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# A Fixed-Node Diffusion Monte Carlo Study of the 1,2,3-Tridehydrobenzene Triradical

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## Abstract

The electronic structure of 1,2,3-tridehydrobenzene was investigated using quantum Monte Carlo (QMC) methods. The radical contains two low-lying electronic states that are nearly degenerate adiabatically (within 2 kcal/mol separation), according to previous coupled cluster calculations. We performed Diffusion Monte Carlo (DMC) calculations starting from Multi-Reference Configuration Interaction (MR-CI) trial wavefunctions, with a complete active space (CAS) containing 9 electrons in 9 orbitals, CAS(9,9). Our converged DMC results are in close agreement with the best coupled-cluster results, and further strengthen the assignment of a  $^2A_1$  ground state.

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## I. INTRODUCTION

Triradicals pose a significant challenge for current electronic structure theories owing to the complicated interactions of three formally unpaired electrons.[1] This can lead to unusual bonding patterns between radical centers, including the preferential occupation of antibonding over non-bonding orbitals in the ground electronic state. The 1,2,3-tridehydrobenzene triradical is a fundamental step in the systematic decomposition of benzene.[2] It is derived from benzene by the removal of three adjacent hydrogen atoms (Fig. 1). Previous theoretical studies on all three triradicals (1,2,3-; 1,3,5-; and 1,2,4-tridehydrobenzene)[3] found the formation of partial bonds between radical centers, due to stabilizing interactions which ranged between 0.5 and 32 kcal/mol. All three isomers contain closed-shell doublet ground states. The largest doublet-quartet splitting occurs in 1,2,3-tridehydrobenzene, indicating strongest interaction between adjacent radical centers. Recently, Sander and coworkers reported the synthesis and partial infrared (IR) spectrum of 1,2,3-tridehydrobenzene isolated in 3 K Ne matrices.[4] Electronic structure calculations indicated the presence of two low-lying states, which are well separated vertically but nearly degenerate adiabatically.[4–6] The inclusion of triple excitations in coupled-cluster methods (CCSD(T) and EOM-SF-CCSD) was required to achieve a converged energy difference between the two states. This energy difference was estimated to be between 0.69 and 2.07 kcal/mol in favor of the  $^2A_1$  state, based on CCSD(T) and EOM-SF(2,3)-CCSD calculations.[5] Comparison of calculated frequencies (corrected for anharmonicity) with the experimental IR spectrum supported the assignment of the  $^2A_1$  ground state.

In this work, we present high-level Diffusion Monte Carlo (DMC) and Variational Monte Carlo (VMC) calculations[7] using trial wavefunctions computed at the Complete Active Space Self-Consistent Field (CASSCF) and Multi-Reference Configuration Interaction with Single and Double excitations (MR-CISD) levels. DMC has the advantage of treating both dynamical and non-dynamical correlation accurately, assuming proper multiconfigurational treatment of the trial wavefunction. With the recent introduction of a highly efficient algorithm for the evaluation of multi determinant wavefunctions in QMC[8, 9], it is now possible to routinely use well converged determinant expansions in QMC calculations, directly capturing static correlation effects at the VMC level. We find that DMC is able to correct large errors in the trial wavefunctions, which are introduced by the lack of dynamical cor-

relation and size-extensivity in CASSCF and MR-CISD, respectively. The converged DMC calculations are in very close agreement with the best coupled-cluster results.

## II. COMPUTATIONAL DETAILS

Minimum-energy geometries for the two doublet states were obtained using the B3LYP density functional[10] and cc-pVTZ basis set.[11] Previous calculations have shown that B3LYP and CCSD(T) optimized geometries yield almost identical CCSD(T) energy differences (within 0.11 kcal/mol).[5] At present, geometry optimizations of large systems using quantum MC methods is prohibitively expensive due to statistical nature of the energy and derivatives; therefore, the B3LYP/cc-pVTZ optimized geometries were used for all calculations in this work. The geometries are shown in Fig. 3; Cartesian coordinates are provided in the Supplementary Information.

