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# An Extended Multireference Study of the Electronic States of Para-benzyne

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An extended multireference study of the electronic states of *para*-benzyneEvan B. Wang,<sup>1</sup> Carol A. Parish,<sup>1,a)</sup> and Hans Lischka<sup>2,b)</sup><sup>1</sup>Department of Chemistry, Gottwald Center for the Sciences, University of Richmond, Richmond, Virginia 23173, USA<sup>2</sup>Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, Vienna A-1090, Austria

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A state-averaged, multireference complete active space (CAS) approach was used for the determination of the vertical excitation energies of valence and Rydberg states of *para*-benzyne. Orbitals were generated with a 10- and 32-state averaged multiconfigurational self-consistent field approach. Electron correlation was included using multireference configuration interaction with singles and doubles, including the Pople correction for size extensivity, multireference averaged quadratic coupled cluster (MR-AQCC), and MR-AQCC based on linear response theory. There is a very high density of electronic states in this diradical system—there are more than 17 states within 7 eV of the ground state including two 3s Rydberg states. All excitations, except 2 <sup>1</sup>A<sub>g</sub>, are from the  $\pi$  system to the  $\sigma\sigma^*$  system. Of the 32 states characterized, 15 were multiconfigurational, including the ground <sup>1</sup>A<sub>g</sub> state, providing further evidence for the necessity of a multireference approach for *p*-benzyne. The vertical singlet-triplet splitting was also characterized using a two-state averaged approach. A CAS(2,2) calculation was shown to be inadequate due to interaction with the  $\pi$  orbitals. © 2008 American Institute of Physics. [DOI: 10.1063/1.2955744]

## INTRODUCTION

1,4 didehydrobenzene, or *para*-benzyne, is a diradical intermediate formed by the Bergman cyclization<sup>1</sup> of (*Z*)-hexa-3-en-1,5-diyne (see Fig. 1). This reaction has been studied extensively using computational<sup>2–15</sup> and experimental methods,<sup>16–24</sup> in part due to the potential for antitumor activity of the diradical intermediates formed from the cyclization of natural product containing enediynes, such as dynemicin and calicheamicin.

Many of the publications which have examined this class of molecules focus theoretically on establishing both efficient and accurate methods to describe the energetics of Bergman reactions,<sup>5,6,9,25–38</sup> while others discuss the effects of substituents on the cyclization.<sup>2,24,28,39–50</sup> The most challenging aspect of a theoretical characterization of the Bergman cyclization, and other similar electrocyclizations, is the resulting diradical intermediate. Radicals and diradicals are difficult to characterize experimentally and equally challenging to electronic structure methods since they mostly possess multireference character.<sup>51–53</sup> For instance, the ground state of *p*-benzyne is a multiconfigurational singlet due to through-bond coupling<sup>54,55</sup> and spin polarization<sup>56</sup> of the radical electrons.

Early studies of the Bergman cyclization and resulting *p*-benzyne intermediate used restricted electron correlation<sup>5</sup> and active space multireference<sup>9,11</sup> methods but with limited success in reproducing the experimentally determined reaction barrier and endothermicity. Previous studies have also explored the use of the density functional theory with pure<sup>2,6</sup>

and hybrid<sup>46</sup> functionals. Around the years 2000–2001 evidence started to appear in the literature that unrestricted density functional theory (DFT) calculations were necessary for describing properly the energetics of the Bergman reaction. Prall *et al.* compared high level Brueckner orbital coupled cluster calculations using double zeta basis sets to unrestricted BLYP/6-31G\* results with good agreement to each other and to the experimental data.<sup>57</sup> Grafenstein *et al.* achieved similar results using unrestricted approaches and local spin density (LSD) and generalized gradient approximation (GGA) functionals.<sup>35</sup> The agreement between experimental and DFT results improved further when broken symmetry approaches, i.e., using a starting wave function in which the highest occupied and lowest occupied orbitals are mixed, were employed.<sup>38</sup> A number of reports have utilized the density functional theory to treat related diradical systems with qualitative success in spite of their multireference character.<sup>4,24,30–32,47–49,58–61</sup> However, unless there are experimental methods available against which to calibrate the results, it is difficult to know *a priori* whether or not the DFT method is capturing properly the physical nature of the systems. In addition, it has recently come to light that DFT often fails to properly characterize isomeric energies of large hydrocarbon systems.<sup>62–64</sup>

There have been numerous studies<sup>14,56,65–73</sup> of the *p*-benzyne singlet ground state (<sup>1</sup>A<sub>g</sub>), however, to our knowledge there have been very few reports of the characterization of the excited states other than the low lying triplet. Slipchenko and Krylov have characterized the ground state singlet and lowest triplet state and reported that there is a high density of states in the range 4–7 eV due to extensive orbital quasidegeneracy.<sup>73</sup> Li *et al.* employed complete active space with second order perturbation theory (CASPT2) to examine the singlet, triplet, and anionic states of *o*-, *m*-, and

