

The second reason is based on the inherent vagueness of HMO, which need not be elaborated. As an example, we take the same problem as quoted in ref 3, i.e., the divergent results of DEPE between HMO butadiene and the HF HCS linear  $H_4$ . Destabilization in HCS is a natural result and may be offset if one considers one or two factors such as long-range interaction and internuclear repulsion, both of which are not taken into account in HMO. Table I shows the total ( $E$ ) and electronic ( $E^F$ ) energies where  $E_A$  and  $E_{AB}$  denote the monocentric and bicentric terms,<sup>1</sup> respectively, and neigh. denotes the sum of the nearest neighboring interactions, e.g., for  $H_4$ , it is ( $E_{12} + E_{23} + E_{34}$ ).

In order to juxtapose the HF HCS model to HMO treatment, the long-range interactions are not incorporated, resulting in that DEPE for  $2H_2 \rightarrow$  linear  $H_4$  is +167 kcal/mol,<sup>3</sup> and internuclear interaction is neglected so that DEPE becomes +172 kcal/mol, showing enormous stabilization. This example shows that if one tries to correlate the HF HCS results with those of HMO, one may not use the total energy but rather partitioned and/or partial energies with apparent physical meaning. Although the detailed analyses along this line may shed light on the role of HMO, it seems for us to be an unimportant task.

The relative stability of the cyclic system to the linear reference is a widely accepted definition of aromaticity.<sup>6</sup> However, considering the sensitivity of ab initio MO theory on geometry, we do not think that such a comparison in the HF HCS model is workable since the geometrical environment between cyclic and linear systems is too different to ignore. Thus we only used the polygonal  $H_n$  systems to show the inherent stabilities of the  $4n + 2$  cyclic HCS compared with the  $4n$  cyclic HCS where the

(6) See ref 6-8 in ref 3.

environment is similar and that such a difference of energy may be correlated to the *kinetic (energy) pressure*.<sup>7</sup>

The foregoing communication<sup>3</sup> also points out that unstability of the  $H_4$  may be due to the higher HF solution (CDW) for singlet state and obtained triplet state ( $H_7^1$ ) of  $H_4$  and  $H_8$  cyclic HCS's. We admit that we only handled the higher solution.

The lowest solutions that we found for  $Dnh$   $H_4$  and  $H_8$  were the spin density wave (SDW) states,<sup>9</sup> which are 31.0 and 34.1 kcal/mol lower than the  $H_4^t$  and  $H_8^t$  solutions, respectively. The order of total energy per atom<sup>10</sup> is the following:  $H_4^t(-0.47511) > H_4^s(\text{SDW: } -0.48747) > H_8^t(-0.50861) > H_8^s(\text{SDW: } -0.51542) > H_{10}(-0.52872)^1 > H_6(-0.53035 \text{ au})^1$ . The unstable nature of  $H_4$  and  $H_8$  systems is again ascertained. Besides, analysis of the partitioned energies led to the same conclusion reported before.<sup>1</sup>

Haddon et al.<sup>3</sup> finally stress the discrepancies in the order for naphthalene, azulene, and [10]annulene geometries using a single common internuclear distance for each system. We have no comment on this, since in addition to the considerable geometrical differences between them, use of a single common H-H length for each system on geometry optimization seems to be an apparent arbitrary factor.

Registry No. Atomic hydrogen, 12385-13-6.

(7) In a previous report,<sup>1</sup> we used the abbreviated term *kinetic pressure* for *kinetic energy pressure* (Feiber, M. J.; Rudenberg, K. *J. Chem. Phys.* **1971**, *54*, 1495).

(8) Whangbo, M. H. *Acc. Chem. Res.* **1983**, *16*, 95.

(9) The total energies were obtained at their optimized structures. The optimized lengths (Å) of side are as follows:  $H_4^t$  (1.1471),  $H_4^s$  (1.2547),  $H_8^t$  (1.0050), and  $H_8^s$  (1.0362).

(10) In terms of au.