CASSCF and MR-CISD calculations were performed with GAMESS[12], using a ROHF reference. The active space for CAS consisted of the three radical center molecular orbitals ( $10a_1$ ,  $7b_2$ ,  $11a_1$ , Fig. 2) and the six  $\pi$  orbitals; e.g., CAS(9,9). MR-CISD calculations were performed from the CASSCF(9,9) wavefunction, with all single and double excitations to the 30 lowest-energy orbitals outside the CAS. Energy-consistent scalar-relativistic Hartree Fock pseudopotentials[13], along with accompanying basis sets, were used in all CASSCF, MR-CISD, VMC and DMC calculations reported in this work.

QMC calculations were performed with the Quantum Monte Carlo Package (QMCPACK)[14]. The trial wavefunctions were of standard Slater-Jastrow form, containing the product of a Jastrow factor and a linear combination of configuration state functions (CSFs). The Jastrow factor contained electron-ion and electron-electron terms, expanded using a B-spline representation. The linear combination contained all CSFs with CI coefficient greater than a given threshold, these were obtained from either CASSCF or MR-CISD wavefunctions. We studied the convergence of the DMC energies with CI thresholds to verify convergence with respect to the number of CSFs, as discussed below. We optimize all variational parameters, including the linear CSF coefficients, using the linear method of Toulouse, *et al.*[15]. All DMC calculations were performed with Casula's T-moves[16] and a timestep of  $0.0025 (Ha)^{-1}$ .

Our criteria for convergence of QMC was made in three ways: 1) reduction of statistical

errors in energy differences; 2) convergence of energies with respect to increasing number of determinants in the wavefunction expansion; and 3) convergence of energies with respect to the size of the atomic basis (DZ, TZ, QZ). The reported DMC energies are converged to within 1 millihartree (0.62 kcal/mol) for all three criteria.

CCSD(T) calculations were performed using the NWChem[17] Tensor Contraction Engine (TCE). Global Arrays was built using ARMC1-MPI, which used the MVAPICH2 and CrayMPI implementations of MPI-3 for one-sided communication.[17] The calculations employed a ROHF reference and a cc-pVXZ basis, for X=2-5. Extrapolation to the Complete Basis Set (CBS) limit was performed with the pVTZ through pV5Z energies using a standard three-point formula.[18]

### III. RESULTS AND DISCUSSION

1,2,3-tridehydrobenzene can be derived from benzene by removing three adjacent hydrogen atoms, leading to three  $sp^2$  hybridized unpaired orbitals. The combination of these atomic orbitals forms three radical center molecular orbitals (MOs), as shown in Fig. 2. The (leading) electronic configuration for the low-lying  $^2A_1$  and  $^2B_2$  states is  $(10a_1)^2(11a_1)^1$  and  $(10a_1)^2(7b_2)^1$ , respectively (Fig. 2). Both states are closed-shell doublets with the fully bonding  $10a_1$  orbital doubly occupied.

The  $7b_2$  and  $11a_1$  orbitals are of nonbonding and antibonding character, respectively. Thus a reasonable candidate for the ground state is the  $^2B_2$  state. However,  $11a_1$  has bonding character between meta radical centers (C1-C3), and deformation of the ring framework can maximize this overlap (Fig. 3, left), whereas no such overlap is possible in  $7b_2$ . Although well separated vertically (about 4.8 and 1.4 eV at  $^2A_1$  and  $^2B_2$  geometry), the states are nearly degenerate adiabatically, due to interactions between the three radical centers. In the  $^2A_1$  state, this can be viewed as competing stabilizing and destabilizing interactions between meta and ortho radical centers.