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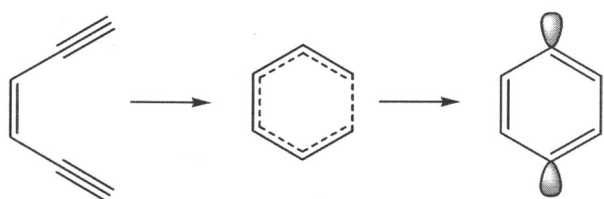


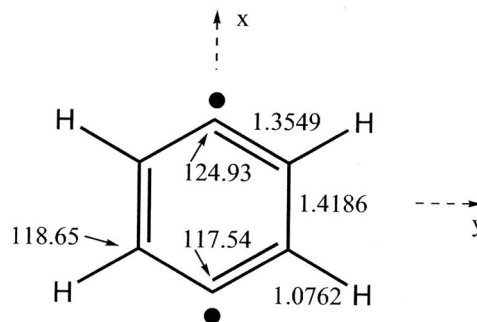
FIG. 1. Bergman cyclization of (Z)-hexa-3-en-1,5-diyne.

*p*-benzyne and the associated adiabatic excitation energies.<sup>74</sup> In their work, they were able to characterize the adiabatic excitation energies for eight low lying  $D_{2h}$  singlet states. Clark *et al.* have reported on a variety of singlet and triplet potential energy surfaces related to the overall Bergman cyclization, including a number of excited states of (Z)-hexa-3-en-1,5-diyne.<sup>44</sup>

State-averaged multiconfigurational self-consistent field (MCSCF) allows the simultaneous determination of multiple electronic states of importance to a particular molecular system. This is particularly useful for systems, such as *p*-benzyne, that possess orbitals that are nearly degenerate or display a high density of low energy electronic states. Orbitals from state-averaged MCSCF are particularly well suited for subsequent multireference configuration interaction with singles and doubles (MR-CISD) calculations on excited states.<sup>75</sup>

It is well known that truncated CI (such as MR-CISD) suffers from the size-extensivity problem.<sup>76</sup> Several methods have been developed in order to remedy this deficiency. A very popular and straightforward approach is the *a posteriori* Davidson correction,<sup>77,78</sup> which has been originally developed for the single reference case, but which has been extended to the multireference case as well.<sup>79,80</sup> Several variants of the Davidson correction have been developed<sup>81</sup> from which the Pople correction (labeled as MR-CISD+Q) will be used in this work.<sup>82</sup> A very good and practical method, which takes size extensivity into account from the very beginning, is given by the multireference averaged coupled pair functional<sup>83</sup> (MR-ACPF) and averaged quadratic coupled cluster<sup>84</sup> (AQCC) methods. The slightly different approximation used in MR-AQCC has been shown to solve the problem of overshooting in MR-ACPF.<sup>84</sup> A review on these and related methods has been published previously.<sup>85</sup> Most recently, MR-AQCC has been successfully applied to bond stretch isomerization in cyclobutadiene, benzo[1,2:4,5]dicyclobutadiene,<sup>51,86</sup> and propellanes.<sup>87</sup> The MR-AQCC method is state-specific and treats each electronic state individually. In order to obtain a balanced description of all electronic states of interest an AQCC version based on the linear response theory (LRT) has been developed (MR-AQCC-LRT),<sup>88</sup> which allows the simultaneous computation of a set of excited states within the AQCC formalism and is expected to give a better balanced energetic description in such cases than the standard, state-specific AQCC method.

In this work we present an application of the multireference methods (MR-AQCC, MR-AQCC-LRT, MR-CISD+Q, and MR-CISD) to the characterization of the *p*-benzyne

FIG. 2. Geometry of *p*-benzyne used for determining vertical excitations.

diradical ground state along with a series of low lying singlet states. As discussed above, we favor the MR-AQCC approach; however, for higher excited states these methods sometimes show convergence problems due to intruder states. These problems could not always be resolved. Fortunately, the standard MR-CISD and MR-CISD+Q orbital occupations and energies, respectively, agree very closely with AQCC results, when available. Therefore, we have made extensive use of these methods as well. A maximum of 26 valence states were computed as listed below with at least one state per irreducible representation, along with a series of relatively low lying  $3s$  Rydberg states. We identify Rydberg states and examine the singlet-triplet splitting.

## COMPUTATIONAL DETAILS

Vertical excitation energies were computed for *p*-benzyne using a  $D_{2h}$  optimized ground state geometry reported by Slipchenko and Krlyov<sup>73</sup> and computed using the spin flip method as implemented into density functional theory, along with the 6-311G\* basis set. [ $D_{2h}$  geometry:  $R_{C-C(H)}=1.3549$  Å,  $R_{C(H)-C(H)}=1.4186$  Å,  $R_{C-H}=1.0762$  Å,  $\angle C(H)-C-C(H)=124.93^\circ$ ,  $\angle C-C(H)-C(H)=117.54^\circ$ ,  $\angle H-C-C=\angle H-C-C(H)=118.65^\circ$ ; see also Fig. 2.] This geometry is in agreement with the structure more recently reported by the Krylov group at the EOM-SF-CCSD/6-31G\* level of theory.<sup>89</sup> The dehydrocarbon atoms are aligned with the  $x$ -axis and the molecular plane coincides with the  $xy$ -plane of the coordinate system.