## Comparison between the *s*-Cis and *Gauche* Conformers of 1,3-Butadiene

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**Abstract:** Geometries of stationary points for *s*-cis-1,3-butadiene and *gauche*-1,3-butadiene have been predicted via molecular electronic structure theory. Both double- $\zeta$  (DZ) and double- $\zeta$  plus polarization (DZ+P) basis sets were used in conjunction with the self-consistent-field (SCF) and configuration interaction (CI) methods. At the DZ SCF level, *s*-cis-1,3-butadiene was characterized as a transition state for the isomerization of the two possible *gauche*-1,3-enantiomers, which were shown to be genuine local minima. The barrier to planarity at this level of theory was predicted to be 0.4 kcal/mol, and the torsional angle for the *gauche* structure is 33.2°. The same qualitative result was found at the DZ+P SCF level, with the rotational barrier being 0.7 kcal and the torsional angle 37.8°.

### Experimental and Theoretical Background

It is now well established that the compound 1,3-butadiene is a mixture of two conformers: the more stable *trans*-1,3-butadiene<sup>1,2</sup> and another structure which is often presented as *s*-cis-1,3-butadiene in textbooks.<sup>3-6</sup> The question as to whether the second stable conformer is actually *s*-cis- or rather *gauche*-1,3-butadiene (twisted) has been the subject of discussion for some time.<sup>7-9</sup>

For experimental chemists, an unequivocal answer to this question has been hindered by the difficulty of obtaining direct evidence concerning the less stable conformer. In 1973, however, Lipnick and Garbisch<sup>10</sup> opted for the *gauche*-1,3-butadiene as the second stable conformer on the basis of NMR spectroscopy. In

his 1975 Raman study, Carreira<sup>11</sup> concluded that the second equilibrium geometry of 1,3-butadiene is the planar *s*-cis structure,

(1) Almenningen, A.; Traetteburg, M. *Acta Chem. Scand.* **1958**, *12*, 1221.

(2) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463.

(3) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 291-292.

(4) Mislow, K. "Introduction to Stereochemistry"; Benjamin: New York, 1966; p 75.

(5) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 61-62.

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(8) Mulliken, R. S. *Rev. Mod. Phys.* **1942**, *14*, 265.

(9) Aston, J. G.; Szasz, G.; Wooley, H. W.; Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67.

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

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which lies only 873 cm<sup>-1</sup> (2.5 kcal) above the trans minimum. The following year Durig, Bucy, and Cole<sup>12</sup> analyzed the observed infrared and Raman spectra and concluded that they were "insufficient to determine uniquely the potential function and the structure of the non-trans conformer". In 1979, Bock, George, Trachtman, and Zanger<sup>13</sup> reassigned spectral lines which had been previously assigned to the s-cis form to the gauche form on the basis of calorimetric, spectroscopic, and ab initio data. Although they did not produce any conclusive evidence for a gauche form, the latter was favored in many respects.

Also in 1979 Squillacote, Sheridan, Chapman, and Anet (SSCA)<sup>14</sup> succeeded in identifying this conformer via matrix isolation spectroscopy. They did not rule out the possibility of a gauche form but rejected any structure with a torsional angle greater than 15° on the basis of electronic (UV) spectra. The most recent paper to address this question appeared in 1983 in which Furukawa and co-workers<sup>15</sup> tend to favor the gauche form. From all these contributions, it appears that the distinction between s-cis and gauche forms is rather difficult to make on an experimental basis. SSCA summarize this enigma with the suggestion that "the energy difference between 0° and ± 15° would then be expected to be so small that the zero-point torsional level would probably lie above the potential energy for the planar geometry, making a strictly geometric distinction almost meaningless".