The equilibrium B3LYP/cc-pVTZ geometries are shown in Fig. 3. Due to the bonding interaction between meta radical centers, the  $^2A_1$  equilibrium structure has short C1-C3 separation of 1.691 Å, compared to 2.342 Å in the  $^2B_2$  state. This bonding interaction in  $^2A_1$  is thus significantly stronger than in the diradical meta-benzyne, where the separation is approximately 2.05 Å.[19]

The calculated adiabatic energy differences between  ${}^2A_1$  and  ${}^2B_2$  are  $\Delta E = E({}^2A_1) - E({}^2B_2)$ . The calculations do not include a zero-point energy correction; this correction to the electronic energies has been estimated to be only about 0.2 kcal/mol.[5] Below, we present results on the convergence of the QMC calculations with respect to the number of configuration state functions (CSFs) and atomic basis sets. The molecular orbitals were not reoptimized within the VMC calculations.

### A. DMC and VMC Convergence with Respect to Number of CSFs

DMC and VMC energy differences were calculated using the MR-CISD wavefunctions and TZ basis, while varying the number of CSFs in the CI expansion. The number of CSFs was controlled by a cutoff for the maximum coefficient in the CI expansion included in the trial wavefunction. QMC calculations were performed with CI expansion thresholds of 1 (single-determinant trial wavefunction), 0.1, 0.01, and 0.001. The results are given in Tables I and II, and shown in Fig. 4.

The inclusion of multi-determinant wavefunctions, even with a small number of CSFs (around 10) was required to converge  $\Delta E$  to within a few kcal/mol. The single-determinant trial wavefunction for QMC (a single determinant using CASSCF-optimized orbitals) led to  $\Delta E$  that strongly overestimated the  ${}^2B_2$  energy, favoring  ${}^2A_1$  by 9.54 kcal/mol. With a CI cutoff of 0.1 (10 and 13 CSFs for  ${}^2A_1$  and  ${}^2B_2$ , respectively),  $\Delta E$  narrowed to -2.58 kcal/mol, due to a larger energy decrease for  ${}^2B_2$ . With a CI cutoff of 0.01 (306 and 485 CSFs for  ${}^2A_1$  and  ${}^2B_2$ ), the DMC  $\Delta E$  becomes -1.55 kcal/mol. By comparing with the two stricter cutoffs, the 0.01  $\Delta E$  is converged to well within 1 millihartree. For 0.005 cutoff (1293 and 1560 CSFs) and 0.001 cutoff (13315 and 17220 CSFs), the DMC  $\Delta E$  are effectively converged, at -1.52 and -1.79 kcal/mol, respectively. We found  $\Delta E$  to converge faster than total energies; between 0.005 and 0.001 CI cutoffs, these decreased by 0.92 and 0.63 kcal/mol for  ${}^2A_1$   ${}^2B_2$ . This same behavior has been noted for DMC calculations of meta-benzyne diradical.[20] The convergence of the  $\Delta E$  are shown in the insets of Fig. 4. Thus, converged CSF expansions are necessary to capture static correlation in the QMC calculations. The use of unoptimized orbitals would require many more CSFs to recover static correlation.

VMC  $\Delta E$  also shows a major improvement going from single- to multi-determinant trial

wavefunction, although the improvement with the addition of CSFs is slower than in DMC. Overall, VMC does predict  ${}^2A_1$  to be the ground state, although by about 0.75-1 kcal/mol less than DMC. Our best VMC result is still not fully consistent with the more accurate DMC result, an improved orbital set and a larger virtual space in the MR-CISD wavefunction is probably needed for fully converged VMC results.

Our best estimate for  $\Delta E$  (with 0.001 cutoff) is -1.79 kcal/mol for DMC. The use of a multideterminant wavefunction was found to be necessary in order to achieve converged energy differences in DMC. The  ${}^2B_2$  state appears to be more sensitive to multireference effects than  ${}^2A_1$ . However, a CSF cutoff of 0.01 is sufficient for converging  $\Delta E$  to within 1 millihartree.