Vertical excitations are uncorrected for zero-point vibrational energy differences and transition moments are not averaged over nuclear motion. Four different basis sets were employed, based on the Dunning all-electron correlation consistent basis sets:<sup>90,91</sup> cc-pVDZ, cc-pVTZ, (with the  $d$  orbitals on H removed for tractability), aug-cc-pVDZ, and d-aug-cc-pVDZ with the most diffuse  $p$ - and  $d$ -functions on C and the most diffuse  $p$ -function on H removed. The first three basis sets aim at an improved description of valence states, whereas the last one is dedicated to the computation of the lowest ( $3s$ ) Rydberg states.

## Computing valence states

The orbital space for the MCSCF calculations was divided into doubly occupied (DOCC) and complete active space (CAS) sections. The DOCC orbitals were constrained to be doubly occupied in all configuration state functions

(CSFs) and in the CAS all possible CSFs were constructed for a given state symmetry. Two sets of complete active spaces were used; CAS(2,2) contains as active orbitals the  $6a_g$  and  $5b_{3u}$  radical centers on the dehydrocarbons while CAS(8,8) includes these orbitals and adds the pi and pi\* orbitals of the aromatic ring ( $1b_{1u}$ ,  $2b_{1u}$ ,  $1b_{2g}$ ,  $2b_{2g}$ ,  $1b_{3g}$ , and  $1a_u$ ). A complete analysis of the molecular orbitals in *p*-benzynes has been published previously.<sup>56</sup>

A variety of state-averaging (SA)-MCSCF schemes were used. We began by averaging over ten singlet states:  $1-3\ ^1A_g$ ,  $^1B_{3u}$ ,  $^1B_{1u}$ ,  $^1B_{2g}$ ,  $^1B_{3g}$ ,  $^1B_{2u}$ ,  $^1A_u$ , and  $^1B_{1g}$ . The three  $^1A_g$  states were chosen in order to represent the two  $^1A_g$  states of the CAS(2,2) calculation plus an additional  $^1A_g$  state since it was found that at the MRCI level the latter was located energetically below the second one. From the other irreducible representations one state per symmetry was chosen.

To more fully characterize the singlet-triplet energy gap we also performed a two-state ( $1\ ^1A_g$  and  $1\ ^3B_{3u}$ ) averaged CASSCF (8,8) calculation. Finally, we performed CASSCF (2,2) calculations using state averaging over four states ( $1-2\ ^1A_g$ ,  $^1B_{3u}$ , and  $^3B_{3u}$ ) for comparison with previously published results for *p*-benzynes.

MR-CISD and MR-AQCC calculations<sup>92</sup> were performed using the orbitals from the state averaged MCSCF procedure described above. The CAS(2,2) and CAS(8,8) reference spaces were identical to the CASSCF spaces defined above. Size-extensivity corrections were computed by means of the Pople method (MR-CISD+Q).<sup>80,82,92,93</sup> Single and double substitutions of reference-occupied orbitals by virtual orbitals in all reference configurations created the total CSF expansion space for the MR-CISD, MR-CISD+Q, MR-AQCC, and MR-AQCC-LRT calculations. In the correlated calculations, electrons in the six core orbitals were kept frozen:  $1-2\ a_g$ ,  $1-2\ b_{3u}$ ,  $1b_{2u}$ , and  $1b_{1g}$ . The interacting space restriction<sup>94</sup> was always used.

## Computing Rydberg states

Following the experience with simultaneous calculation of valence and Rydberg states for formaldehyde,<sup>95,96</sup> the CAS(8,8) orbital space of the MCSCF calculations for the valence states was augmented by one auxiliary (AUX) orbital for the description of the  $3s$  ( $7a_g$ ) Rydberg orbital. Individual Rydberg configurations were constructed as single excitations from the valence orbitals into the  $3s$  AUX Rydberg orbital.

Our SA-MCSCF for the Rydberg calculations included 32 states, with four states per irreducible representation. The reference space for the MR-CISD calculations was identical to the CSF space of the MCSCF calculation. Otherwise procedures were performed as for the valence state calculations described above.

The calculations were carried out using the COLUMBUS program system<sup>97-99</sup> employing the atomic orbital integral package from DALTON.<sup>100</sup>

