and *EE*-HD, it is mitigated by the twist in the s-cis conformer. The steric strain in the s-trans rotamer of DMB is the sum of the increase in energy of the s-cis rotamer and the 1 kcal/mol decrease in the s-trans/s-cis enthalpy difference compared with the $\Delta H_{t\rightleftharpoons c}$ of "unperturbed" dienes. Indeed, s-trans DMB has two of the 1,3 $H-CH_3$ steric interactions present in s-trans 2-MB. However, these interactions will be stronger than in 2-MB because, as indicated in Figure 13, a buttressing effect prevents opening of the diene angle opposite the methyl group. Opening up the C2−C3−C4 angle in an attempt to relieve the 1,3 $H-CH_3$ steric interaction will close down the $CH_3-C3-C2$ angle and thereby increase the other 1,3 $H-CH_3$ interaction. This buttressing effect is demonstrated in Figure 14 where the calculated geometries of s-trans 2-MB and DMB are compared. Note the smaller C4−C3−C2 angle and the closer approach of H6 and H7 in s-trans DMB as compared with s-trans 2-MB. Because of this buttress-

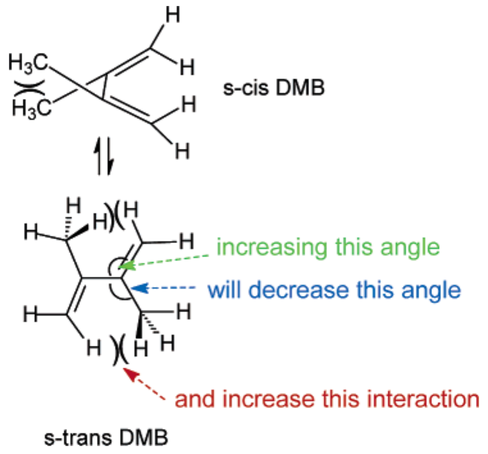
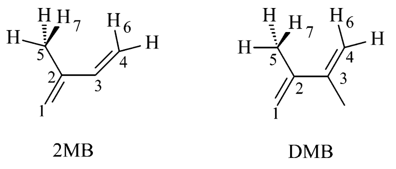


FIGURE 13. Steric interactions in s-cis and s-trans DMB.



	2MB	DMB
∠ $C_5C_2C_3$	118.7°	118.5°
∠ $C_4C_3C_2$	125.4°	121.5°
r H_6, H_7	2.459 Å	2.350 Å

FIGURE 14. Calculated geometries of 2-MB and DMB.

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[42] (a) Hehre, W. J.; Pople, J. A.; Devaquet, A. J. P. *J. Am. Chem. Soc.* **1976**, *98*, 664. (b) Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253.

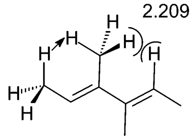

FIGURE 15. Buttressing effect in s-trans *EE*-DMH.

ing effect, s-trans DMB should be raised more than twice the 0.5 kcal/mol increase seen for s-trans 2-MB, as is observed.

Although, in general, terminal (*E*)-substituted methyl groups have marginal effects on the potential function of dienes, the potential function of (*E*,*E*)-3,4-dimethyl-2,4-heaxadiene, *EE*-DMH, is significantly different from that for DMB because of the existence of the cis interaction between the internal and terminal (*E*)-methyl groups. Here, again, a buttressing effect changes the steric interaction. As seen in Figure 15, the cis methyl interaction in *EE*-DMH increases the inner methyl vinyl hydrogen interaction. The calculated geometry shows a 2.2-Å separation between the hydrogens of the inner methyl group and the opposite vinyl hydrogen, which is over 0.15 Å less than this same interaction in DMB. This increase in steric interaction raises the energy of the s-trans form. The gauche form avoids any substantial increase in steric energy by twisting slightly more with a central dihedral angle of 51 °C as compared with the calculated 47 °C dihedral angle of DMB. So, the enthalpy difference between the conformers of *EE*-DMH is less. The gauche s-cis/s-trans enthalpy difference is about 2 kcal/mol for DMB, whereas it is only about 1 kcal/mol for *EE*-DMH, making *EE*-DMH the only acyclic diene we studied that had substantial amounts of the s-cis form present at room temperature (∼25%).

ZZ-HD and 2,5-DMH were the two dienes examined that could not be effectively trapped using our technique. Matrix isolated high-temperature depositions of *ZZ*-HD diluted in N_2 at a ratio of 1:1000 showed only a very weak additional set of bands not present in room-temperature depositions. As with all matrix isolation experiments, the CsI window must be kept near 22 K as lower window temperatures always result in an opaque sample. Neat depositions use nearly 1000 times less material, producing only very, very thin films, so in these depositions, lower window temperatures can be used. Neat high-temperature depositions onto a CsI window held at 20 K again resulted in a set of only very weak additional bands, but carrying out these neat high-temperature depositions at the lower window temperature of 14 K (our lower limit) showed a discernible increase in these additional bands. These bands decayed at significantly lower temperatures than previous dienes (below 30 K), and these decays gave a very low value (1.68 kcal/mol) for $\Delta G_0^{\ddagger} - 3\sigma$. This matches well with the calculated barrier of 1.72 kcal/mol, and the incomplete trapping seen for this molecule sets a lower limit of the barrier "protecting" the metastable conformer for successful conformational trapping experiments. Indeed, in the case of 2,5-DMH, where calculations suggest only a 1.56 kcal/mol barrier, we find no trapping of the minor conformer even in neat depositions at 14 K.

