

# A Multiconfigurational SCF and Correlation-Consistent CI Study of the Structures, Stabilities, and Singlet–Triplet Splittings of *o*-, *m*-, and *p*-Benzyne

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**Abstract:** The structures, total energies, singlet–triplet splittings, and absolute heats of formation of *o*-, *m*-, and *p*-benzyne have been calculated with the use of a variety of multiconfigurational self-consistent field (MCSCF) and configuration-interaction (CI) methods. The performance of each method is evaluated by comparison of the calculated singlet–triplet energy difference and absolute heat of formation for *o*-benzyne with the experimentally-determined values. Correlation-consistent CI (CCCI) methods, when used in conjunction with relatively large basis sets and molecular structures derived from MCSCF-based geometry optimizations, are found to give the best agreement, although the performance of larger-scale CI (e.g., CISD) calculations is comparable. All three benzyne isomers are found to have singlet biradical ground states at each of the levels of theory used. The most probable values for the singlet–triplet splittings in *o*-, *m*-, and *p*-benzyne derived from the CI calculations are  $36 \pm 2$ ,  $17 \pm 1$ , and  $2.2 \pm 0.5$  kcal/mol, respectively. The energetics of the hypothetical isodesmic reaction between each of the benzyne and benzene to produce two phenyl radicals have been evaluated. These energy changes are discussed in terms of the stabilization or destabilization of the singlet and triplet states of each biradical with respect to simple bond-strength additivity models. The calculated energy differences have also been combined with the experimentally-determined heats of formation of benzene and the phenyl radical in order to derive the absolute heats of formation for the three benzyne isomers. The value obtained for *o*-benzyne using CCCI methods is in excellent agreement with the experimental value; the predicted heats of formation for the singlet ground states of *o*-, *m*-, and *p*-benzyne are 107, 125, and 138 kcal/mol, respectively. A comparison of the theoretically-predicted heats of formation with the experimental values recently determined in this laboratory (Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* 1991, 113, 7414) suggests that the measured heats of formation for *m*- and *p*-benzyne are both too low by 9–10 kcal/mol.

Determining accurate physical properties for open-shell organic molecules such as carbenes, carbynes, and biradicals continues to be one of the most challenging experimental tasks in chemistry. Whereas the assignment of ground-state multiplicities for many of these species has been made relatively routine by the development of low-temperature matrix electron-spin resonance (ESR) techniques,<sup>1</sup> the reliable measurement of energy differences among the low-lying electronic states can still be extremely difficult.<sup>2</sup> Moreover, the determination of the *absolute* energies (heats of formation) for such highly reactive molecules almost always requires indirect thermokinetic methods, since the usual equilibrium and calorimetric procedures are inapplicable.<sup>3</sup> Negative ion photoelectron spectroscopy offers a fairly general, direct means for measuring accurate electronic state splittings for open-shell organic species, provided that intense beams of the needed organic anions can be generated with known structures and internal energy content.<sup>4</sup> This method has been successfully applied in the determination of the singlet–triplet splittings for *o*-benzyne<sup>5</sup> and various carbenes and nitrenes<sup>6</sup> and the doublet–quartet splitting in methylidyne.<sup>7</sup> For a few carbenes, the measured electron affinities could be combined with additional

thermochemical data derived from gas-phase ion/molecule reactions to derive the absolute heats of formation.<sup>8</sup>

Electronic structure calculations for carbenes and biradicals also pose special challenges. It has long been recognized that although the triplet states of carbenes and biradicals are adequately represented by single-determinant wave functions, the proper description of the singlet states of these species requires, at the very least, a two-determinant approach.<sup>9</sup> Accordingly, restricted open-shell Hartree–Fock (ROHF)<sup>10</sup> calculations for triplet states and two-configuration self-consistent field (TC-SCF)<sup>11</sup> or generalized valence bond with one perfect pair (GVB-(1/2)-PP)<sup>12</sup> calculations for singlet states are usually employed for biradicals with degenerate or near-degenerate nonbonding

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molecular orbitals. However, these simple descriptions can still lead to incorrect ground-state assignments and state splittings because electron correlation is incompletely represented in the wave functions. Configuration-interaction (CI)<sup>13</sup> and multiconfigurational self-consistent field (MCSCF)<sup>14</sup> techniques are most often used to account for the electron correlation in biradicals because they are variational (unlike perturbational methods) and allow the use of multideterminant (i.e., TCSCF) zeroth-order wave functions.