## RESULTS

### Characterizing the valence states of singlet *p*-benzynes

We have characterized ten valence-excited singlet states ( $1-3\ ^1A_g$ ,  $^1B_{3u}$ ,  $^1B_{1u}$ ,  $^1B_{2g}$ ,  $^1B_{3g}$ ,  $^1B_{2u}$ ,  $^1A_u$ , and  $^1B_{1g}$ ) and associated vertical excitations of *p*-benzynes using MCSCF state-averaging and MR-CISD, MR-CISD+Q, MR-AQCC, and MR-AQCC-LRT methods. In what follows we will refer to these calculations as SA(10)-MR-CISD, SA(10)-MR-AQCC, etc. The ten-state averaged MCSCF calculations were performed in order to provide adequate orbitals for the subsequent correlated calculations. We chose a ten-state averaging scheme as there are eight states possible under  $D_{2h}$  symmetry and preliminary results indicated that inclusion of two additional  $A_g$  states was necessary for convergence. Calculations with different state averaging schemes (3-SA and 5-SA, not reported here) and 32-SA (*vide infra*), some including the  $B_{3u}$  triplet state, indicate that there was little dependence of the results on the averaging scheme chosen. Vertical excitation energies, leading electron configurations (contributors greater than 10%) and oscillator strengths for all valence singlet states of *p*-benzynes using the ten-state averaging scheme and the cc-pVTZ basis set are given in Table I. Results using the cc-pVDZ and aug-cc-pVDZ basis sets can be found in the supplementary materials. Excitations are characterized by the symmetry of the excited state. At all levels of theory the ground state singlet of *p*-benzynes is two-configurational. At the CAS(8,8) cc-pVTZ SA-10 MR-CI level the leading configurations are 51%  $\sigma^0(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^2$  and 24%  $\sigma^2(\sigma^*)^0\pi_1^2\pi_2^2\pi_3^2$ . (in Table I,  $\sigma$  is the  $6a_g$  symmetric molecular orbital, and  $\sigma^*$  is the  $5b_{3u}$  antisymmetric molecular orbital.  $\pi_1$ ,  $\pi_2$ , and  $\pi_3$  are the pi bonding orbitals  $1b_{1u}$ ,  $1b_{2g}$ , and  $1b_{3g}$ , and  $\pi_4$ ,  $\pi_5$ , and  $\pi_6$  are the antibonding orbitals of symmetry  $2b_{1u}$ ,  $1a_u$ , and  $2b_{2g}$ , respectively.) It is no surprise that the CSF with a doubly occupied  $\sigma^*$  is the leading configuration—through bond coupling between diradical electrons via the intervening sigma bonds results in a highest occupied molecular orbital of  $b_{3u}$  symmetry.<sup>54-56</sup>

As shown in Table I and Fig. 3, including electron correlation (MCSCF→MRCI) and Pople corrections for size extensivity generally lowers the state energies in all cases except for the  $2\ ^1A_g$  and  $^1B_{2u}$  states. The Pople correction stabilizes the  $3\ ^1A_g$  and  $^1B_{3u}$  states most significantly, lowering the MRCI energy by 0.54 and 1.1 eV, respectively. At the AQCC level, there were two states that were not convergent due to an inadequate reference space,  $3\ ^1A_g$  and  $^1B_{3u}$ ; therefore, these states are missing in the AQCC results in Table I and Fig. 3. Generally, there is very good agreement between CISD+Q and AQCC so in cases where AQCC is not convergent the +Q results will be used. There is some state reordering with different methods, particularly the relative positioning of the  $2\ ^1A_g$ ,  $3\ ^1A_g$ , and  $^1B_{3u}$  energies in the overall manifold of states. For instance, the  $2\ ^1A_g$  state lies at 4.22 eV in the MCSCF results but then climbs higher in the manifold of states as the methods progress from MCSCF→MRCISD→AQCC but is then again stabilized to 4.54 eV with AQCC-LRT. However, in the AQCC-LRT results there is a significant stabilization of the  $^1B_{3u}$  and  $3\ ^1A_g$  states. This results in the  $2\ ^1A_g$  state as the seventh highest lying valence



TABLE I. SA(10)-MC-SCF, MR-CISD, MR-CISD+Q, MR-AQCC, and MR-AQCC/LRT vertical excitation energies (eV) from the  ${}^1A_g$  ground state using CAS(8,8) reference wave function and the cc-pvTZ basis set. MCSCF oscillator strengths are provided in parenthesis for transitions allowed by symmetry.

State	Dominant configuration in MRCI	MC-SCF <sup>a</sup> $E_{\text{exc}}$	MR-CISD <sup>a</sup> $E_{\text{exc}}$	MR-CISD+Q <sup>a</sup> $E_{\text{exc}}$	AQCC <sup>a</sup> $E_{\text{exc}}$	LRT <sup>a</sup> $E_{\text{exc}}$
$1\ {}^1A_g$	51% $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^2+$ 24% $\sigma^2\pi_1^2\pi_2^2\pi_3^2$					
${}^1B_{2g}$	68% $\sigma^1(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^2$	3.65	3.44	3.30	3.27	3.33
${}^1B_{3g}$	69% $\sigma^1(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^1$	3.99	3.69	3.45	3.42	3.52
${}^1B_{1u}$	58% $\sigma^2(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^2+15\%$ $\sigma^1(\sigma^*)^2\pi_1^1\pi_2^2\pi_3^2$	4.26 ( $1.685 \times 10^{-3}$ )	4.20	4.17	4.18	4.18
${}^1A_u$	67% $\sigma^2(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^1$	4.56	4.39	4.25	4.22	4.28
$2\ {}^1A_g$	72% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^1(\pi_5^*)^1$	4.22	4.46	4.60	4.63	4.54
$3\ {}^1A_g$	29% $\sigma^2\pi_1^2\pi_2^2\pi_3^2+$ 19% $\sigma^2(\sigma^*)^2\pi_1^2\pi_3^2+$ 12% $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^2+$ 11% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$	5.32	4.98	4.44	<sup>b</sup>	4.34
${}^1B_{3u}$	58% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^2+11\%$ $(\sigma^*)^2\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$	6.19 ( $1.119 \times 10^{-2}$ )	5.08	3.98	<sup>b</sup>	4.10
${}^1B_{2u}$	27% $(\sigma^*)^2\pi_1^2\pi_2^1\pi_3^2(\pi_5^*)^1$ 19% $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^1(\pi_4^*)^1+$ 12% $\sigma^2\pi_1^2\pi_2^1\pi_3^2(\pi_5^*)^1$	5.23 ( $1.504 \times 10^{-3}$ )	5.36	5.38	5.35	5.36
${}^1B_{1g}$	54% $\sigma^1(\sigma^*)^1\pi_1^2\pi_3^1\pi_3^2(\pi_5^*)^1+$ 20% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^1(\pi_4^*)^1$	6.35	6.14	5.96	5.94	6.01