In the field of ab initio molecular electronic structure theory, several studies have been devoted to this question, and all of these have been restricted to the self-consistent-field (SCF) level of theory. As early as 1970, Radom and Pople<sup>16</sup> suggested the existence of minima for both the s-cis and gauche forms, but using STO-3G (minimum basis) calculations and incomplete optimizations. In 1976, Skaarup, Boggs, and Skancke<sup>17</sup> performed geometry optimizations for four rotamers with fixed dihedral angles 0° (trans), 90°, 140°, and 180° (cis), using a (7s3p/5s3p) basis set for carbon and three uncontracted s functions for hydrogen. The only constraint in the optimization was that the two ethylene-like fragments of the molecule remain planar while rotating about the C-C bond. They pointed out that the gauche structure was energetically lower lying than the s-cis, but by only 0.6 kcal/mol, a result which they did not consider to be conclusive. With the same type of constraint, De Mare<sup>18,19</sup> optimized butadiene geometries with STO-3G, 3-21G (split-valence), and 6-31G\* (split-valence and polarization d functions on C atoms) basis sets and predicted likewise an energetic preference for the gauche conformer over the s-cis. Before leaving the general area of computational chemistry, it should be noted that Tai and Allinger<sup>20</sup> have used molecular mechanics to predict a planar s-cis equilibrium structure.

Here we extend this series of ab initio studies by full SCF geometrical optimizations of s-cis-1,3-butadiene and gauche-1,3-butadiene with larger basis sets. A discussion of the nature of the different stationary points will be made possible by means of vibrational frequency analyses. The effects of electron correlation were explicitly taken into account by using configuration interaction (CI),<sup>21</sup> and these results will be of value in discussing the energetics of the s-cis vs. gauche competition.

### Theoretical Approach

The structures of s-cis- and gauche-1,3-butadiene were optimized at the SCF level of theory by means of analytic gradient

**Table I.** Geometrical Description of the s-cis-1,3-Butadiene (C<sub>2v</sub>) Transition State (See Figure 1 for Atom Numbering)

parameter	present research		
	DZ SCF	DZ+P SCF	4-31G SCF <sup>a</sup>
Bond Lengths <sup>b</sup>			
C <sub>2</sub> =C <sub>3</sub>	1.337	1.328	1.323
C <sub>3</sub> -C <sub>4</sub>	1.482	1.484	1.472
H <sub>2</sub> C <sub>2</sub>	1.074	1.078	1.079
H <sub>4</sub> C <sub>2</sub>	1.073	1.078	1.078
H <sub>5</sub> C <sub>4</sub>	1.076	1.080	1.079
Bond Angles <sup>c</sup>			
C <sub>4</sub> C <sub>3</sub> C <sub>2</sub>	127.2	127.2	127.1
H <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	116.3	116.7	115.9
H <sub>4</sub> C <sub>2</sub> C <sub>3</sub>	120.9	120.6	121.2
C <sub>1</sub> C <sub>4</sub> H <sub>5</sub>	118.1	118.0	118.1

<sup>a</sup> Bock, Trachtman, and George, ref 28. <sup>b</sup> Bond lengths in Å. <sup>c</sup> Bond angles in degrees.

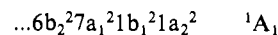
**Table II.** Geometrical Description of the gauche-1,3-Butadiene (C<sub>2</sub>) Conformer (See Figure 1 for Atom Numbering)<sup>a</sup>

parameter	present research	
	DZ SCF	DZ+P SCF
Bond Lengths		
C <sub>2</sub> =C <sub>3</sub>	1.337	1.328
C <sub>3</sub> -C <sub>4</sub>	1.481	1.482
H <sub>1</sub> C <sub>1</sub>	1.0743 <sup>a</sup>	1.0783 <sup>a</sup>
H <sub>3</sub> C <sub>1</sub>	1.0737 <sup>a</sup>	1.0779 <sup>a</sup>
H <sub>5</sub> C <sub>3</sub>	1.076	1.081
Bond Angles <sup>b</sup>		
C <sub>1</sub> C <sub>3</sub> C <sub>4</sub>	125.8	125.5
C <sub>1</sub> C <sub>3</sub> H <sub>5</sub>	118.7	118.8
H <sub>3</sub> C <sub>1</sub> H <sub>1</sub>	116.7	117.2
H <sub>1</sub> C <sub>1</sub> C <sub>3</sub>	122.1	121.9
H <sub>3</sub> C <sub>1</sub> C <sub>3</sub>	121.2	120.9
H <sub>5</sub> C <sub>3</sub> C <sub>4</sub>	115.4	115.7
Dihedral Angles <sup>b</sup>		
C <sub>1</sub> C <sub>3</sub> C <sub>4</sub> C <sub>2</sub>	33.2	37.8
H <sub>1</sub> C <sub>1</sub> C <sub>3</sub> C <sub>4</sub>	1.8	1.6
H <sub>3</sub> C <sub>1</sub> C <sub>3</sub> C <sub>4</sub>	179.3	179.2
H <sub>5</sub> C <sub>3</sub> C <sub>4</sub> H <sub>5</sub>	31.1	35.3