### B. DMC and VMC Convergence with Respect to Basis Set

DMC and VMC calculations were also performed using CASSCF(9,9) trial wavefunctions with a CI determinant cutoff of 0.001, while varying the basis set size between DZ and QZ. Calculations using a QZ basis with MR-CISD trial wavefunctions were found to require excessively large CI expansions to be computationally feasible. The resulting energies and  $\Delta E$  are shown in Tables III and IV, and in Fig. 5.

In contrast with a strong dependence on CI expansion size, the DMC  $\Delta E$ s had a much lower dependence on basis set. For all three basis sets tested, the DMC  $\Delta E$  was already converged within 1 millihartree, equaling -1.31, -1.81, and -1.46 kcal/mol for DZ, TZ, and QZ respectively. Using QZ, the DMC  $\Delta E$  with a CASSCF trial wavefunction (-1.46 kcal/mol) is also in very close agreement with the MR-CISD/TZ result (-1.79 kcal/mol).

In contrast, VMC was found to show a much stronger basis set dependence. For the DZ basis, VMC predicts the wrong ground state, with  ${}^2B_2$  being lower by 1.64 kcal/mol. In VMC,  ${}^2A_1$  appears to be very sensitive to basis set. At the TZ and QZ levels, this problem is partially alleviated, with  ${}^2A_1$  predicted to be lower, but by over 1 kcal/mol less than the corresponding DMC results. In order to assess whether adding more determinants could improve the small-basis VMC, we performed a VMC calculation with an MR-CISD/DZ trial wavefunction. This gave  $\Delta E$  of -1.14 kcal/mol, which fixed the qualitatively wrong order predicted using CASSCF, and gave very close agreement with the MR-CISD/TZ VMC energy difference. This suggests that for VMC, the use of adequately multideterminen-

tal wavefunctions may be a more important factor than basis set, at least for energies of hydrocarbon triradicals.

### C. Wavefunction based methods

The results of single-point CCSD(T) calculations using cc-pVXZ (X=2-5) basis sets are shown in Table V. As discussed in Ref. ([5]), the leading coefficients in the CC expansions at the two equilibrium geometries are close to unity, enabling the use of the single-reference CCSD(T) method. The calculated CCSD(T)/CBS estimate is -1.52 kcal/mol. This is in very close agreement with the best DMC calculations, which obtain -1.46 kcal/mol using CASSCF/QZ, and -1.79 kcal/mol using MR-CISD/TZ wavefunctions.

Table V also shows the energies of the trial wavefunctions used for DMC and VMC calculations. Particularly, both CASSCF and MR-CISD reverse the ordering of the two states. CASSCF predicts a  $^2B_2$  ground state by 16.1 kcal/mol using TZ basis. MR-CISD partially improves this description, leading to an energy separation of 12.4 kcal/mol. This latter result indicates that size-extensivity plays an important role in describing the energy of hydrocarbon triradicals. Size-extensivity corrections (including Davidson correction and ACPF) lead to a nearly vanishing energy gap, as discussed in Ref. ([5]). Both DMC and VMC calculations thus overcome sizable deficiencies in their CASSCF and MR-CISD trial wavefunctions.

### D. Conclusions

High-level DMC and VMC calculations were employed to accurately characterize relative energies of the two low-lying electronic states of 1,2,3-tridehydrobenzene. Our best estimates for  $\Delta E$  are -1.46 and -1.79 kcal/mol, calculated with DMC using CASSCF/QZ and MR-CISD/TZ trial wavefunctions, respectively. These results are in excellent agreement with the CCSD(T)/CBS limit of -1.52 kcal/mol. They are also in excellent agreement with the EOM-SF(2,3)-CCSD/6-311G(2df) extrapolated value of -0.69 kcal/mol. Both wavefunction methods utilize triple excitations. CCSD(T) is highly accurate for systems with single-configurational wavefunctions, whereas EOM-SF-CCSD provides a balanced description of a general triradical wavefunction, including in limits of small and large energy separations

between frontier MOs. Our QMC calculations thus confirm the assignment of the  $^2A_1$  ground state by a very small energy gap. The close splitting between these two electronic states suggests that the character of the ground state can likely be manipulated in substituted trihydrobenzenes. Furthermore, DMC is likely to be a highly useful method for describing open-shell interactions in other hydrocarbon triradicals.

