

Isomer Energy Differences for the C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> Isomers Using Diffusion Monte Carlo<sup>†</sup>Dominik Domin,<sup>‡</sup> William A. Lester, Jr.,<sup>\*,‡,§</sup> Russell Whitesides,<sup>||,⊥</sup> and Michael Frenklach<sup>||,⊥</sup>

Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California at Berkeley, Berkeley, California 94720-1460, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, and Department of Mechanical Engineering, University of California at Berkeley, Berkeley, California 94720-1740

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A new diffusion Monte Carlo study is performed on the isomers of C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> emulating the methodology of a previous study (*Int. J. Chem. Kinet.* **2001**, 33, 808). Using the same trial wave function form of the previous study, substantially different isomerization energies were found owing to the use of larger walker populations in the present work. The energy differences between the *E* and *i* isomers of C<sub>4</sub>H<sub>3</sub> were found to be 10.5 ± 0.5 kcal/mol and for C<sub>4</sub>H<sub>5</sub>, 9.7 ± 0.6 kcal/mol. These results are in reasonable accord with recent MRCI and CCSD(T) findings.

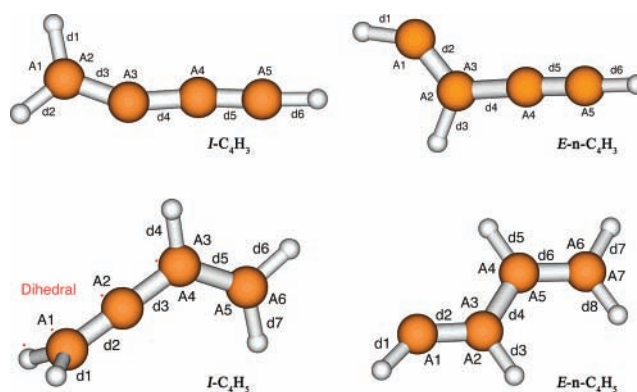
## 1. Introduction

For well over a decade there has been considerable debate over the relative importance of even-carbon-atom pathways for the formation of aromatics. The addition of acetylene to *n*-C<sub>4</sub>H<sub>3</sub> and *n*-C<sub>4</sub>H<sub>5</sub> was dismissed as unlikely by Miller and Melius on the basis of BAC-MP4 calculations of the energy differences between the *normal* and *iso* isomers.<sup>1</sup> Significantly smaller normal and iso isomer energy differences for C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> were calculated using diffusion Monte Carlo (DMC) in a study by Krokidis, Moriarty, Lester, and Frenklach, hereafter KMLF,<sup>2</sup> and led Frenklach<sup>3</sup> to advocate the importance of such even-carbon-atom pathways in the formation of the first aromatic. The substantially lower isomer energy differences predicted by the KMLF DMC calculations recently generated controversy as they were outliers compared to CCSD(T) calculations by Wheeler *et al.*<sup>4</sup> and MRCI calculations by Klippenstein and Miller.<sup>5</sup> The consistency of the results of the latter studies and their disagreement with the KMLF DMC results has spurred this re-examination of the previous DMC results. We have repeated KMLF's DMC calculations as closely as possible to ascertain their validity.

This paper is organized as follows. Section 2 summarizes the DMC method to the extent needed for the present purpose. It is followed in section 3 by computational details, and in section 4 by results and discussion.

## 2. Diffusion Monte Carlo

Diffusion Monte Carlo solves the time-independent Schrödinger equation by stochastically simulating the time-dependent Schrödinger equation in imaginary time. The method is well described elsewhere (see, for example, refs 6–12), and therefore



**Figure 1.** Isomer geometries. The numerical values for the different geometry parameters are located in Tables 1 and 2. Bond angles (denoted A1–A7) and the dihedral angle are in degrees. Bond lengths (denoted d1–d8) are in angstroms.

we make comments about the method as needed for the present purpose. Although the DMC energy is primarily dependent on the nodes of the trial wave function and not the trial wave function itself, the quality of the trial wave function greatly influences the variance of the energy (and therefore its error bar). The simulation bias of using a finite time step can be reduced by extrapolating several DMC time step runs to zero time step, or by using a sufficiently small time step that this bias is negligible. However, time steps that are too small, can make it difficult to converge calculations, and the energies obtained from such calculations can be unreliable. Walker population size may also introduce bias and produce irreproducible energies if the population is too small.