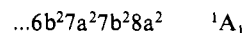
<sup>a</sup> All bond distances are given in Å. CH bond distances are reported to four decimal places, since they are indistinguishable to three decimals. <sup>b</sup> Bond angles in degrees.

methods.<sup>22</sup> The gradient method has been applied with sufficient precision to yield bond angles to within 0.1° and bond distances to within 0.001 Å of the exact values for the levels of theory adopted.

The standard Huzinaga-Dunning<sup>23,24</sup> double- $\zeta$  (DZ in the text) basis set, C(9s5p/4s2p) and H(4s/2s), was used in the initial phases of this research. Subsequently, polarization functions were added to this basis set: one set of d functions on each carbon atom ( $\alpha = 0.75$ ) and one set of p functions on each hydrogen atom ( $\alpha = 0.75$ ). This double- $\zeta$ -plus polarization (DZ+P) basis set thus includes 94 contracted Gaussian functions for butadiene. The geometry of s-cis-1,3-butadiene was constrained to have C<sub>2v</sub> symmetry during the optimization. The cis electron configuration at the optimized DZ geometry is



No constraint at all was introduced in the optimization of the gauche-1,3-butadiene at the DZ level. However, the optimized geometry was ultimately found to have the symmetry of the point group C<sub>2</sub>, with configuration



The C<sub>2</sub> symmetry was subsequently retained for the DZ+P SCF optimization. The stationary points obtained at the DZ level were

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(15) Furukawa, Y.; Takeuchi, H.; Harada, I.; Tasumi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 392.

(16) Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4786.

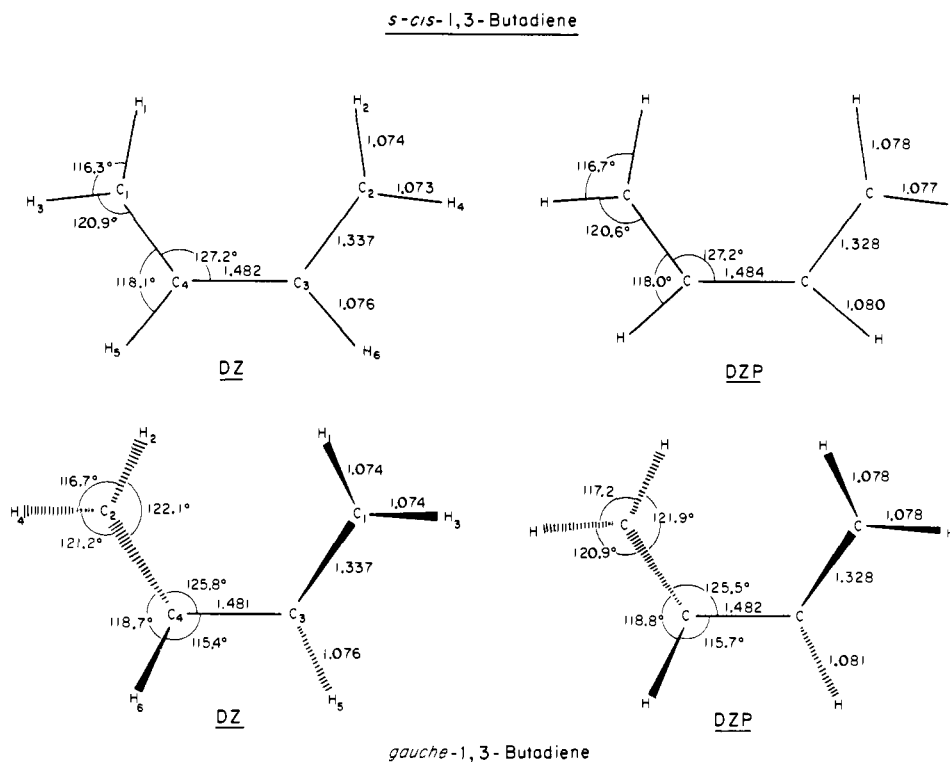
(17) Skaarup, S.; Boggs, J. E.; Skancke, P. N. *Tetrahedron* **1976**, *32*, 1179.