<sup>a</sup>Total ground state energies (a.u.): -229.538 19 (MCSCF), -230.247 77 (MR-CISD), -230.401 55 (MR-CISD+Q), -230.393 85 (MR-AQCC), and -230.364 81 (MR-AQCC-LRT).

<sup>b</sup>Calculation not converged; reference space is not adequate.

state in the LRT manifold, as opposed to lying as the third, fifth, and fifth highest lying state with MCSCF, MRCISD, and AQCC, respectively. There is a particularly high density of states between 4.0 and 4.6 eV in the LRT results. This can be seen most clearly in Fig. 3. MRCISD+Q and AQCC stabilize all states relative to MRCI except for the  $2\ {}^1A_g$  state. In most cases AQCC-LRT energies are higher than AQCC energies. Overall, basis set effects were not significant. As expected, increasing basis set diffuseness lowers the energy of all states as does increasing from double-zeta to triple-zeta. When discussing the 10-SA results below, all energies cited are MRCI+Q/TZ energies unless otherwise noted.

In addition to identifying the two-configurational  ${}^1A_g$

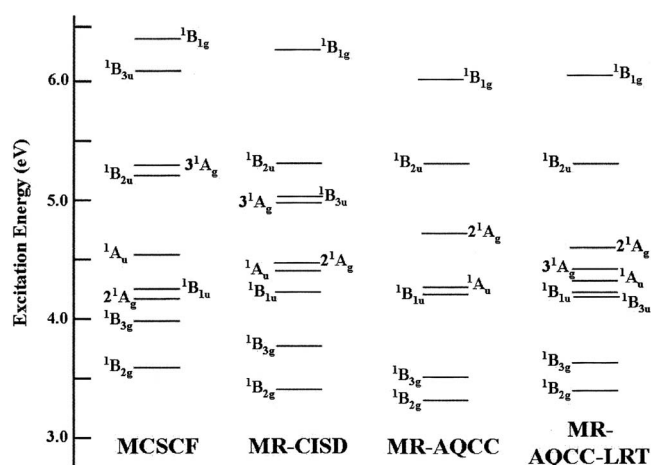


FIG. 3. A comparison of valence states for *p*-benzyne calculated using 10-SA, MCSCF, MR-CISD, AQCC, and AQCC-LRT. Results are not shown for MRCISD+Q as they are within 0.03 eV agreement of the AQCC results.

state as the ground state, all methods used herein predict a high density of valence states above the ground state; there are eight states within a 3.0–5.5 eV window of excitation energy from the ground state. This is in good agreement with the estimate given previously by Slipchenko and Krylov—using their spin-flip method they predicted more than seven states in a 4–7 eV energy window.<sup>101</sup> In our work, the two lowest excited states are the single-configurational  ${}^1B_{2g}$  and  ${}^1B_{3g}$  states at 3.30 and 3.45 eV, respectively, followed by a two-configurational  ${}^1B_{3u}$  state at 3.98 eV, a two-configurational  ${}^1B_{1u}$  state at 4.17 eV, and a single configurational  ${}^1A_u$  state at 4.25 eV. The lowest excited  ${}^1A_g$  state is four-configurational and occurs at 4.44 eV while the next excited  ${}^1A_g$  state is single-configurational and comes in at 4.60 eV. The remaining states ( ${}^1B_{2u}$  and  ${}^1B_{1g}$ ) are three- and two-configurational at 5.38 and 5.96 eV, respectively. Oscillator strengths were calculated using MC-SCF. The most prominent transition is predicted to occur at 3.98 eV, corresponding to the  ${}^1B_{3u}$  state. Visualization of the active orbitals confirms the similarity of the *p*-benzyne  $\pi$  orbitals to the  $\pi$  orbitals of benzene. However, in the case of *p*-benzyne, all excitations in the window from  $\sim 3.3$  to 4.4 eV, except for the  $2\ {}^1A_g$  and  ${}^1B_{3u}$  states, are from the  $\pi$  system to the  $\sigma\sigma^*$  system. Therefore, the spectrum cannot be seen in analogy to the  $\pi$ - $\pi^*$  transitions of the benzene electronic spectrum. Li *et al.* employed CASPT2 to examine the adiabatic excitation energies for eight low lying singlet states of *p*-benzyne. A direct energetic comparison with our results is not possible due to the geometry optimized nature of their excited states; however, the energetic orderings and electronic nature, i.e., dominant configurations, are similar. While it was not the

