Fixed-node diffusion Monte Carlo study of the structures of m-benzyne

W. A. Al-Saidi and C. J. Umrigar
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA.
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Diffusion Monte Carlo (DMC) calculations are performed on the monocyclic and bicyclic forms of m-benzyne, which are the equilibrium structures at the CCSD(T) and CCSD levels of coupled cluster theory. We employed multi-configuration self-consistent field trial wave functions which are constructed from a carefully selected 8-electrons-in-8-orbitals complete active space [CAS(8,8)], with CSF coefficients that are reoptimized in the presence of a Jastrow factor. The DMC calculations show that the monocyclic structure is lower in energy than the bicyclic structure by 1.9(2) kcal/mole, in excellent agreement with the best coupled cluster results.

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I. INTRODUCTION

Quantum chemistry methods used to study 1,3-Didehydrobenzene, commonly known as meta-benzyne or m-benzyne, do not agree upon its geometrical structure. The issue at question is, which of the structures shown in Fig. 1, the monocyclic (a) or the bicyclic (b), is lower in energy. These two structures differ mostly in the distance between the radical centers, C1 and C3; the single occupied orbitals on carbon atoms 1 and 3 form a bond in (b) which decreases the biradical nature of (a).

At the time of its synthesis [1], coupled cluster calculations with single and double excitations plus a perturbative treatment of triple excitations CCSD(T), with a small 6-31G(d,p) basis [2] were used in identifying the structure of m-benzyne. The computed infrared frequencies of the monocyclic structure, (a), were in good agreement with the experimental one, thus indicating that this structure is the stable one. Subsequent calculations using larger basis sets also supported this conclusion [2,4,5].

In an extensive recent study, Smith, Crawford, and Cremer [5] performed coupled cluster CCSD (single and double excitations), CCSD(T), and CCSDT (single, double and triple excitations) calculations on m-benzyne. The CCSD and CCSD(T) calculations were done with 6-31G(d,p) [2] and cc-pVTZ [6] basis sets with reference determinants from restricted Hartree-Fock (RHF), unrestricted Hartree-Fock (UHF) and Bruekner orbitals. They found that CCSD favors the bicyclic form (b) as the ground state with a C1C3 bond length ≈ 1.56 Å. On the other hand, CCSD(T) predicted (a) as the stable structure with a C1C3 bond length ≈ 2.10 Å. With the small 6-31G(d,p) basis set and with RHF orbitals, CCSDT also favored the structure (a). One of the conclusions of their study is that the inclusion of triple excitations (as in CCSD(T) or CCSDT) is essential to obtain a correct energy ordering of the structures of m-benzyne, and, inclusion of d- and f-type polarization functions in the basis is needed for a quantitatively correct energy difference.

The structural predictions of density functional theory (DFT) are inconclusive, depending strongly on the choice of the approximate exchange-correlation func-
two geometries of (a) and (b) with a cc-pVTZ basis set from Ref. [5]. The first geometry was optimized using CCSD(T) and the second one with CCSD. Bond distances are in angstroms and angles are in degrees.

|        | (a)       | (b)       |
|--------|-----------|-----------|
| $r_{13}$ | 2.026     | 1.551     |
| $r_{23}$ | 1.364     | 1.343     |
| $r_{34}$ | 1.372     | 1.376     |
| $r_{45}$ | 1.398     | 1.404     |
| $r_{2H}$ | 1.072     | 1.074     |
| $r_{4H}$ | 1.076     | 1.071     |
| $r_{5H}$ | 1.080     | 1.078     |
| $\theta_{123}$ | 95.9      | 70.5      |
| $\theta_{145}$ | 116.7     | 107.7     |
| $\theta_{456}$ | 113.4     | 111.7     |
| $\theta_{14H}$ | 120.7     | 126.3     |

the RHF theory which predicts that structure (b) is more stable than structure (a) by about 18 kcal/mole [5]. This shows the importance of a multi-determinant description of m-benzyne; and, in order to get reliable energy differences it is essential to have an accurate description of both static and dynamic correlations.