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**Figure 1.** Predicted self-consistent-field molecular structures for 1,3-butadiene in its *s-cis* and *gauche* conformations. DZP refers to the use of a double- $\zeta$ -plus polarization basis set. All bond distances are in Å.

characterized by vibrational frequencies analyses carried out by means of analytic second derivative methods.<sup>25,26</sup> At both stationary points, CI wave functions including all single and double excitations (CISD) with respect to the SCF reference function (four lowest occupied and four highest unoccupied atomic carbon 1s-like orbitals being frozen) were determined by using the "shape-driven" graphical unitary group approach.<sup>27</sup> Those CI wave functions included 19 482 ( $C_{2v}$ ) and 33 306 ( $C_2$ ) configurations with the DZ basis set; 93 262 ( $C_{2v}$ ) and 170 982 ( $C_2$ ) configurations are included when the larger DZ+P basis set was used.

### Predicted Structures and Energetics

Tables I and II along with Figure 1 present the fully optimized geometries for the *s-cis* and *gauche* structures of 1,3-butadiene at both DZ and DZ+P SCF levels of theory. For the *s-cis* form, a comparison with previous 4-31G SCF results<sup>28</sup> is also possible. To a greater degree than found for the latter calculation, we found that the C=C bond length is plausibly predicted at the DZ SCF level of theory, if one compares the present 1.337 Å with the experimental bond length of *trans*-butadiene, 1.342 Å. Of course, there is no experimental geometry available for the second stable conformer of 1,3-butadiene.

There is no fundamental difference between the bond distances of *s-cis*- and *gauche*-1,3-butadiene. The only substantive distinction resides in the torsional angle C=C—C, which is predicted here to be 33.2°, much larger than the 15° value suggested as acceptable by SSCA.<sup>14</sup> It may be noted in this regard that De Mare<sup>18</sup> found 38.1° at the 3-21G (SCF) level. The constraint of keeping the ethylene-like fragments planar during optimization is found to be basically acceptable as shown by the very small dihedral angles C=C—C—H obtained in our complete optimizations.

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**Table III.** Estimation of the Barrier to Planarity of *gauche*-1,3-Butadiene (in kcal/mol)

	SCF	CISD <sup>a</sup>	CISD + unlinked <sup>b</sup>
DZ	0.43	0.81	0.82
DZ+P	0.71	0.82	0.81
absolute energies, hartrees			
	DZ SCF	DZ CI	DZ+P SCF
<i>s-cis</i>	-154.87252	-155.20060	0.81
<i>gauche</i>	-154.87321	-155.20190	-154.94540
			DZ+P CI
<i>s-cis</i>			-155.43809
<i>gauche</i>			155.43939

<sup>a</sup>CI wave function (including single and double excitations) determined at the corresponding SCF optimized geometry. <sup>b</sup>Includes Davidson's correction<sup>29</sup> for unlinked clusters.

As found in earlier ab initio calculations<sup>17-19</sup> these two stationary points are almost isoenergetic. Indeed, for the *cis* form we find  $E(\text{DZ SCF}) = -154.87252$  and for the *gauche* form  $E(\text{DZ SCF}) = -154.87321$ , giving rise to an energy difference of only 0.43 kcal/mol.

The inclusion of electronic correlations does not qualitatively modify this finding. As shown in Table III, the energy difference remains within 1 kcal/mol at the DZ CI level of theory. Furthermore, this conclusion is qualitatively unaffected by the appendage of Davidson's correction<sup>29</sup> for unlinked clusters.