## 3. Computational Methodology.

**3.1. Geometries.** In this study optimized molecular geometries were obtained in the B3LYP/cc-pVTZ approach using the Gaussian 03 *ab initio* package<sup>13</sup> and are essentially the same as the B3LYP/cc-pVQZ geometries of the KMLF study. Wheeler *et al.* reported restricted open-shell coupled-cluster singles doubles with perturbation triples [ROCCSD(T)] geom-

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<sup>\*</sup> Corresponding author. E-mail: walester@lbl.gov.

<sup>‡</sup> Kenneth S. Pitzer Center for Theoretical Chemistry, University of California at Berkeley.

<sup>§</sup> Chemical Sciences Division, Lawrence Berkeley National Laboratory.

<sup>||</sup> Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory.

<sup>⊥</sup> Department of Mechanical Engineering, University of California at Berkeley.

**TABLE 1: Geometries of the C<sub>4</sub>H<sub>3</sub> Isomers**

	<i>E-n-C<sub>4</sub>H<sub>3</sub></i>		<i>i-C<sub>4</sub>H<sub>3</sub></i>	
	B3LYP/cc-pVTZ	ROCCSD(T) <sup>a</sup>	B3LYP/cc-pVTZ	ROCCSD(T) <sup>a</sup>
	Bond Length (Å)			
d1	1.077	1.079	1.088	1.088
d2	1.314	1.326	1.088	1.084
d3	1.094	1.091	1.303	1.319
d4	1.422	1.434	1.315	1.347
d5	1.201	1.214	1.229	1.233
d6	1.061	1.064	1.061	1.064
	Bond Angle (deg)			
A1	136.6	135.2	116.1	117.2
A2	118.6	119.1	121.9	121.3
A3	125.6	124.4	180.0	156.0
A4	177.6	177.9	180.0	185.8
A5	180.8	180.8	180.0	177.9

<sup>a</sup> ROCCSD(T)/TZ(2d1f,2p1d) geometry parameters taken from ref 4.

**TABLE 2: Geometries of the C<sub>4</sub>H<sub>5</sub> Isomers**

	<i>E-n-C<sub>4</sub>H<sub>5</sub></i>		<i>i-C<sub>4</sub>H<sub>5</sub></i>	
	B3LYP/cc-pVTZ	ROCCSD(T) <sup>a</sup>	B3LYP/cc-pVTZ	ROCCSD(T) <sup>a</sup>
	Bond Length (Å)			
d1	1.077	1.079	1.087	1.086
d2	1.313	1.326	1.296	1.311
d3	1.095	1.093	1.346	1.357
d4	1.458	1.465	1.087	1.086
d5	1.084	1.084	1.390	1.396
d6	1.333	1.343	1.079	1.080
d7	1.081	1.082	1.080	1.081
d8	1.083	1.084		
	Bond Angle (deg)			
A1	138.0	136.6	121.9	121.5
A2	118.4	118.7	179.7	179.7
A3	125.7	124.8	118.0	118.6
A4	116.2	116.8	125.8	124.6
A5	123.8	123.0	121.2	120.9
A6	121.5	121.3	118.3	118.6
A7	117.0	117.5		
	Dihedral Angle (deg)			
			90.1	90.0

<sup>a</sup> ROCCSD(T)/TZ(2d1f,2p1d) geometry parameters taken from ref 4.

eries using augmented triple- $\zeta$  basis sets [TZ(2d1f,2p1d)]. For all the isomers except *i-C<sub>4</sub>H<sub>3</sub>*, the differences between B3LYP/cc-pVTZ and ROCCSD(T)/TZ(2d1f,2p1d) bond angles were at most 1.5° and those for bond lengths were at most 0.015 Å. These differences amount to 1.0% for both bond lengths and bond angles.

