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Publication Date

2008-06-03

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Isomer energy differences for the C_4H_3 and C_4H_5 isomers using diffusion Monte Carlo

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Abstract

A new diffusion Monte Carlo study is performed on the isomers of C_4H_3 and C_4H_5 emulating the methodology of a previous study [Int. J. Chem. Kinetics 33, 808 (2001)]. 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_4H_3 were found to be 10.5 ± 0.5 kcal/mol and for C_4H_5, 9.7 ± 0.6 kcal/mol. These results are in reasonable accord with recent MRCI and CCSD(T) findings.

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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_4H_3 and n-C_4H_5 was dismissed as unlikely by Miller and Melius based on BAC-MP4 calculations of the energy differences between the *normal* and *iso* isomers [1]. Significantly smaller *normal* and *iso* isomer energy differences for C_4H_3 and C_4H_5 were calculated using diffusion Monte Carlo (DMC) in a study by Krokidis, Moriarty, Lester, and Frenklach, hereafter KMLF [2], and led Frenklach [3] 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.* [4] and MRCI calculations by Klippenstein and Miller [5]. 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 extend needed for the present purpose. It is followed in Sec. 3 by computational details, and in Sec. 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, 7, 8, 9, 10, 11, 12]) and therefore we make comments about the method as 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 the error bar). The simulation bias of using a finite time step can be reduced by extrapolating several DMC time step run 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 [13] 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)] geometries. For all the isomers except I-C_4H_3, the differences between B3LYP and ROCCSD(T) bond angles were at most 1.5° and those for bond lengths were at most 0.015Å. These differences amount to 1.0% for both bond lengths and bond angles.

For I-C_4H_3, the maximal differences of the B3LYP/cc-pVTZ and ROCCSD(T) approaches were 24.0° and 0.032Å, but as Wheeler *et al.* noted, this molecule has a relatively flat potential energy surface about its CCC angle (labeled "A3"; see Fig. 1 for geometry definitions). We confirmed the insignificance of the effect of the geometry on the energy of the I-C_4H_3 by computing the DMC energy at both the published ROCCSD(T) and the B3LYP/cc-pVTZ arrangements and found the differences statistically insignificant (0.4 ± 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 [2], incorrectly designated MCSCF(3,3). This notation means that the highest-lying 9 electrons were distributed among the 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 Stevens-Basch-Krauss (SBK) effective core potential (ECP) [14] 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 the Appendix.

In the present study, we carried out MCSCF calculations using the GAMESS *ab initio* package [15]. 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) [16]. 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 VMC and DMC computations. The parameters of the SMBH correlation function were optimized by minimization of the absolute deviation functional [17, 18] of the local energy on a fixed sample of 12800 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.* [6] algorithm using single-electron moves, 128 processor runs with 100 walkers per processor and the small time step of $0.0050H^{-1}$ 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 $0.0025H^{-1}$. 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 [19] and 0.9537 for QCISD [20]. 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,

$$C_4H_x \rightarrow 4C + xH \tag{1}$$
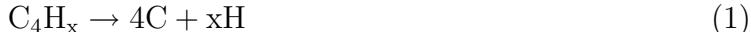
as

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

where β_i is the stoichiometric coefficient of atom i and method corresponds to either DMC or other *ab initio* level of theory. For DMC, zero-point energies (E_{ZPE}^{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 in 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 [21]) yields the enthalpy of formation at 0K;

$$\Delta_f H_0 = \sum_{i}^{N} \beta_i \Delta_f H_{0,i}^o - E_A \tag{3}$$

Applying temperature corrections (ΔH_{298K}), one obtains the enthalpy of formation at 298K,