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- [1] A. I. Krylov, Triradicals, *J. Phys. Chem. A*, **109**, 10638–10645 (2005).
- [2] P. G. Wenthold, Toward the systematic decomposition of benzene, *Angew. Chem. Int. Ed.*, **44**, 7170–7172 (2005).
- [3] A. M. C. Cristian, Y. Shao, and A. I. Krylov, Bonding patterns in benzene triradicals from structural, spectroscopic, and thermochemical perspectives, *J. Phys. Chem. A*, **108**, 6581–6588 (2004).
- [4] S. Venkataramani, M. Winkler, and W. Sander, 1,2,3-Tridehydrobenzene, *Angew. Chem. Int. Ed.*, **44**, 6306–6311 (2005).
- [5] L. Koziol, M. Winkler, K. N. Houk, S. Venkataramani, W. Sander, and A. I. Krylov, The 1,2,3-tridehydrobenzene triradical: 2B or not 2B? the answer is 2A!, *J. Phys. Chem. A*, **111**, 5071–5080 (2007).
- [6] P. U. Manohar, L. Koziol, and A. I. Krylov, Effect of a heteroatom on bonding patterns and triradical stabilization energies of 2,4,6-tridehydropyridine versus 1,3,5-tridehydrobenzene, *J. Phys. Chem. A*, **113**, 2591–2599 (2009).
- [7] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Quantum Monte Carlo simulations of solids, *Rev. Mod. Phys.*, **73**, 33–83 (2001).
- [8] Bryan K. Clark, Miguel A. Morales, Jeremy B. McMinis, Jeongnim Kim, and Gustavo E. Scuseria, Computing the energy of a water molecule using multideterminants: a simple, efficient algorithm., *J. Chem. Phys.*, **135**(24), 244105 December 2011.
- [9] Miguel A. Morales, Jeremy McMinis, Bryan K. Clark, Jeongnim Kim, and Gustavo E. Scuseria, Multideterminant Wave Functions in Quantum Monte Carlo, *J. Chem. Theory Comput.*, **8**(7), 2181–2188 July 2012.
- [10] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **98**, 5648–5652 (1993).
- [11] R. A. Kendall, Jr. T. H. Dunning, and R. J. Harrison, Electron affinities of the first row atoms revisited. systematic basis sets and wave functions, *J. Chem. Phys.*, **96**, 6796–6806 (1992).
- [12] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery Jr., General atomic and molecular electronic structure system, *J. Comput. Chem.*,

- 14**, 1347–1363 (1993).
- [13] M. Burkatzki, C. Filippi, and M. Dolg, Energy-consistent pseudopotentials for quantum Monte carlo calculations, *J. Chem. Phys.*, **126**, 234105 (2007).
- [14] Jeongnim Kim, Kenneth P Esler, Jeremy McMinis, Miguel A Morales, Bryan K Clark, Luke Shulenburger, and David M Ceperley, Hybrid algorithms in quantum Monte Carlo, *Journal of Physics: Conference Series*, **402**(1), 012008 (2012).
- [15] J. Toulouse and C. J. Umrigar, Full optimization of JastrowSlater wave functions with application to the first-row atoms and homonuclear diatomic molecules, *J. Chem. Phys.*, **128**, 174101 (2008).
- [16] Michele Casula, Beyond the locality approximation in the standard diffusion Monte Carlo method, *Phys. Rev. B*, **74**, 161102(R) (2006).
- [17] J. Dinan, P. Balaji, J. R. Hammond, S. Krishnamoorthy, and V. Tipparaju, Supporting the global arrays PGAS model using MPI one-sided communication, In proceeding of: Proc. 26th Intl. Parallel and Distributed Processing Symp. (IPDPS), **DOI: <http://dx.doi.org/10.1109/IPDPS.2012.72>** (2012).
- [18] K. A. Peterson, D. E. Woon, and T. H. Dunning Jr., Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the H+H<sub>2</sub>H<sub>2</sub>+H reaction, *J. Chem. Phys.*, **100**, 7410–7415 (1994).
- [19] M. Winkler and W. Sander, The structure of meta-benzyne revisited: a close look into sigma-bond formation, *J. Phys. Chem. A*, **105**, 10422–10432 (2001).
- [20] W. A. Al-Saidi and C. J. Umrigar, Fixed-node diffusion Monte Carlo study of the structures of m-benzyne, *J. Chem. Phys.*, **128**, 154324 (2008).