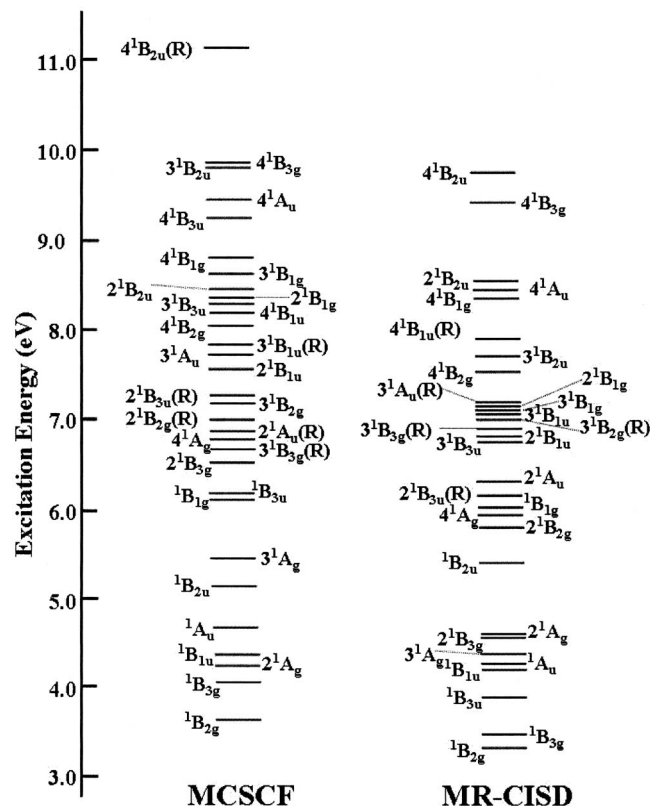


FIG. 4. A comparison of valence and Rydberg states for *p*-benzyne calculated using 32-SA, MCSCF, and MR-CISD.

major focus of their work, they also provided a CASPT2(12,12) vertical excitation of 3.11 eV for the lowest lying excited state singlet. Our result of 3.30 eV (MRCISD+Q) is in reasonable agreement with this.<sup>74</sup>

### Characterizing 3s Rydberg states of *para*-benzynes

We have performed a 32-state averaged CAS(8,8) MCSCF calculation to identify low lying 3s Rydberg states of *p*-benzyne. The states were selected for averaging by including four states for each of the eight irreducible representations under  $D_{2h}$  symmetry. The MCSCF results provided orbitals for the subsequent MR-CISD and MR-CISD+Q calculations. MR-AQCC was not included in the analysis of Rydberg states because of convergence problems with higher excited states. The states and computed transitions are displayed graphically in Figs. 4 and 5, respectively. A listing of excitation energies, dominant configurations, and  $\langle Z^2 \rangle$  quadrupole values for each state can be found in the supplementary materials.

The 32-SA results are comparable to the 10-SA results for the ten lowest lying valence states characterized in Table I and Fig. 3, i.e., states computed with different averaging schemes possess the same orbital character and very similar excitation energies. In addition, the 32-SA results provide information about higher lying states including the identification of six and five Rydberg states, at the MCSCF and MRCI levels, respectively. Rydberg states were characterized as those states having dominant configurations with either a sigma or a pi electron excited into the 3s orbital, for

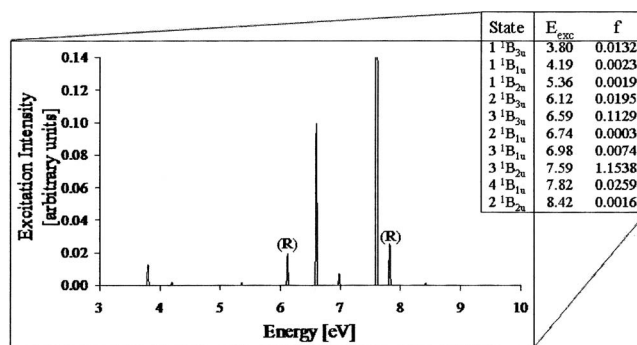


FIG. 5. Calculated spectrum for *p*-benzyne using oscillator strengths ( $f$ ) from MCSCF and excitation energies from the 32-SA CAS(8,8)+AUX MR-CISD+Q/d-aug-ccpVDZ level of theory. Transitions associated with Rydberg states are indicated with a boldface (R).

example, the lowest Rydberg state at the MRCISD+Q level was  $2^1B_{3u}$  at 6.12 eV with a configuration of 70%  $\sigma^1\pi_1^2\pi_2^2\pi_3^23s^1$ . Rydberg states were also identified by calculating the expectation values of the  $\langle Z^2 \rangle$  component (perpendicular to the  $xy$ -molecular plane) of the quadrupole tensor for each state. In all cases identified as Rydberg states by an examination of electron configurations, the corresponding  $\langle Z^2 \rangle$  value was almost twice as large as for non-Rydberg states.