$$\Delta_f H_{298} = \Delta_f H_0 + \Delta H_{298} \tag{4}$$

The temperature correction contains the difference of the classical approximations for the rotational, translational and vibrational energies evaluated at the two temperatures (0K and 298K), 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 which are the non-relativistic Born-Oppenheimer energy differences (which do not contain the zero- point vibrational energies) between the E and I isomers (ΔE_e) for the C_4H_3 and C_4H_5 systems. This is the most fundamental comparison one can readily make to the published CCSD(T) results [4], and does not introduce energy differences due to vibrational zero point energies. As seen from Table 4, the choice of ab initio method used to compute the frequencies changes enthalpies of formation by at least a few tenths 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 ± 0.5 kcal/mol for C_4H_3 and 9.7 ± 0.6 kcal/mol for C_4H_5, are in good agreement with the complete basis set limit ROCCSD(T) calculations of Wheeler *et al.* (11.1 kcal/mol and 9.9 kcal/mol, respectively) and in poor agreement with isomerization energies deduced from the KMLF study (6.2 ± 1.2 kcal/mol for $C_4H_3$and 6.7 ± 1.2 kcal/ mol for C_4H_5). Furthermore, VMC energies of the trial wave functions used in the present DMC study where found to be 9.6 ± 0.4 kcal/ mol for C_4H_3 and 10.8 ± 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 $0.0025H^{-1}$ time step yielding a ΔE_e of 10.1 ± 0.7 kcal/mol C_4H_3 and 9.5 ± 0.5 kcal/mol for C_4H_5, so 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 0K and Table 6 gives them at 298K for the

various approaches. These include those of Miller and Melius BAC-MP4 [1], Klippenstein and Miller QCISD(T) and MRCI [5], 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 ± 0.2 kcal/mol larger than the former for all the isomers. This is a common occurrence since experience shows that larger percentage of the correlation energy is often recovered for atoms (carbon here) than for molecules, and thus enthalpies of formation based on atomization energies are frequently too large. This emphasizes the importance of comparing underlying energy differences rather than individual enthalpies of formation.

The DMC error bars that are reported 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 [22]. 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 these 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 ± 3.2 kcal/mol (E-C_4H_3), 122.8 ± 3.2 kcal/mol (I-C_4H_3), 92.9 ± 3.3 kcal/ mol (E-C_4H_5), and 82.7 ± 3.3 kcal/mol (I-C_4H_5).

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 relaxing 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 MCSCF calculations and refute previous DMC calculations with a similar trial wave function.

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10

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Table 1: Geometries of the C_4H_3 isomers

	E-n-C_4H_3		I-C_4H_3	
	B3LYP/cc-pVTZ	ROCCSD(T)[a]	B3LYP/cc-pVTZ	ROCCSD(T)[a]
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 (°)				
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

[a] Geometry parameters taken from Ref. [4]

12

Table 2: Geometries of the C_4H_5 isomers

	E-n-C_4H_5		I-C_4H_5	
	B3LYP/cc-pVTZ	ROCCSD(T)[a]	B3LYP/cc-pVTZ	ROCCSD(T)[a]
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 (°)				
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			90.1	90.0

[a] Geometry parameters taken from Ref. [4]

Table 3: Isomerization Energies (ΔE_e in kcal/mol).

Molecule	VMC[a]	DMC[b]	ROCCSD(T)[c]	DMC[a]
C_4H_3	9.6(0.4)	6.2(1.2)	11.1	10.5(0.5)
C_4H_5	10.8(0.6)	6.7(1.2)	9.9	9.7(0.6)

[a]Present work using SBK ECP for C and MCSCF trial wave functions.

[b]Values deduced from Ref.[2].

[c]Values from Ref.[4].

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

Molecule	B3LYP/cc-pVTZ[a]	QCISD/6-31(d)[b]
E-n-C_4H_3	28.4	28.5
I-C_4H_3	27.4	27.9
E-n-C_4H_5	43.0	43.2
I-C_4H_5	42.4	42.5

[a]Harmonic B3LYP/cc-pVTZ frequencies scaled by 0.9650.

[b]Harmonic QCISD/6-31(d) frequencies scaled by 0.9537.

Table 5: Enthalpies of formation at 0K ($\Delta_f H_0$ in kcal/mol).

Molecule	ROCCSD(T)[a]	QCISD(T)[b]	DMC[c]	DMC[d]
E-n-C_4H_3	130.8	131.1	126.6(0.6)	135.0(0.3)
I-C_4H_3	119.0	119.1	119.8(0.6)	122.9(0.3)
E-n-C_4H_5	89.1	89.0	84.0(0.6)	92.9(0.4)
I-C_4H_5	78.4	78.7	76.6(0.6)	82.8(0.4)

[a]Values from Ref.[4].

[b]Values from Ref.[23].

[c]Values deduced from Ref.[2].

[d]Present work using scaled QCISD/6-31(d) zero-point vibrational energies.