TABLE I. Convergence of DMC energies with respect to the CI determinant threshold, using MRCI/TZ trial wavefunctions. Absolute energies for the two states are given in hartree; the energy difference  $\Delta E = E(^2A_1) - E(^2B_2)$  is given in kcal/mol. Statistical errors are shown in parentheses.

CI threshold	$^2A_1$	$^2B_2$	$\Delta E$
1(CASSCF)	-35.687299(0.00014)	-35.672098(0.00013)	-9.54(0.17)
0.1	-35.692322(0.00008)	-35.688215(0.00008)	-2.58(0.10)
0.01	-35.699333(0.00014)	-35.696865(0.00016)	-1.55(0.19)
0.005	-35.700330(0.00017)	-35.697900(0.00012)	-1.52(0.18)
0.001	-35.701800(0.00018)	-35.698951(0.00020)	-1.79(0.24)

TABLE II. Convergence of VMC energies with respect to the CI determinant threshold, using MRCI/TZ trial wavefunctions. Absolute energies for the two states are given in hartree; the energy difference  $\Delta E = E(^2A_1) - E(^2B_2)$  is given in kcal/mol. Statistical errors are shown in parentheses.

CI threshold	$^2A_1$	$^2B_2$	$\Delta E$
1(CASSCF)	-35.593571(0.00040)	-35.574297(0.00038)	-12.09(0.49)
0.1	-35.605056(0.00019)	-35.604258(0.00016)	-0.50(0.22)
0.01	-35.621506(0.00024)	-35.621478(0.00031)	-0.02(0.35)
0.005	-35.625741(0.00030)	-35.624679(0.00014)	-0.67(0.28)
0.001	-35.629068(0.00015)	-35.627400(0.00014)	-1.05(0.18)

TABLE III. Convergence of DMC energies with respect to basis set, using CASSCF trial wavefunctions and a 0.001 CI determinant threshold. Absolute energies for the two states are given in hartree; the energy difference  $\Delta E = E(^2A_1) - E(^2B_2)$  is given in kcal/mol. Statistical errors are shown in parentheses.

	Basis $^2A_1$	$^2B_2$	$\Delta E$
DZ	-35.684242(0.00011)	-35.682152(0.00011)	-1.31(0.13)
TZ	-35.698602(0.00012)	-35.695721(0.00014)	-1.81(0.16)
QZ	-35.700628(0.00007)	-35.698309(0.00008)	-1.46(0.09)

TABLE IV. Convergence of VMC energies with respect to basis set, using CASSCF trial wavefunctions and a 0.001 CI determinant threshold. Absolute energies for the two states are given in hartree; the energy difference  $\Delta E = E(^2A_1) - E(^2B_2)$  is given in kcal/mol. Statistical errors are shown in parentheses.