Finally, these two unsuccessful trapping experiments point out the one disagreement between our experimental results and the calculations. As previously mentioned, the s-cis to s-trans barriers for DMB and *EE*-DMH calculated at the G3 level are much smaller than we observed experimentally in the solid-state and are essentially the same as the barriers calculated at the same level for *ZZ*-HD and 2,5-DMH, both of which could not be successfully trapped. Yet, the minor forms of DMB and *EE*-DMH are trapped quite well. Calculations using the composite G3B3 level of theory show only slightly higher barriers for these two dienes. Treating the methyl groups as hindered rotors changed both the calculated energy difference and the barrier of DMB by less than 0.1 kcal/mol, so the ultimate cause of this discrepancy is unknown.

Conclusions

We have demonstrated that high-temperature conformational equilibrium trapping by a high-vacuum cryogenic deposition technique can be used to obtain very accurate conformational enthalpy differences even when the conformers are, like acyclic 1,3-dienes, separated by quite small barriers. Further, when a Gaussian distribution of activation energies is used to describe the site-specific decay barriers of the minor form, good estimates of gas-phase barriers can be obtained. Ab initio calculations at the G3 level reproduce with high accuracy the experimentally determined enthalpy differences between the s-cis and s-trans conformers of the methyl-substituted 1,3-dienes studied. The gas-phase s-cis to s-trans barriers determined from solid-state decays are, with the exception of those dienes containing methyl groups on the inner carbons of the diene unit, replicated by the calculations quite well. The changes in the 1,3-diene conformeric energy differences can be understood by a variety of steric interactions which can be modified by buttressing effects. In particular, a terminal *E*-substituted methyl group will affect the torsional profile very little, whereas, surprisingly, a terminal *Z*-substituted methyl group raises the energy of the s-trans conformer as much as the gauche s-cis conformer, about 1 kcal/mol. The s-trans conformer of 1,3-dienes with methyl groups on the inner carbons is also raised in energy relative to the corresponding s-cis conformer but much less than previously believed, on the order of only 0.5 kcal/mol per methyl group.

Experimental Section

All 1,3-dienes were purchased excepting those listed below. Final purifications were performed by preparative gas chromatography using a 20 ft, 1/8 in. 15% OV-17 on chromsorb W column.

All infrared spectra were recorded on a Fourier transform spectrometer, equipped with a Globar source, a KBr beam splitter, and a broadband DTGS detector. All spectra were recorded at 0.5 or 1.0 cm^{-1} resolution. For all spectra, 2000 interferograms were co-added, Blackman−Harris 3 term apodized, and Fourier transformed with a zero-filling factor of 4.

Low-temperature IR spectra were taken by using a displex equipped with a temperature controller using a gold−chromel thermocouple. The matrix isolation experiments were performed as described in the text. Depositions of neat samples were performed similarly. NMR spectra of deposited samples were obtained by warming the system to room temperature overnight while pumping the nitrogen/sample mixture through a liquid N_2 trap which was warmed and rinsed with NMR solvent (CD_3CN) to obtain the sample.

2,5-Dimethyl-2,4-hexadiene (2,5-DMH) was obtained from Dr. R. S. H. Liu from the University of Hawaii. Final purification was performed by preparative gas chromatography.

3,4-Dimethyl-3,4-hexanediol.[43] A solution of mercuric chloride ($HgCl_2$) (10.5 g, 0.0387 mmol) in 2-butanone (63.0 g, 0.875 mol) was added slowly to magnesium turnings (10 g, 0.42 mol) in 120 mL of dried benzene until the reaction mixture began to reflux spontaneously. The remainder of the solution of mercuric chloride in 2-butanone was added over a 45-min period at such a rate that a vigorous reflux was maintained. After the reaction mixture had been refluxed for an additional 1.5 h, 40 mL of distilled water was added and the mixture was heated to reflux for 30 min.

The gray solid which formed upon addition of water was separated from benzene solution by filtration and then returned to the reaction flask, together with 100 mL of fresh benzene. This mixture was refluxed and filtered. After the benzene filtrates were combined and concentrated, 16.11 g of oil (25.2% yield on starting ketone) was obtained. NMR spectra showed it was an approximately 1:1 mixture of meso and DL isomer of the pinacol 3,4-dimethyl-3,4-hexanediol (bp 108−114 °C, 32 mm).

Dehydration of 3,4-Dimethyl-3,4-hexanediol. A 25-mL three-necked flask was charged with 15 mL of propionic anhydride, 15 mg of iodine, and 6.0 g of the DL−meso mixture of the 3,4-dimethyl-3,4-hexanediols. The mixture was stirred with a magnetic stirrer and heated for 2 h at 125 °C. A stream of N_2 was passed through the reaction flask to sweep the volatile products through a water-cooled condenser into a receiving flask immersed in an ice−salt mixture. The propionic anhydride that distilled along with the diene fraction was removed by shaking with a saturated sodium bicarbonate solution. The resulting diene mixture was produced with a 70% yield.

(*E,E*)-3,4-Dimethyl-2,4-hexadiene. The mixture of several dienes and ketones produced via the pinacol rearrangement obtained above was purified by preparative GC using a 2-m long, 6.3-mm o.d., 10% Carbowax column. The *EE*-DMH purified had the following characteristics: bp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 1.71 (d, $J = 6.6$ Hz), 1.76 (s), 5.58 (q, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 13.5, 14.0, 119.1, 137.1; UV (pentane) λ_{max}, nm (ϵ) 237 (17 000).

All calculations were performed using the Gaussian 03 program.[44]

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Supporting Information Available: s-trans and s-cis IR bands for each diene and a comparison of G3 and G3B3 results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Reeve, W.; Reichel, D. M. *J. Org. Chem.* **1972**, *37*, 68.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Guassian 03*; Gaussian, Inc.: Wallingford, CT, 2004.