In this paper we use variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) to study this issue. These methods have the advantage that both static and dynamic correlation can be described accurately, provided that well optimized, multi-determinant trial wave functions are employed. Further, the results have only a weak dependence on the size of the basis. Currently, it is still expensive to optimize the geometry of large molecules using QMC methods mainly because of their stochastic nature. Thus, we limited our study to the two geometries of (a) and (b) which are respectively the equilibrium geometries for CCSD(T) and CCSD with a cc-pVTZ basis [5]. The geometrical parameters are reproduced in Table I for convenience.

### II. QMC METHODS

We employ two QMC methods, variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) which have been reviewed before [12, 13, 14]. In both methods the expectation values are obtained by a Monte Carlo integration and consequently there is great freedom in the choice of the trial wave function. VMC yields expectation values for the trial wave function, whereas in DMC the trial wave function serves as a starting point for a stochastic projection onto the ground state. Although DMC is exact for Bosonic ground states, for Fermionic systems the projection is performed while imposing the boundary condition that the nodes of the many-body wave function are the same as those of the trial states. Consequently, the DMC energy is also an upper bound to the true energy and the fixed-node error depends crucially on the quality of the trial wave function. In practice, we use an accelerated Metropolis algorithm with a very small auto-correlation time [15] and a DMC algorithm [16], that takes into account the singularities in the time-evolution operator and allows one to use large time steps while still having an acceptably small time-step error. All the QMC calculations are performed using the program package CHAMP [17].

The trial wave function is of the standard Jastrow-Slater form consisting of a Jastrow factor $J(R) = e^{J(R)}$ times a linear combination of determinants. Specifically,

$$
\Psi_T(R) = J(R) \sum_i c_i C_i(R)
$$

where $R = (r_1, r_2, \ldots, r_N)$ is a 3N-dimensional vector, $r_k$ is the position vector of the kth electron, $C_i(R)$ is the ith configuration state function (CSF), which is a symmetry-adapted linear combination of Slater determinants, and $c_i$ are the CSF linear expansion coefficients. The Jastrow part includes explicitly electron-nucleus, electron-electron, and electron-electron-nucleus correlation functions [18]. The statistical and the systematic errors in the VMC and DMC energies depend on the quality of the trial wave function. The Jastrow and CSF variational parameters are optimized using recently developed energy minimization methods [19, 20, 21].

To eliminate the core electrons, we employ the energy-consistent scalar-relativistic Hartree-Fock pseudopotentials of Burkatzki, Filippi and Dolg [22] and the accompanying basis sets. For the DMC calculations, we use the standard locality approximation which [23] introduces another small systematic error.

### III. CONVERGENCE TESTS

Before performing the final calculations, we studied the convergence of the energy with respect to a) the size of the basis, b) the cutoff used for selecting which CSFs are included in the expansion, and c) the Trotter time-step used to evolve the system. All of our DFT and MCSCF calculations are performed using GAMESS [24].

1. **Basis set convergence**

The VMC and DMC energies depend on the quality of the basis used to expand the orbitals in the determinants. One of the advantages of both QMC methods, particularly DMC, is that the dependence on the basis size is much weaker than for other quantum chemistry methods.

Figure 2 shows the QMC energies obtained, with the determinant part of the wave function chosen to be a B3LYP single determinant, for various basis sets. DZ denotes a double-zeta basis set, TZ a triple-zeta basis set without the $f$-functions of the carbon atoms, TZ is a
triple-zeta basis, and QZ$^*$ denotes a quadruple-zeta basis without the carbon $g$-functions. As expected, the VMC and DMC energies improve as the basis is improved. The DMC energies obtained from DZ and TZ bases differ by about 8 milli Hartree (mHa) and those obtained from TZ and QZ$^*$ bases by less than 2 mHa. The $\approx 4$ mHa difference in DMC energy between the TZ and QZ$^*$ basis sets shows that it helps to include the polarization $f$-functions.

The quantity of interest is the difference in the energies of the two structures and this converges faster than the individual total energies. The inset of Fig. 2 shows the energy difference $\Delta E = E_b - E_a$ is already converged within statistical errors even with the double-zeta basis. In the rest of our QMC calculations, we employ only double- and triple-zeta basis sets.