For *i-C<sub>4</sub>H<sub>3</sub>*, the maximal differences of the B3LYP/cc-pVTZ and ROCCSD(T)/TZ(2d1f,2p1d) approaches were 24.0° and 0.032 Å, but as Wheeler *et al.* noted, this molecule has a relatively flat potential energy surface about its CCC angle (labeled “A3”; see Figure 1 for geometry definitions). We confirmed the insignificance of the effect of the geometric differences on the energy of the *i-C<sub>4</sub>H<sub>3</sub>* by computing the DMC energy at both the published ROCCSD(T)/TZ(2d1f,2p1d) and the B3LYP/cc-pVTZ arrangements and found the differences statistically insignificant ( $0.4 \pm 0.4$  kcal/mol). The various bond lengths and angles are presented in Tables 1 and 2.

**3.2. Trial Wave Function Construction and DMC Specifications.** KMLF used single-determinant trial wave functions constructed from the natural orbitals of MCSCF(9,9) calculations,<sup>2</sup> incorrectly designated MCSCF(3,3). This notation means that the highest-lying 9 electrons were distributed among the

**TABLE 3: Isomerization Energies ( $\Delta E_c$  in kcal/mol)**

molecule	VMC <sup>a</sup>	DMC <sup>b</sup>	ROCCSD(T) <sup>c</sup>	DMC <sup>a</sup>
C <sub>4</sub> H <sub>3</sub>	9.6(0.4)	6.2(1.2)	11.1	10.5(0.5)
C <sub>4</sub> H <sub>5</sub>	10.8(0.6)	6.7(1.2)	9.9	9.7(0.6)

<sup>a</sup> Present work using SBK ECP for C and MCSCF trial wave functions. <sup>b</sup> Values deduced from ref 2. <sup>c</sup> Values from ref 4.

five highest occupied and four lowest unoccupied canonical Hartree–Fock orbitals in all possible ways that retain configurations with 1 singly and 4 doubly occupied orbitals. The 9 electron and 9 orbital active space was chosen on the basis of the number of electrons in nonbonding and  $\pi$  bonding orbitals in the C<sub>4</sub>H<sub>3</sub> isomers and the same size active space was used for the C<sub>4</sub>H<sub>5</sub> isomers for consistency. The Stevens–Basch–Krauss (SBK) effective core potential (ECP)<sup>14</sup> was used for carbon in conjunction with a large contracted Gaussian basis set obtained as a fit to numerical Hartree–Fock atomic orbitals and are listed in Tables 7 and 8.

In the present study, we carried out MCSCF calculations using the GAMESS *ab initio* package.<sup>15</sup> The DMC trial wave functions were of the form of a Slater determinant (constructed from the MCSCF natural orbitals) multiplied by a 10-parameter Schmidt–Moskowitz correlation function (SMBH).<sup>16</sup> The latter contains terms with explicit dependence on electron–electron, electron–nucleus, and electron–other-nucleus distances. The correlation function serves to reduce the variance in the local energy of both variational Monte Carlo (VMC) and DMC computations. The parameters of the SMBH correlation function were optimized by minimization of the absolute deviation functional<sup>17,18</sup> of the local energy on a fixed sample of 12 800 walkers. Three cycles of optimization and VMC were performed for each isomer and the correlation function parameters from the last optimization were used in subsequent DMC calculations. The calculations were performed following the Reynolds *et al.*<sup>6</sup> algorithm using single-electron moves, 128 processor runs with 100 walkers per processor and the small time step of 0.0050 hartree<sup>-1</sup>, which is not expected to have a substantial time step bias. This assumption was tested in DMC calculations that were performed using a time step of 0.0025 hartree<sup>-1</sup>. Decorrelated energies from blocks of 200 steps were averaged across the processors and outliers lying more than 4 standard deviations from the mean were removed during the final statistical averaging.

