

# Energetics of carbon clusters $C_8$ and $C_{10}$ from all-electron quantum Monte Carlo calculations

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The energetics of carbon clusters  $C_8$  and  $C_{10}$  in several configurations have been determined in all-electron fixed-node quantum Monte Carlo calculations. The total electronic energies obtained are 0.4–1.2 hartrees lower than those of the lowest-energy analytic variational and coupled-cluster calculations, and they are only 0.2 to 0.4 hartrees above the experimentally based total energies. The recovery of correlation energy is 89%–94%. For  $C_8$ , relative values are found to be in agreement with earlier calculations: the cyclic  $C_{4h}^1A_g$  structure, the linear  $^3\Sigma_g^-$  (cumulenic), and the linear  $^1\Sigma_g^+$  (cumulenic) structures are found lowest in energy and within 10 kcal/mol of each other. For  $C_{10}$ , relative values are found to be in agreement with earlier calculations: the cyclic  $D_{5h}^1A_1'$  (distorted cumulenic) and  $D_{10h}^1A_{1g}$  (cumulenic) structures are found to be lowest in energy, within 5 kcal/mol of each other, 60 kcal/mol below the linear  $^3\Sigma_g^-$  (cumulenic) structure. An analysis of the scaling of computational effort with the number of electrons  $N_e$  for these quantum Monte Carlo calculations indicates a third-power dependence  $N_e^3$ . © 1999 American Institute of Physics. [S0021-9606(99)30122-7]

## I. INTRODUCTION

The ubiquitous carbon clusters—which seem to occupy much of interstellar space, various hot and cold spots of the earth, and a place in every nanoscale materials laboratory—provide an interesting and challenging testing ground for modern methods of quantum chemistry. Early semiempirical calculations favored linear structures for clusters smaller than about  $C_{10}$  and monocyclic rings for larger clusters up to about  $C_{20}$ . More recent calculations suggest that monocyclic rings are also favored for  $C_4$ ,  $C_6$ , and  $C_8$ . For  $C_{20}$  the ring, bowl, and cage structures are each favored by one or another of the available theoretical methods. For the smaller clusters both linear and cyclic forms have been detected and characterized spectroscopically.

The most recent comprehensive review of experiment and theory for small carbon clusters is that of Van Orden and Saykally.<sup>1</sup> Earlier reviews have been given by Weltner and Van Zee<sup>2</sup> and by Martin, Francois, and Gijbels.<sup>3</sup>

We report here all-electron fixed-node quantum Monte Carlo calculations for several structures of  $C_8$  and  $C_{10}$ . For each of these there exist several low-energy structures very close in energy, and it is clear that electron correlation plays an important role in determining their relative energies. Results of earlier high-level calculations of several types are available for comparison and one may hope for experimental determinations of relative energies within a few years.

The earliest calculations for  $C_8$  and  $C_{10}$  were carried

out by Pitzer and Clementi,<sup>4</sup> Hoffmann,<sup>5</sup> Slanina and Zahradnik,<sup>6</sup> Ewing and Pfeiffer,<sup>7</sup> Joyes and Leleyter,<sup>8</sup> and Bernholc and Phillips,<sup>9</sup> using either semiempirical methods or self-consistent field (SCF) calculations with small basis sets.

High-level *ab initio* calculations have been carried out more recently by Raghavachari and Binkley<sup>10</sup> using fourth-order Möller–Plesset (MP4) perturbation theory; by Liang and Schaefer<sup>11,12</sup> using configuration interaction with single and double excitations (CISD); by Parasuk and Almlöf<sup>13</sup> using several methods including coupled-cluster calculations with single and double excitations and an estimate of triple [CCSD(T)]; by Watts and Bartlett<sup>14</sup> using MP4 and CCSD(T); by Martin and Taylor<sup>15,16</sup> using CCSD(T); and by Grossman, Mitas, and Raghavachari<sup>17</sup> using fixed-node quantum Monte Carlo with pseudopotentials. A partial list of results of these calculations is given in Tables I–IV.