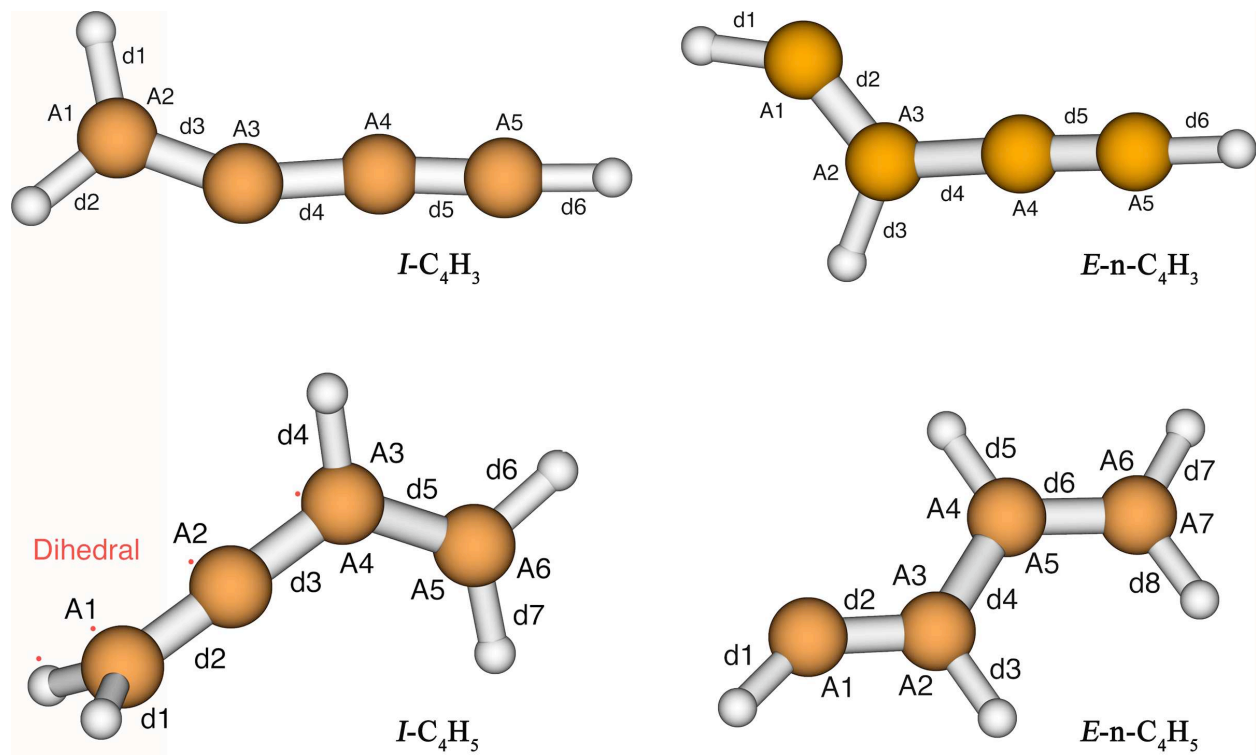Table 6: Enthalpies of formation at 298K ($\Delta_f H_{298}$ in kcal/mol).

Molecule	BAC-MP4[a]	QCISD(T)[b]	MRCI[b]	DMC[c]	DMC[d]
E-n-C_4H_3	129.9(8.6)	130.8	131.9	126.0(0.6)	134.3(0.3)
I-C_4H_3	111.3(15.9)	119.3	120.8	119.4(0.6)	122.5(0.3)
E-n-C_4H_5	86.1(9.1)	-	-	83.5(0.6)	90.3(0.4)
I-C_4H_5	74.1(7.3)	-	-	76.2(0.6)	80.3(0.4)

[a]Values from Ref.[1].

[b]Values from Ref.[5].

[c]Values from Ref.[2].

[d]Present work using scaled QCISD/6-31(d) zero-point vibrational energies.

Figure Captions

Figure 1 The numerical values for the different geometry parameters are located in Tables 1 and 2

[a] Bond angles (denoted A1-A7 and Dihedral angle) are in degrees.

[b] Bond lengths (denoted d1-d8) are in Angstroms.

APPENDIX

Table 1: Gaussian Basis Set used for C Atom[a].

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

[a]See Ref. [24].

Table 2: Gaussian Basis Set used for H Atom[a].

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	1.0000000
S	0.102741	1.0000000
P	0.757000	1.0000000

[a]See Ref. [24].