Basis	$^2A_1$	$^2B_2$	$\Delta E$
DZ	-35.589151(0.00016)	-35.591759(0.00018)	1.64(0.21)
TZ	-35.621161(0.00020)	-35.620638(0.00017)	-0.33(0.23)
QZ	-35.626671(0.00007)	-35.626218(0.00009)	-0.28(0.10)

TABLE V.  $\Delta E^{\text{ad}}$  calculated from electronic structure methods (kcal/mol).

	${}^2A_1$	${}^2B_2$	$\Delta E$
CCSD(T)/cc-pVDZ	-229.584230	-229.581631	-1.63
CCSD(T)/cc-pVTZ	-229.796724	-229.794128	-1.63
CCSD(T)/cc-pVQZ	-229.860297	-229.857800	-1.57
CCSD(T)/cc-pV5Z	-229.879545	-229.877100	-1.53
CCSD(T)/CBS extrap.	-229.890702	-229.888287	-1.52
CASSCF(9,9)/TZ	-34.779128	-34.804840	16.13
CASSCF(9,9)/QZ	-34.784944	-34.810396	15.97
MR-CISD/TZ	-34.814470	-34.834212	12.39
EOM-SF(2,3)/6-311G(2df), extrap.			-0.69

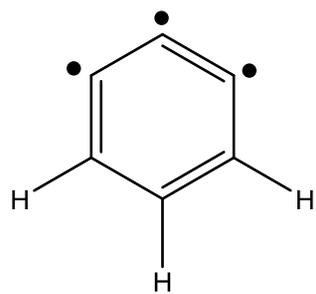


FIG. 1. 1,2,3-tridehydrobenzene.

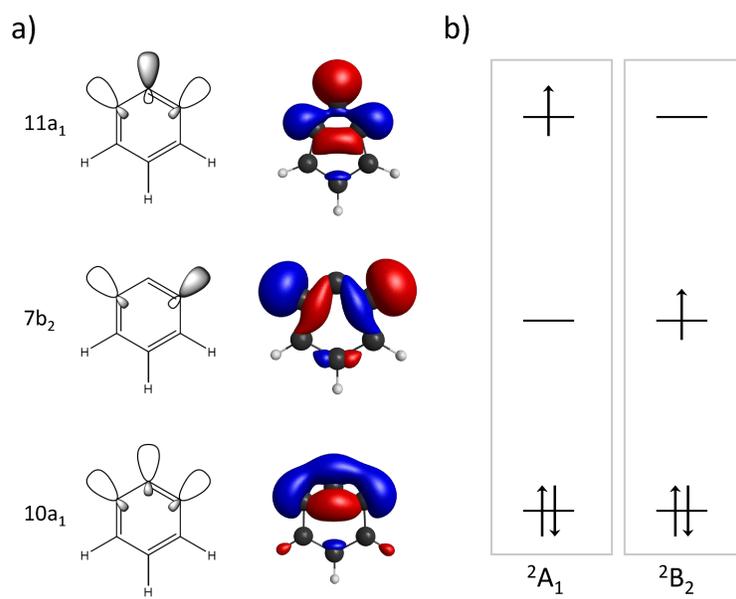


FIG. 2. a) Frontier molecular orbitals, and b) leading electronic configurations of the low-lying  ${}^2A_1$  and  ${}^2B_2$  states of 1,2,3-tridehydrobenzene.