The likely stable structures for  $C_8$  and  $C_{10}$  include the singlet and triplet states of the linear and cyclic structures with either acetylenic ( $-C\equiv C-C\equiv C-$ ) or cumulenic ( $=C=C=C=C=$ ) bonding—a total of eight possibilities for each. However, as shown in Tables I–IV the lowest-energy structures given by the earlier high-level *ab initio* calculations are the linear cumulenic  $^3\Sigma_g^-$  and the cyclic acetylenic  $C_{4h}^1A_g$  structures for  $C_8$  and the cyclic cumulenic  $D_{10h}^1A_{1g}$ , the cyclic acetylenic  $D_{5h}^1A_1'$  and the cyclic cumulenic  $D_{5h}^1A_1'$  structures for  $C_{10}$ . These structures are shown in Figs. 1 and 2.

Since these geometries are located at or near fairly broad minima in the potential energy surfaces, the energies are in-

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TABLE I. Energies of  $C_8$  structures.

	Total energy (hartrees)			Relative energy (kcal/mol)	
	$^1\Sigma_g^+$ linear, cum	$^3\Sigma_g^-$ linear, cum	$^1A_g$ $C_{4h}$ , acet	$^3\Sigma_g^-$ linear, cum	$^1A_g$ $C_{4h}$ , acet
Raghavachari and Binkley (Ref. 10) (1987)					
HF/6-31G*		-302.529	-302.477	0.0	+33.0
MP4/6-31G*		-303.527	-303.549	0.0	-13.9
Liang and Schaefer (Ref. 11) (1990)					
CISD/DZP		-303.254			
CISD+Q/DZP		-303.398			
Parasuk and Almlöf (Ref. 13) (1992)					
MRCI/4s3p1d		-303.414	-303.403	0.0	+7.2
CISD/5s4p2d		-303.416	-303.436	0.0	-12.5
MCPF/5s4p2d		-303.694	-303.710	0.0	-10.0
+ correction				0.0	0.0
Martin and Taylor (Refs. 15 and 16) (1995,1996)					
CCSD(T)/cc-pVDZ		-303.552	-303.559	0.0	-4.1
+ correction				0.0	-15.3
CCSD(T)/cc-pVTZ		-303.811	-303.821	0.0	-6.1
+ correction				0.0	-10.1
This work					
VQMC/SCF+Jastrow	-303.45	-303.27	-303.56	0.0	-119
+/-	(0.02)	(0.02)	(0.02)		(17)
FN-QMC	-304.229	-304.242	-304.28	0.0	+8.8
+/-	(0.005)	(0.004)	(0.004)		(3.5)
Experiment (see the text)			-304.361		

sensitive to small variations in the nuclear positions. Thus, for example, energies calculated by the same method for geometries optimized by different methods differ typically by only a few microhartrees.

## II. COMPUTATIONAL DETAILS

We carried out fixed-node all-electron quantum Monte Carlo (FN-QMC) calculations for  $C_8$  and  $C_{10}$  using proce-

TABLE II. Total energies of  $C_{10}$  structures.

	Total energy (hartrees)				
	$^3\Sigma_g^-$ linear, cum	$^3\Sigma_u^+$ linear, acet	$^1A_{1g}$ $D_{10h}$ , cum	$^1A'_1$ $D_{5h}$ , acet	$^1A'_1$ $D_{5h}$ , cum
Raghavachari and Binkley (Ref. 10) (1987)					
HF/6-31G*					-378.236
MP4/6-31G*					-379.598
Liang and Schaefer (Ref. 12) (1990)					
CISD/DZP	-379.074	-379.074	-379.150	-379.151	-379.179
CISD+Q/DZP	-379.264	-379.256	-379.351	-379.348	-379.371
Parasuk and Almlöf (Ref. 13) (1992)					
CISD+Q/4s3p1d	-379.498		-379.587	-379.586	-379.602
MCPF/4s3p1d	-379.605		-379.694	-379.698	-379.702
CCSD(T)			-379.777	-379.777	-379.779
Watts and Bartlett (Ref. 14) (1992)					
MBPT(2)/4s3p1d			-379.662	-379.645	-379.593
CCSD+T(CCSD)/4s3p1d			-379.698	-379.694	-379.701
Martin and Taylor (Refs. 15 and 16) (1995,1996)					
CCSD(T)/cc-pVDZ					-379.594
CCSD(T)/cc-pVTZ					-379.926
This work					
VQMC/SCF+Jastrow	-379.472		-379.372		-379.495
+/-	(0.020)		(0.018)		(0.019)
FN-QMC	-380.313		-380.413		-380.406
+/-	(0.008)		(0.006)		(0.006)
Experiment (see the text)					-380.603