2. CSF convergence

As seen from Figure 2, when a B3LYP single-determinant is employed in the wave function, the energy of the (b) structure is lower than that of the (a) structure. However, since this is a system where static correlation is important, it is imperative to employ multi-determinant wave functions in QMC. In fact inclusion of additional determinants results in reversing the ordering of the energies. To this end, we employed truncated complete active space self consistent field (CASSCF) wave functions to construct the determinant part of our trial wave functions, which yield lower VMC and DMC energies than the single-determinant wave functions. The active space was carefully selected such that it contains the six $\pi$ electrons and the two unpaired electrons in structure (a) that form the C1C3 bridging bond in structure (b).

In order to reduce the number of determinants in the QMC calculations, we include only CSFs which have a coefficient larger in absolute magnitude than a cutoff parameter, $\eta$, in the MCSCF wave function. The CSF coefficients are then reoptimized within VMC in the presence of the Jastrow; typically, all the CSF coefficients (except the dominant one) get smaller in absolute magnitude upon reoptimization because of the presence of the Jastrow factor. Table III shows the QMC energies for several values of the cutoff $\eta$. With a cutoff of $\eta = 0.01$, the DMC total energies are converged to better than 1 mHa, and this is the value of $\eta$ we used in the rest of our calculations. Moreover, there is a good degree of cancellation of error between the energies of the two structures, so that the energy differences are converged, within statistical errors, even with larger values of $\eta$.

3. Time-step convergence

The imaginary-time evolution operator used in DMC is exact only in the limit of zero Trotter time step, $\delta \tau$. Consequently, energies evaluated at finite $\delta \tau$ have a time-step error which may be positive or negative. Table III shows the DMC energies for the two structures and their difference for various values of $\delta \tau$. The time-step errors of the energies of the two structures cancel out within statistical error upon taking the energy difference. Consequently, we employed a time step of $\delta \tau = 0.1$ Hartree$^{-1}$ in the rest of our calculations.

IV. RESULTS

Table IV shows the energy difference of the two structures $\Delta E = E_b - E_a$ obtained from the BLYP and B3LYP density functional methods and from MCSCF/CAS(8,8) theory. The density functional calculations are converged with respect to basis size; the difference between the triple- and quadruple-zeta basis sets being less than 0.1 kcal/mole. In the CAS(8,8) calculations, we used double- and triple-zeta basis sets. In agreement with previous papers, B3LYP favors structure (b), BLYP favors structure (a), and MCSCF greatly favors structure (a).

The energy differences $\Delta E$ at the B3LYP and BLYP levels of theory are in good agreement with the values of $-2.9$ and $3.0$ kcal/mole obtained using an all electron 6-311++G(3df,3pd) basis set [1]. Also, the CAS(8,8) energy difference with the triple-zeta basis is in very good agreement with the all-electron value, 12.9 kcal/mole, obtained using a 6-31+G(2df,2p) basis value at the same level of theory [4]. This is a testament to the good quality of the Burkatski et al. [22] pseudopotentials and basis sets employed in our calculations. The geometries we used from [1] are sufficiently close to those of Ref. [1] that they should not appreciably affect the energy differences.
TABLE II: The convergence of the QMC energies for structures (a) and (b) with respect to the threshold \( \eta \) used to select the CSFs included in the trial wave function. The determinant part of the wave function comes from the MCSCF/CAS(8,8) wave function with a double-zeta basis. Statistical errors on the last digit are shown in parentheses.

| \( \eta \) | \( E_a \) (Ha) | \( E_b \) (Ha) | \( \Delta E = E_b - E_a \) (kcal/mole) |
|----------|-----------|-----------|-----------------|
|         | VMC       | DMC       | VMC             | DMC            |
| 0.05     | -36.2832(5) | -36.3519(3) | -36.2757(5) | -36.3465(3) | 4.7(4) | 3.4(3) |
| 0.01     | -36.2855(5) | -36.3526(2) | -36.2801(5) | -36.3487(2) | 3.4(4) | 2.4(2) |
| 0.005    | -36.2869(5) | -36.3531(4) | -36.2798(3) | -36.3489(2) | 4.5(4) | 2.6(3) |