As with the 10-SA results, the state ordering depended on the method employed (Fig. 4). Unlike the 10-SA results, the character of many of the higher lying states also changed with inclusion of electron correlation. For example, using MCSCF the fourth  $1^1A_g$  state, at 6.79 eV, exhibited the character 55%  $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$  whereas at the MRCI level the same state was 53%  $\sigma^2(\sigma^*)^2\pi_1^2\pi_3^2$ . All together, there are 12 states that change character:  $2^1B_{2g}$ ,  $4^1A_g$ ,  $2^1A_u$ ,  $3^1B_{2g}$ ,  $3^1B_{1u}$ ,  $2^1B_{1g}$ ,  $3^1A_u$ ,  $4^1B_{3u}$ ,  $4^1B_{1u}$ ,  $4^1B_{1g}$ , and  $4^1B_{2u}$ . Of these, nine states display Rydberg character at one or both of these levels of theory. For instance, six Rydberg states were identified at the MCSCF level:  $2^1B_{2g}$ ,  $2^1B_{3u}$ ,  $2^1A_u$ ,  $3^1B_{3g}$ ,  $3^1B_{1u}$ , and  $4^1B_{2u}$ . The lowest MCSCF Rydberg state  $3^1B_{3g}$  is two-configurational, appears at 6.72 eV, and has a dominant configuration of 56%  $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^13s^1+32\%\sigma^2\pi_1^2\pi_2^2\pi_3^13s^1$ . Five Rydberg states were identified at the MR-CI level:  $2^1B_{3u}$ ,  $3^1B_{3g}$ ,  $3^1B_{2g}$ ,  $3^1A_u$ , and  $4^1B_{1u}$ ; only two of these ( $2^1B_{3u}$ ,  $3^1B_{3g}$ ) were also Rydberg in character using MCSCF. This is mainly a state reordering effect. At the MRCI level the other MCSCF Rydberg states,  $2^1B_{2g}$ ,  $2^1A_u$ , and  $3^1B_{1u}$ , adopt non-Rydberg character while the state of corresponding symmetry one level higher ( $3^1B_{2g}$ ,  $3^1A_u$ , and  $4^1B_{1u}$ ) adopts the same Rydberg character as previously exhibited at the MCSCF level. The only Rydberg state found at the MCSCF level without a higher lying partner in the MRCI manifold of states is  $4^1B_{2u}$ . More information regarding the character and excitation energies for all 32 states may be found in the supplementary materials.

Oscillator strengths were calculated using MC-SCF. The most prominent transition is predicted to occur at 7.59 eV (MR-CISD+Q) corresponding to the  $3^1B_{2u}$  state. Of those

TABLE II. Vertical excitation energies for the singlet-triplet transition (eV) for *p*-benzynes using MC-SCF, MR-CISD, MR-CISD+Q, MR-AQCC, and MR-AQCC/LRT CAS(8,8) cc-pvDZ, aug-cc-pvDZ, and cc-pvTZ and averaging over two states ( $1^1A_g$  and  $3^3B_{3u}$ ).

Method	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ
MCSCF	0.1713	0.1713	0.1640
CISD	0.2274	0.2277	0.2138
CISD+Q	0.3031	0.3095	0.2901
AQCC	0.3496	0.3613	0.3482
AQCC-LRT	0.2990	0.3032	0.2870
Comparison with previous results			Ref.
EOM-SF-CCSD/6-31G*	0.22		89
REKS-B3LYP/6-31G(D)	0.21		72
CASSCF(8,8)/6-31G*	0.13		44
CASSCF(2,2)/6-31G*	0.04		44

states characterized as Rydberg using MRCI, only  $2^1B_{3u}$  and  $4^1B_{1u}$  have nonzero transition probabilities. The simulated spectrum is shown in Fig. 5.

It should be noted that in this work we have examined only 3s Rydberg states in order to determine where the series of Rydberg states begins. In view of the high density of states for *p*-benzynes, we abstained from including higher Rydberg states in our calculations.

### Characterizing the singlet-triplet gap in *para*-benzynes

In order to more fully characterize the singlet-triplet splitting in *p*-benzynes, and to compare with previous results, we have performed a two-state averaged CAS(8,8) MCSCF calculation, averaging over the ground  $1^1A_g$  state along with the low lying  $3^3B_{3u}$  state. The MCSCF results provided orbitals for the subsequent MR-CISD, MR-CISD+Q, MR-AQCC, and MR-AQCC-LRT calculations (Table II).