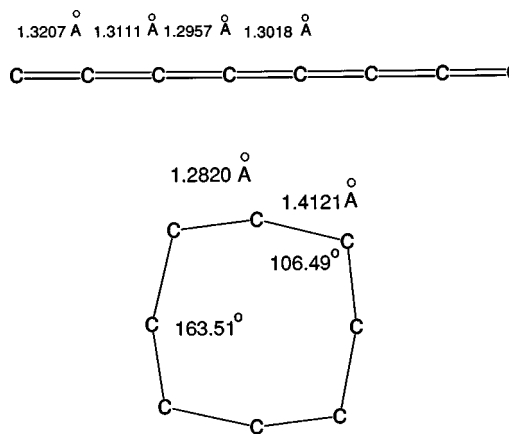
TABLE III. Energies of  $C_{10}$  structures relative to  $D_{10h}$ .

	Relative energy (kcal/mol)		
	${}^1A_{1g}$ $D_{10h}$ , cum	${}^1A'_1$ $D_{5h}$ , acet	${}^1A'_1$ $D_{5h}$ , cum
Liang and Schaefer (Ref. 12) (1990)			
CISD/DZP	0.0	-0.7	-18.5
CISD+Q/DZP	0.0	+1.8	-12.9
Parasuk and Almlöf (Ref. 13) (1992)			
CISD+Q/4s3p1d	0.0	+0.7	-9.7
MCPF/4s3p1d	0.0	-2.4	-5.2
CCSD(T)	0.0	-0.5	-1.2
Watts and Bartlett (Ref. 14) (1992)			
MBPT(2)/4s3p1d	0.0	+10.3	+43.0
CCSD+T(CCSD)/4s3p1d	0.0	+2.2	-2.2
Martin and Taylor (Refs. 15 and 16) (1995,1996)			
CCSD(T)/cc-pVDZ	0.0		-2.9
CCSD(T)/cc-pVTZ	0.0		-1.0
Grossman <i>et al.</i> (Ref. 17) (1996)			
FN-QMC/pseudopotential	0.0		-6.9
+/-			(2.3)
This work			
FN-QMC	0.0		+4.4
+/-			(5.3)

dures described previously.<sup>18-20</sup> The algorithm was the same as that for earlier calculations<sup>21</sup> in our laboratory using importance sampling, with an added acceptance/rejection step.<sup>20</sup> The calculations were executed on parallel IBM SP2 machines located at the Pennsylvania State University.

The calculations were carried out for fixed nuclear geometries given by earlier high-level calculations with optimization. For linear and cyclic  $C_8$  and for cyclic  $C_{10}$ , the geometries were those from Martin and Taylor,<sup>15,16</sup> and the geometry for linear  $C_{10}$  was that from Parasuk and Almlöf.<sup>13</sup> These geometries are shown in Figs. 1 and 2. No additional optimizations were performed.

The trial wave functions for importance sampling were single-determinant SCF functions multiplied by ten-term Schmidt-Moskowitz<sup>22</sup> "Jastrow" functions to introduce an explicit electron correlation. The SCF functions were obtained in GAUSSIAN<sup>23</sup> and GAMESS<sup>24</sup> calculations with 10-31G\* basis sets. To satisfy the cusp condition at each nucleus and avoid large errors in local energies at the cusps,