TABLE III: DMC energies for different Trotter time steps \( \delta \tau \), using a CAS trial wave function and a double-zeta basis. Total energies, \( E_a \), \( E_b \), of structures (a) and (b) are in Hartrees, and the energy difference, \( \Delta E = E_b - E_a \), is in kcal/mole. Statistical errors of the last digit are shown between parentheses. \( \Delta E \) has a negligible time-step error because the errors in \( E_a \) and \( E_b \) nearly cancel.

| \( \delta \tau \) | \( E_a \) (Ha) | \( E_b \) (Ha) | \( \Delta E \) (kcal/mole) |
|--------|-----------|-----------|-----------------|
| 0.2    | -36.3572(3) | -36.3533(4) | 2.4(3) |
| 0.1    | -36.3526(2) | -36.3487(2) | 2.4(2) |
| 0.07   | -36.3519(3) | -36.3483(3) | 2.3(3) |
| 0.05   | -36.3529(3) | -36.3487(3) | 2.6(3) |
| 0.01   | -36.3563(5) | -36.3528(6) | 2.2(5) |

TABLE IV: Energy differences, \( \Delta E = E_b - E_a \) (in kcal/mole) obtained from BLYP, B3LYP, MCSCF/CAS(8,8) methods, and, from VMC and DMC using wave functions constructed from the BLYP, B3LYP, MCSCF/CAS(8,8) methods. For MCSCF both double-zeta (DZ) and triple-zeta (TZ) bases are used. The geometries are the same as in Table 1. Statistical errors of the last digit are shown in parentheses.

|        | DFT/MCSCF | VMC         | DMC         |
|--------|-----------|-------------|-------------|
| B3LYP/TZ | -3.75     | -7.3(4)     | -3.4(2)     |
| B3LYP/TZ | 1.59      | -6.2(4)     | -3.5(2)     |
| MCSCF/CAS(8,8)/DZ | 14.72     | 3.3(4)     | 2.4(2)     |
| MCSCF/CAS(8,8)/TZ | 13.17     | 3.4(5)     | 1.9(2)     |

Table IV shows also the QMC energies obtained using DFT and CAS(8,8) determinants to construct the QMC wave functions. Note that the QMC energy differences obtained using the two single determinants in the trial wave functions agree within statistical error, despite the fact that B3LYP favors structure (b) and BLYP favors structure (a). It appears that it is necessary for this system to employ multi-determinant wave functions to obtain the correct energy ordering in QMC.

The best DMC result is obtained with the CAS(8,8) wave function; this wave function captures the static correlations that are important for this system and has a lower energy and lower root-mean-square fluctuations of the energy than the single determinant wave functions. We show in Table IV the values obtained with the double- and triple-zeta basis sets; there is no dependence on the basis size within statistical error. Our best estimate is that structure (a) has a lower energy than structure (b) by 1.9(2) kcal/mole. This result is in excellent agreement with the best existing quantum chemistry calculations, namely 1.0 kcal/mole from CCSD(T) using a 6-311++G(3df,3pd) basis [4] and \( \approx 1.6 \) kcal/mole from CCSD(T) using a cc-pVTZ basis [5]. The result is also in reasonable agreement with the 4.7 kcal/mole energy difference obtained using a CASSCF(8,8)/6-31+G(2df,2p) wave function followed by second order perturbation theory (CASPT2) [5].

In summary, our DMC results support the CCSD(T) and CCSDT conclusions [4, 5] that the cyclic structure (a) is the ground state of the system. We find that accurate fixed-node DMC energy differences for the structures of m-benzyne require multi-determinant wave functions; the fixed-node error in the energy difference with a single determinant from restricted B3LYP or BLYP calculations is \( \approx 5 \) kcal/mole. Our best DMC estimate, obtained with a reoptimized MCSCF/CAS(8,8) trial wave function, shows that the proposed monocyclic structure of m-benzyne is lower in energy than the bicyclic structure by 1.9(2) kcal/mole, in very good agreement with previous coupled cluster estimates.

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