**3.3. Thermochemistry.** The zero-point energies and thermal corrections were computed using Gaussian 03 at the B3LYP/cc-pVTZ and QCISD/6-31(d) levels of theory. The harmonic frequencies were scaled by 0.965 for B3LYP<sup>19</sup> and 0.9537 for QCISD.<sup>20</sup> Enthalpies of formations were computed from the atomization energies and standard experimental enthalpies of formation for the atoms, and not from isodesmic reactions that benefit from cancellation of errors with other *ab initio* methods. With DMC, the statistical error of each of the constituent molecules that are part of an isodesmic calculation would lead to a large overall error.

The atomization energy ( $E_A$ ) is defined for the present systems for the general reaction



as

$$E_A^{\text{method}} = \sum_{i=1}^N \beta_i E_{\text{atom}(i)}^{\text{method}} - E_{\text{molecule}}^{\text{method}} - E_{\text{ZPE}}^{\text{method}} \quad (2)$$

**TABLE 4: Zero-Point Vibrational Energies (in kcal/mol)**

molecule	B3LYP/cc-pVTZ <sup>a</sup>	QCISD/6-31(d) <sup>b</sup>
<i>E-n</i> -C <sub>4</sub> H <sub>3</sub>	28.4	28.5
<i>i</i> -C <sub>4</sub> H <sub>3</sub>	27.4	27.9
<i>E-n</i> -C <sub>4</sub> H <sub>5</sub>	43.0	43.2
<i>i</i> -C <sub>4</sub> H <sub>5</sub>	42.4	42.5

<sup>a</sup> Harmonic B3LYP/cc-pVTZ frequencies scaled by 0.9650. <sup>b</sup> Harmonic QCISD/6-31(d) frequencies scaled by 0.9537.

**TABLE 5: Enthalpies of Formation at 0 K ( $\Delta_f H_0$  in kcal/mol)**

molecule	ROCCSD(T) <sup>a</sup>	QCISD(T) <sup>b</sup>	DMC <sup>c</sup>	DMC <sup>d</sup>
<i>E-n</i> -C <sub>4</sub> H <sub>3</sub>	130.8	131.1	126.6(0.6)	135.0(0.3)
<i>i</i> -C <sub>4</sub> H <sub>3</sub>	119.0	119.1	119.8(0.6)	122.9(0.3)
<i>E-n</i> -C <sub>4</sub> H <sub>5</sub>	89.1	89.0	84.0(0.6)	92.9(0.4)
<i>i</i> -C <sub>4</sub> H <sub>5</sub>	78.4	78.7	76.6(0.6)	82.8(0.4)

<sup>a</sup> Values from ref 4. <sup>b</sup> Values from ref 23. <sup>c</sup> Values deduced from ref 2. <sup>d</sup> Present work using scaled QCISD/6-31(d) zero-point vibrational energies.

**TABLE 6: Enthalpies of Formation at 298 K ( $\Delta_f H_{298}$  in kcal/mol)**

molecule	BAC-MP4 <sup>a</sup>	QCISD(T) <sup>b</sup>	MRCI <sup>b</sup>	DMC <sup>c</sup>	DMC <sup>d</sup>
<i>E-n</i> -C <sub>4</sub> H <sub>3</sub>	129.9(8.6)	130.8	131.9	126.0(0.6)	134.3(0.3)
<i>i</i> -C <sub>4</sub> H <sub>3</sub>	111.3(15.9)	119.3	120.8	119.4(0.6)	122.5(0.3)
<i>E-n</i> -C <sub>4</sub> H <sub>5</sub>	86.1(9.1)			83.5(0.6)	90.3(0.4)
<i>i</i> -C <sub>4</sub> H <sub>5</sub>	74.1(7.3)			76.2(0.6)	80.3(0.4)

<sup>a</sup> Values from ref 1. <sup>b</sup> Values from ref 5. <sup>c</sup> Values from ref 2. <sup>d</sup> Present work using scaled QCISD/6-31(d) zero-point vibrational energies.