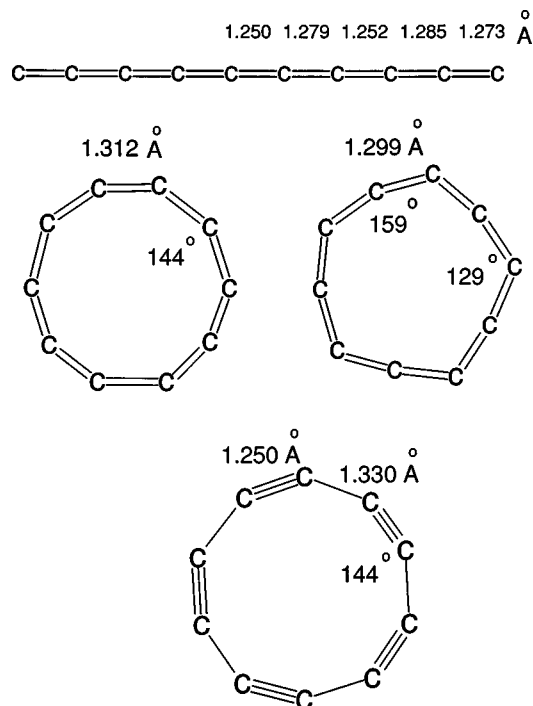
FIG. 1. Geometries of  $C_8$  used in the calculations.

we replaced each  $1s$  contracted Gaussian orbital with a corresponding Slater-type  $1s$  orbital. This takes advantage of the unique ability of QMC to use any form of wave function (since analytical integration is not required). The exponential coefficient  $\zeta = 5.75 \text{ bohr}^{-1}$  was determined in optimization to minimize the expectation value of the energy for a single carbon atom. For each of the molecules the GAUSSIAN or GAMESS calculation was run with the ten term GTO replacing the  $1s$  STO. The expectation value for the trial function is essentially the same with STO replacement. The coefficients of the Jastrow terms were optimized by minimizing the variance in local energies with the SCF determinant fixed. The standard deviation in individual local energies was about 3.0 hartrees for  $C_8$  structures and 3.5 hartrees for  $C_{10}$  structures.

Fixed-node QMC calculations are variational with respect to the locations of the nodal surfaces. For the calculations reported here, the nodes are those given by the single-determinant SCF function. The Jastrow function lowers the expectation value of the energy to a value (typically well below the Hartree-Fock limit), which may be determined in variational QMC calculations (VQMC) using Metropolis sampling. The VQMC energies so determined are listed in Tables I-II. The FN-QMC calculations give the energies corresponding to exact solutions of the Schrödinger equation for the nodal surfaces (i.e., boundary conditions) specified. These energies are expected to be higher than the true ener-

TABLE IV. Energies of  $C_{10}$  structures relative to linear.

	Relative energy (kcal/mol)				
	${}^3\Sigma_g^-$ linear, cum	${}^3\Sigma_u^+$ linear, acet	${}^1A_{1g}$ $D_{10h}$ , cum	${}^1A'_1$ $D_{5h}$ , acet	${}^1A'_1$ $D_{5h}$ , cum
Liang and Schaefer (Ref. 12) (1990)					
CISD/DZP	0.0	-0.3	-47.4	-48.2	-66.0
CISD+Q/DZP	0.0	+4.9	-54.2	-52.5	-67.2
Parasuk and Almlöf (Ref. 13) (1992)					
CISD+Q/4s3p1d	0.0		-55.6	-54.9	-65.3
MCPF/4s3p1d	0.0		-38.5	-58.4	-61.0
This work					
FN-QMC	0.0		-63.		-58.
+/-			(6.)		(6.)

FIG. 2. Geometries of  $C_{10}$  used in the calculations.

gies by 10–20 kcal/mol per carbon atom. In comparing the energies of similar systems most of the fixed-node error is expected to cancel, so that energy differences are expected to be more accurate than total energies.

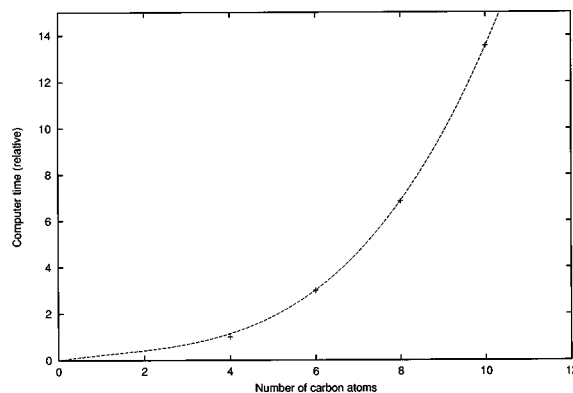
Calculations for each system were performed with several different time-step sizes and the results were extrapolated to a time step of zero. The statistical or sampling errors associated with the QMC calculations were estimated from results of repeated calculations. The FN-QMC energies reported in Tables I–IV include in parentheses the estimated statistical errors.