The adiabatic singlet-triplet splitting was measured by Wenthold *et al.* to be  $-3.8 \pm 0.5$  kcal/mol using negative-ion photoelectron spectroscopy. In that same report, an alternative value of  $-2.1 \pm 0.4$  kcal/mol was also presented.<sup>102</sup> There have been a number of theoretical calculations on the adiabatic singlet-triplet splitting and taken together these reveal a significant dependence on basis set and geometry employed.<sup>3,6,7,10,14,24,27,28,33,35,37,44,68-74,89,102-111</sup> There have been fewer reports on the vertical energy gap between the ground state singlet and the lowest triplet states.<sup>44,72,89</sup> Vertical singlet-triplet values calculated in this study using three

different basis sets (cc-pvDZ, aug-cc-pvDZ, and cc-pvTZ) are reported in Table II. Our CAS(8,8) two-state averaged MRCISD results are in good agreement with previously published equation-of-motion spin-flip CCSD results<sup>89</sup> as well as with spin-restricted ensemble-referenced Kohn-Sham (REKS) B3LYP values.<sup>72</sup> The MRCISD+Q values predict a splitting that is 0.08 eV larger than these results. Our MCSCF results are in better agreement with these higher, correlated calculations than previously published CASSCF(8,8)/6-31G\* results.<sup>44</sup> This could be due to the larger basis sets employed in this study or the benefits obtained from a state-average approach.

### Results obtained using the smaller CAS(2,2) active space

One of the simplest, and most common, approaches to describing diradicals is to use the two-electrons in two-orbital model<sup>112,113</sup> and this active space has been used previously for studying properties of *p*-benzynes.<sup>9,14,44,111</sup> For comparison purposes, we also performed a series of calculations using the CAS(2,2) minimum reference space. This leads to three possible orbital occupations of  $6a_g^2$ ,  $6a_g 5b_{3u}$ , and  $5b_{3u}^2$  and four resulting electronic states of  $1, 2^1A_g$ ,  $3^3B_{3u}$  and  $1^3B_{3u}$ . The first and the last occupations give rise to states  $1-2^1A_g$ . The second orbital occupation gives rise to singlet and triplet states of  $B_{3u}$  symmetry. We began by including these four states into the state-averaging scheme; however, interaction with the  $\pi$  orbitals (states derived from a larger active space) indicated that the (2,2) approach was not adequate. The inadequacy was apparent from the large change in energy between the MRCI and MRCI+Q values (see Table III). In particular, the  $2^1A_g$  and  $1^3B_{3u}$  states were not well represented. The results indicated that a configuration containing a  $1b_{2g} \rightarrow 2b_{2g}$  orbital excitation appeared in the CI wavefunction that was not included in the CAS(2,2) reference space. This one and other  $\pi$  orbital related configurations are included in the CAS(8,8) treatments described above. The details of all vertical excitation energy calculations are reported in the supplementary material.<sup>114</sup>

### SUMMARY

The ground and singlet excited states of *p*-benzynes have been determined using a variety of multireference methods MR-CISD, MR-CISD+Q, MR-AQCC, and MR-AQCC-LRT, and utilizing orbitals obtained from CAS(8,8) and 10-

TABLE III. CAS(2,2) SA(4)-MC-SCF, MR-CISD, MR-CISD+Q, and MR-AQCC vertical excitation energies (eV) from the  $1^1A_g$  ground state using CAS(2,2) reference wavefunction and the cc-pvTZ basis set (cc-pvDZ results are in the supplemental information).

State	Dominant configuration in MRCI	MC-SCF <sup>a</sup>	MR-CISD <sup>a</sup>	MR-CISD+Q <sup>a</sup>	AQCC <sup>a</sup>
$1^1A_g$	57% $(\sigma^*)^2 + 25\% \sigma^2$				
$3^3B_{3u}$	83% $\sigma^1(\sigma^*)^1$	0.02	0.15	0.26	0.28
$1^3B_{3u}$	80% $\sigma^1(\sigma^*)^1$	7.51	5.78	4.35	3.72
$2^1A_g$	56% $\sigma^2 + 24\% (\sigma^*)^2$	7.93	6.16	4.63	<sup>b</sup>

<sup>a</sup>Total ground state energies (a.u.): -229.434 31 (MCSCF), -230.192 56 (MR-CISD), -230.374 03 (MR-CISD+Q), and -230.368 91 (MR-AQCC).

<sup>b</sup>Calculation is not converged; reference space is not adequate.



and 32-state averaged MCSCFs. These results indicate that there is a high density of electronic states above the two-configurational singlet ground state including other states that are multiconfigurational. The seven lowest excitations are from the  $\pi$  system to the in-plane  $\sigma\sigma^*$  system on the dehydrocarbons except for  $2^1A_g$  and  $1^1B_{3u}$ . The ordering of electronic states was dependent on the inclusion of electron correlation and in some cases the character of the states changed as well. Five Rydberg states were identified at the MRCI level; two of which display nonzero transition probabilities. The  $3s$  Rydberg states were shown to arise from either excitation of a  $\sigma/\sigma^*$  or  $\pi$  electron. The vertical singlet-triplet gap for *p*-benzynes was computed to be 0.29 eV using a two state-averaged CAS(8,8) MRCISD + Q/cc-pVTZ treatment. Finally, our investigation into the reliability of a CAS(2,2) approach for *p*-benzynes showed that at least one important configuration characterized by a  $\pi \rightarrow \pi^*$  orbital excitation is missing in the CAS(2,2) reference wave function for the calculation of the  $2^1A_g$  and  $1^1B_{3u}$  states.

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