where  $\beta_i$  is the stoichiometric coefficient of atom  $i$  and method corresponds to either DMC or another *ab initio* level of theory. For DMC, zero-point energies ( $E_{\text{ZPE}}^{\text{method}}$ ) were generated from QCISD/6-31(d) frequency calculations performed at the QCISD/6-31(d) minimum geometry. Scaled zero-point energies were used with the present DMC calculations and are given in Table 4. Subtracting the atomization energy of the isomer from the standard heats of formation of the atoms at 0K ( $\Delta_f H_{0,i}^o$  is the experimental enthalpy of formation at 0 K of atom  $i$ )<sup>21</sup> yields the enthalpy of formation at 0 K:

$$\Delta_f H_0 = \sum_i^N \beta_i \Delta_f H_{0,i}^o - E_A \quad (3)$$

Applying temperature corrections ( $\Delta H_{298}$ ), one obtains the enthalpy of formation at 298 K:

$$\Delta_f H_{298} = \Delta_f H_0 + \Delta H_{298} \quad (4)$$

The temperature correction contains the difference of the classical approximations for the rotational, translational, and vibrational energies evaluated at the two temperatures (0 and 298 K), and the experimental elemental corrections. Our computed  $\Delta_f H_0$  are presented in Table 5, and the  $\Delta_f H_{298}$  are given in Table 6.

#### 4. Results and Discussion

In this study we focus primarily on comparing isomerization energies that are the nonrelativistic Born–Oppenheimer energy differences (which do not contain the zero-point vibrational energies) between the *E* and *i* isomers ( $\Delta E_c$ ) for the C<sub>4</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>5</sub> systems. This is the most fundamental comparison one can readily make to the published CCSD(T) results<sup>4</sup> and does not introduce energy differences due to vibrational zero-point

**TABLE 7: Gaussian Basis Set used for C Atom<sup>a</sup>**

shell	exponent	coefficient	
S	819.2000	−0.0000620	
	409.6000	0.0001158	
	204.8000	−0.0002879	
	102.4000	−0.0000447	
	51.2000	−0.0006288	
	25.6000	−0.0027651	
	12.8000	0.0037249	
	6.4000	−0.0369135	
	3.2000	−0.1205673	
	1.6000	−0.0179754	
	0.8000	0.1736282	
	0.4000	0.4120941	
	0.2000	0.3651538	
	0.1000	0.1884090	
	P	819.2000	0.0000191
		409.6000	0.0000100
		204.8000	0.0000776
102.4000		0.0003556	
51.2000		0.0007104	
25.6000		0.0036337	
12.8000		0.0088456	
6.4000		0.0290517	
3.2000		0.0560032	
1.6000		0.1438918	
0.8000		0.2102160	
0.4000		0.3376644	
0.2000		0.2361849	
0.1000		0.2119805	
S		0.2718000000	1.00000000
P		0.2718000000	1.00000000
S		0.1213000000	1.00000000
P	0.1213000000	1.00000000	
D	0.8582000000	1.00000000	

<sup>a</sup> See ref 24.

**TABLE 8: Gaussian Basis Set used for H Atom<sup>a</sup>**

shell	exponent	coefficient
S	25600.00	0.0000036
	12800.00	−0.0000081
	6400.000	0.0000199
	3200.000	−0.0000207
	1600.000	0.0000571
	800.0000	−0.0000314
	400.0000	0.0002032
	200.0000	−0.0000061
	100.0000	0.0008849
	50.0000	0.0004022
	25.0000	0.0042053
	12.0000	0.0043356
	6.0000	0.0211119
	3.0000	0.0253706
	1.5000	0.1010152
	0.7000	0.1493879
	0.3500	0.3339335
	0.1600	0.3131527
	0.0800	0.1892405
	S	0.325840
S	0.102741	1.0000000
P	0.757000	1.0000000

<sup>a</sup> See ref 24.