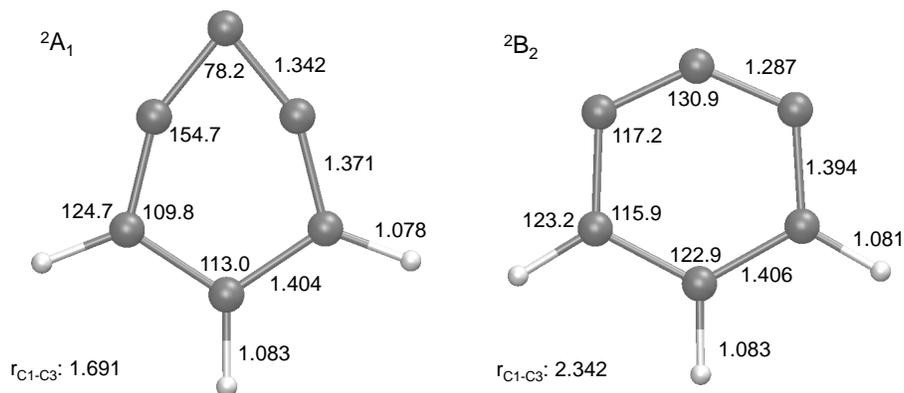


FIG. 3. Calculated equilibrium geometries for the  ${}^2A_1$  (left) and  ${}^2B_2$  (right) states, at B3LYP/cc-pVTZ level. Bond lengths are in Angstroms and angles are in degrees.

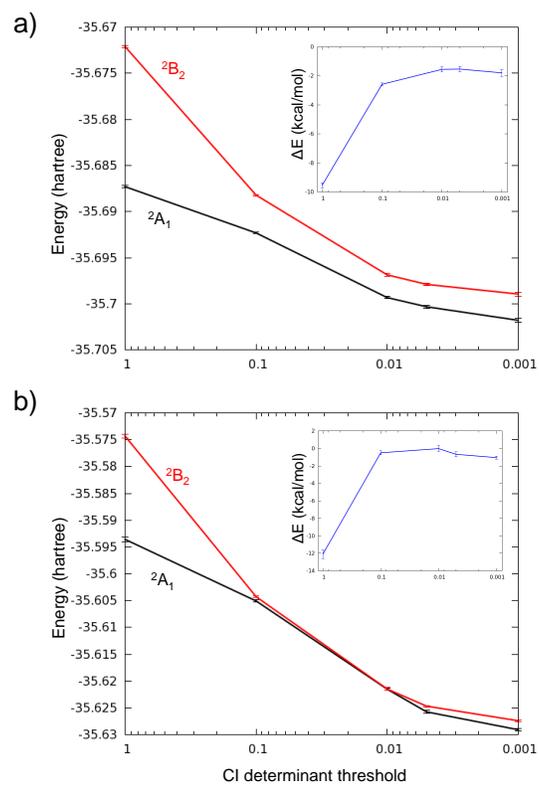


FIG. 4. DMC and VMC energies for different CI determinant cutoffs. The convergence of  $\Delta E$  is shown in the inset.

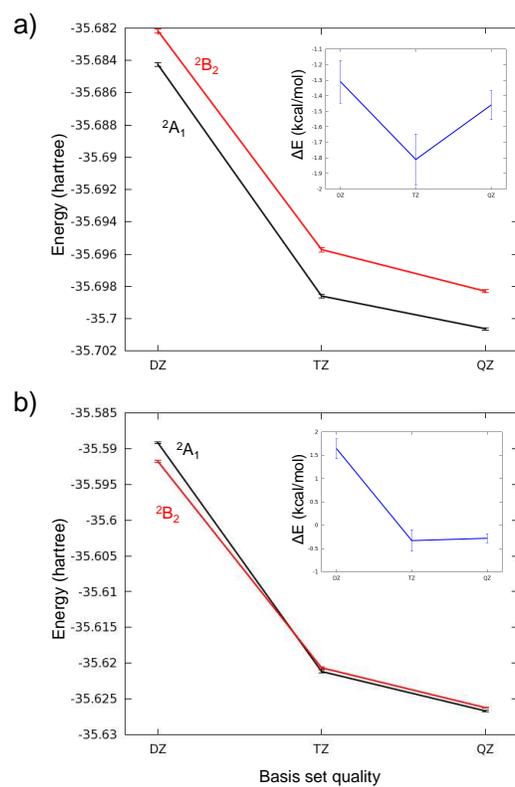


FIG. 5. DMC and VMC energies for different basis sets. The convergence of  $\Delta E$  is shown in the inset.