Additional calculations were performed for  $C_4$  and  $C_6$  clusters in order to investigate the scaling of the computational effort with the size of the system for these all-electron FN-QMC calculations. No attempt was made to obtain highly accurate results for  $C_4$  and  $C_6$ .

### III. RESULTS AND DISCUSSION

Results of the calculations for  $C_8$  and  $C_{10}$  are listed in Tables I–IV. For  $C_8$ , the energies given by FN-QMC are about 0.8 hartrees lower than the lowest analytic variational energies, and about 0.4 hartrees lower than recent coupled-cluster and Møller–Plesset energies. For  $C_{10}$ , the FN-QMC energies are about 1.2 hartrees lower than the lowest analytic variational energies and about 0.8 hartrees lower than recent coupled-cluster and Møller–Plesset energies.

Total energies for  $C_8$  and  $C_{10}$  may be estimated from their binding energies together with the energies of free carbon atoms. Martin and Taylor<sup>16</sup> have compiled recent estimates of these binding energies. Adjusted for zero-point energies, these are in the range of 1000–1040 kcal/mol for  $C_8$  and 1360–1400 kcal/mol for  $C_{10}$ . Combined with an electronic energy of  $-37.842$  hartrees for the C atom (experi-

FIG. 3. Scaling of QMC computational time with a system size. The dotted line varies as  $N^3$ .

mental less the relativistic correction),<sup>25,26</sup> these give total energies of  $-304.33$  to  $-304.39$  hartrees for  $C_8$  and  $-380.59$  to  $-380.65$  hartrees for  $C_{10}$ . The recovery of correlation energy by the FN-QMC calculations is found to be 89%–94%.

The three  $C_8$  structures—linear  ${}^3\Sigma_g^-$ , linear  ${}^1\Sigma_g^+$ , and cyclic  $C_{4h}{}^1A_g$ —were found nearly equal in energy in FN-QMC calculations. This is in agreement with the results of prior high-level calculations, which predict these energies within about 10 kcal/mol of each other. The FN-QMC calculations place the cyclic  ${}^1A_g$  about 9 kcal/mol higher than the linear  ${}^3\Sigma_g^-$ , with a statistical uncertainty of about 4 kcal/mol.

For  $C_{10}$ , the cyclic structures are predicted to be 55–65 kcal/mol lower in energy than the linear  ${}^3\Sigma_g^-$  structure. This is in good agreement with prior results. The cyclic  $D_{5h}{}^1A_1'$  (distorted cumulenic) is found very slightly higher than the cyclic  $D_{10h}{}^1A_{1g}$  (cumulenic) structure, i.e., 4.4 kcal/mol higher but with an uncertainty of about that amount. Most other calculations indicate the  $D_{5h}{}^1A_1'$  structure to be somewhat lower, i.e., typically 1–10 kcal/mol lower. These include the FN-QMC calculations by Grossman *et al.*<sup>17</sup> using pseudopotentials.

Overall, the results for all forms of  $C_8$  and  $C_{10}$  are in good agreement with the results of earlier high-level calculations. No surprises were found. Improving the accuracies in total energies by as much as 1.2 hartrees gave no indication of significant changes in relative energies for the various isomers investigated. We are left with an increased level of confidence in each of the higher-level methods.

The results of investigation of the scaling with system size are illustrated in Fig. 3 as a plot of the computation time versus the cluster size for a fixed number of FN-QMC time steps. The points fit well to a pure cubic curve showing  $N^3$  scaling, where  $N$  is the number of carbon atoms. This is to be expected, since most of the computational effort is spent in evaluating the determinants occurring in the trial wave function and its first and second derivatives and these evaluations scale with  $N^3$ . For analytic methods with large basis sets, the number of basis functions is roughly proportional to (the number of electrons and) the number of atoms. We note that  $N^3$  scaling is more favorable than the  $N^5$  scaling for MP2

calculations, the  $N^6$  scaling for CCSD calculations, and the  $N^7$  scaling for CCSD(T) calculations.<sup>27</sup>

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