energies. As seen from Table 4, the choice of *ab initio* method used to compute the frequencies changes the enthalpies of formation by at least a few tenths of kcal/mol and can potentially obscure the underlying DMC energy differences between the isomers. From Table 3 we see that our DMC isomerization energies of  $10.5 \pm 0.5$  kcal/mol for C<sub>4</sub>H<sub>3</sub> and  $9.7 \pm 0.6$  kcal/mol for C<sub>4</sub>H<sub>5</sub>, are in good agreement with the complete basis set limit ROCCSD(T) calculations of Wheeler *et al.* (11.1 and 9.9 kcal/mol, respectively) and in poor agreement with isomer-



ization energies deduced from the KMLF study ( $6.2 \pm 1.2$  kcal/mol for  $C_4H_3$  and  $6.7 \pm 1.2$  kcal/mol for  $C_4H_5$ ). Furthermore, VMC energies of the trial wave functions used in the present DMC study were found to be  $9.6 \pm 0.4$  kcal/mol for  $C_4H_3$  and  $10.8 \pm 0.6$  kcal/mol for  $C_4H_5$ , suggesting that the single determinantal wave functions used in this study should give isomerization energies that are in agreement with ROCCSD(T). The DMC isomerization energies do not change substantially with the smaller  $0.0025$  hartree $^{-1}$  time step, yielding a  $\Delta E_e$  of  $10.1 \pm 0.7$  kcal/mol for  $C_4H_3$  and  $9.5 \pm 0.5$  kcal/mol for  $C_4H_5$ , suggesting that time step error is not a likely source of the discrepancy of the present results with KMLF.

Table 5 presents enthalpies of formation at 0 K and Table 6 gives them at 298 K for the various approaches. These include those of Miller and Melius BAC-MP4,<sup>1</sup> Klippenstein and Miller QCISD(T) and MRCI,<sup>5</sup> KMLF DMC, along with present DMC values. Although the current DMC isomerization energies are consistent with ROCCSD(T) isomerization energies, the computed DMC  $\Delta_f H_0$  are consistently  $4.0 \pm 0.2$  kcal/mol larger than the former for all the isomers. This is a common occurrence because experience shows that a larger percentage of the correlation energy is often recovered for atoms (carbon here) than for molecules, leading to enthalpies of formation based on atomization energies that are frequently too large. This emphasizes the importance of comparing underlying energy differences rather than individual enthalpies of formation.

The reported DMC error bars do not take into account the fixed-node error that is expected to be an order of magnitude larger than the statistical error reported in the present calculations. The nodal accuracy of the KMLF trial wave functions was not fully characterized. The closest systematic DMC study is that of Grossman of the G1 set.<sup>22</sup> He found the mean absolute deviation of the DMC atomization energies from experiment to be 2.9 kcal/mol for single determinant (with SBK ECPs) trial wave functions. Because the present trial wave functions similarly consist of single determinants used with the SBK ECPs, we expect the accuracy of the present DMC studies to be comparable to that of the Grossman study. Therefore, with the conservative assumption that all errors are additive, DMC (single time step) estimates of  $\Delta_f H_0$  of the isomers are  $134.9 \pm 3.2$  kcal/mol (*E-n-C<sub>4</sub>H<sub>3</sub>*),  $122.8 \pm 3.2$  kcal/mol (*i-C<sub>4</sub>H<sub>3</sub>*),  $92.9 \pm 3.3$  kcal/mol (*E-n-C<sub>4</sub>H<sub>5</sub>*), and  $82.7 \pm 3.3$  kcal/mol (*i-C<sub>4</sub>H<sub>5</sub>*).

During the present study, it was found that the various isomers had different rates of initial decay to the ground state energy. Therefore, if one were not careful in fully equilibrating individual isomers, then isomerization energies were found to be smaller than those of the fully relaxed systems. It was also found that the trial wave functions did not yield reproducible DMC results unless walker populations of at least 6400 walkers were used. We note that it was typical practice around the time of the KMLF study to run DMC calculations with substantially smaller walker populations than is present practice. In light of the present findings, we believe that small walker populations are the basis of the discrepancies between the present DMC results and those of KMLF.

## 5. Conclusions

New DMC calculations of  $C_4H_3$  and  $C_4H_5$  have yielded isomerization energies in good agreement with recent ROCCSD(T) and MRCI calculations and refute previous DMC calculations with a similar trial wave function.

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