The DZ+P SCF structures are qualitatively similar to those obtained at the less complete DZ SCF level of theory. Rather than decrease the torsional angle, the DZ+P SCF method increases it, from 33.2° (DZ SCF) to 37.8°. This DZ+P SCF value, resulting from a complete optimization of all geometrical parameters, is in close agreement with the value 38.5° predicted at the 6-31G\* SCF level via an incomplete structural optimization.<sup>19</sup> The DZ+P SCF total energies in Table III also indicate that the energy difference between the *cis* and *gauche* conformers is increased, from 0.43 kcal (DZ SCF) to 0.71 kcal (DZ+P SCF).

The central C—C bond length is virtually unaffected by the addition of polarization functions to the basis set. For the *s-cis* structure it increases by 0.002 Å, and for the *gauche* conformer

(29) Davidson, E. R. "The World of Quantum Chemistry"; Daudel, R., Pullman, B., Eds.; Dordrecht: Holland, 1974; pp 17-30.

**Table IV.** Comparison of Observed and Calculated (DZ SCF) Vibrational Frequencies (in  $\text{cm}^{-1}$ ) for *s-cis*-1,3- and *gauche*-1,3-Butadiene<sup>a</sup>

largest contrib. to normal mode		<i>s-cis</i> -1,3-butadiene			<i>gauche</i> -1,3-butadiene			
		symmetry	DZ SCF	diff. <sup>a</sup>	symmetry	obsd	DZ SCF	diff. <sup>a</sup>
CH <sub>2</sub> asymmetric stretch	in phase	A <sub>1</sub>	3441	10.9	A	3103	3441	10.9
	out of phase	B <sub>2</sub>	3436	10.7	B	3103	3437	10.8
CH stretch	in phase	A <sub>1</sub>	3372	11.9	A	3014	3365	11.6
	out of phase	B <sub>2</sub>	3350	11.1	B	3014	3347	11.0
CH <sub>2</sub> symmetric stretch	in phase	A <sub>1</sub>	3341	11.9	A	2986	3336	11.7
	out of phase	B <sub>2</sub>	3335	11.7	B	2986	3332	11.6
C=C stretch	out of phase	B <sub>2</sub>	1828	13.4	B	1612	1821	13.0
	in phase	A <sub>1</sub>	1826	11.8	A	1633	1829	12.0
CH <sub>2</sub> scissors	in phase	A <sub>1</sub>	1611	13.1	A	1425	1607	12.8
	out of phase	B <sub>2</sub>	1584	12.9	B	1403	1579	12.5
CH in-plane bend	in phase	A <sub>1</sub>	1484		A		1465	
	out of phase	B <sub>2</sub>	1436		B		1431	
CH <sub>2</sub> rock	out of phase	B <sub>2</sub>	1220		B		1214	
	in phase	A <sub>1</sub>	1163	7.0	A	1087	1176	8.2
CH out-of-plane bend	out of phase	A <sub>2</sub>	1159	17.9	A	983	1140	16.0
	in phase	B <sub>1</sub>	1152	15.7	B	996	1147	15.2
CH <sub>2</sub> wag	in phase	B <sub>1</sub>	1112	21.7	B	914	1113	21.8
	out of phase	A <sub>2</sub>	1099	20.1	A	915	1103	20.5
C—C stretch		A <sub>1</sub>	940		A		946	
CH <sub>2</sub> twist	in phase	A <sub>2</sub>	832	14.4	A	727	833	14.6
C=C—C deformation		B <sub>2</sub>	620	4.0	B	596	676	13.4
CH <sub>2</sub> twist	out of phase	B <sub>1</sub>	573	21.9	B	470	524	11.5
C=C—C deformation	in phase	A <sub>1</sub>	318		A		299	
C—C torsion		A <sub>2</sub>	131i		A	136	156	14.7

<sup>a</sup>The percentage differences between theoretical and observed vibrational frequencies.

by 0.001 Å. The C=C bond distances decrease slightly in going to the larger basis set, the differences being 0.009 Å for both the *s-cis* and *gauche* forms. All C—H distances increase with the addition of polarization functions, by 0.004–0.005 Å. The DZ+P SCF predictions should be the more reliable, with bond distances correct to within  $\pm 0.02$  Å and bond angles (other than the torsional angle) to within  $\pm 3^\circ$ . The reliability of the torsional angle is much more difficult to assess, but we may estimate the DZ+P prediction of  $37.8^\circ$  to be good to within  $\pm 10^\circ$ .

### Vibrational Analyses

The basic distinction between the *s-cis* and *gauche* structures is apparent when one predicts the vibrational frequencies. As may be seen in Table IV, *s-cis*-1,3-butadiene has one DZ SCF imaginary vibrational frequency ( $131i \text{ cm}^{-1}$ ), with normal mode corresponding to rotation about the C—C single bond. This makes the *s-cis* form a transition state, rather than a genuine local minimum at this level of theory. This is actually the transition state for the interconversion between the two possible enantiomers of *gauche*-1,3-butadiene, characterized here as genuine local minima. For the *gauche* structure the torsional motion or C—C internal rotation corresponds to a real vibrational frequency ( $156 \text{ cm}^{-1}$ ). This is the first time to our knowledge that the *s-cis* form has been ruled out as the second stable conformer on such a rigorous theoretical basis. Of course, the extremely flat shape of the curve makes the distinction a rather subtle matter, as pointed out by Durig, Bucy, and Cole<sup>12</sup> and by SSCA.<sup>14</sup>

The comparison with the observed frequencies requires some comment. One must consider the possibility that the set of observed frequencies of Furukawa et al.<sup>15</sup> may be assigned to either conformer. However, as pointed out by these authors, the  $a_2$  modes are infrared inactive in  $C_{2v}$ . The fact that they are observed requires a symmetry lowering to  $C_2$ . Assigning the observed frequencies to *s-cis*-butadiene also implicitly requires the assumption that it is a genuine minimum. That is why a question mark appears in Table IV for the C=C—C torsional mode in *cis*-1,3-butadiene.

There is only one difference in the assignments of the frequencies to normal modes between our predictions and the experimental work.<sup>15</sup> It concerns the "CH out-of-plane bends" and

the "CH<sub>2</sub> twists" which are switched in our assignment. But as may also be seen in Table IX of Furukawa's paper, these two modes are almost equally mixed. One may also notice that the theoretical vibrational frequencies are more consistently higher than the observed ones for the case of *gauche*-1,3-butadiene than for the case of *s-cis*-1,3-butadiene. It is furthermore worth noting here that the zero-point vibrational energy correction reduces the barrier height between the two conformers by an amount of 0.12 kcal/mol.

To the extent that the DZ SCF level of theory may be trusted, the second stable conformer of butadiene is therefore a *gauche* conformer with a torsional angle of  $33.2^\circ$ . Since this angle is twice as big as the value of  $15^\circ$  suggested by Squillacote et al.<sup>14</sup> and since it is well-known that inclusion of polarization in the basis set can reduce that kind of torsional angle, we also optimized, as noted above, both isomers at the DZ+P SCF level. Although no vibrational frequencies were predicted with the DZ+P SCF method, the energetics (discussed above) support the view that the *gauche* structure is a minimum and the *cis* is a transition state.

### Concluding Remarks

Reported here is the first ab initio vibrational characterization of the *s-cis* and *gauche* conformations of 1,3-butadiene. At the higher of the two levels of theory adopted, the equilibrium structure is twisted by  $37.8^\circ$  relative to the planar *s-cis* structure. It seems highly unlikely that geometry optimization at the CI level would reduce this angle to a value close to the  $15^\circ$  suggested as an upper limit by Squillacote, Sheridan, Chapman, and Anet.<sup>14</sup> It would also be surprising should basis set improvements produce such a decrease in the torsional angle. We therefore conclude that the second stable conformer of butadiene is *gauche*-1,3-butadiene with a torsional angle of about  $35^\circ$ .

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