Numerous computational recipes for performing CI calculations on biradicals have been described in the literature. One of the more commonly used approaches is to allow all single and double excitations from the valence orbitals of the TCSCF (or ROHF) wave function into the virtual orbitals. This approach, referred to as CISD,<sup>15</sup> has been used by Schaefer and co-workers to study Closs's diradical (cyclopentane-1,3-diyl)<sup>16</sup> as well as other open-shell systems.<sup>17</sup> Borden and co-workers have employed related CI methods that emphasize  $\sigma$ - $\pi$  electron correlation in their studies of various biradicals, including 2,4-dimethylenecyclobutane-1,3-diyl,<sup>18</sup> oxyallyl,<sup>19</sup> and *m*-quinone.<sup>20</sup> MCSCF formalisms, such as the fully-optimized reaction space MCSCF (FORS-MCSCF) method<sup>21</sup> and the complete active space SCF (CASSCF) procedure,<sup>22</sup> have also been used for biradical calculations by several groups, for example, by Johnson and co-workers in investigations of bent-planar allene and strained cyclic allenes<sup>23</sup> and by Jordan and co-workers in studies of tetramethyleneethane and its derivatives.<sup>24</sup> MCSCF and CISD may be combined to give a second-order CI (MCSCF-SOCI) calculation.<sup>25</sup> For example, Bauschlicher and Taylor used MCSCF-SOCI methods with a large basis set to compute the singlet-triplet gap in methylene to within 0.2 kcal/mol of the experimental value.<sup>26</sup> Goddard and co-workers have emphasized the need for a balanced CI treatment wherein nearly equal numbers of excited configurations contribute to both the singlet and triplet states of the open-shell system. The correlation-consistent CI (CCCI)<sup>27</sup> and dissociation-consistent CI (DCCI)<sup>28</sup> methods developed by this group have shown impressive accuracy in calculations of singlet-triplet energy gaps for substituted carbenes and silylenes.

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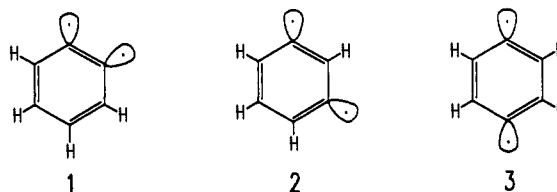
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It is because of the inherent difficulties in both measuring and calculating accurate energetics for open-shell organic species that complementary approaches involving experiment and theory have become so important. The colorful history of the determination of the singlet-triplet splitting in methylene<sup>29</sup> nicely illustrates this synergism, and it is also evident in the current status of our knowledge of the dihydrobenzenes (benzyne) (1-3). *o*-Ben-



zyne, **1**, has been recognized as an important reactive intermediate for over 40 years and has been the subject of several spectroscopic<sup>5,30</sup> and theoretical<sup>31-38</sup> investigations. This pseudobiradical is known to have a <sup>1</sup>A<sub>1</sub> singlet ground state, with the first excited <sup>3</sup>B<sub>2</sub> triplet state lying 37.7 ± 0.6 kcal/mol higher in energy.<sup>5</sup> Numerous attempts to generate *m*-benzyne, **2**, and *p*-benzyne, **3**, have been reported.<sup>39-42</sup> *p*-Benzyne analogues can be formed by electrocyclic ring closure of *cis*-3-ene-1,5-diyne (Bergman cyclizations)<sup>40</sup> and have been proposed as intermediates in the DNA-cleaving action of calicheamicins and esperamicins.<sup>43,44</sup> Chemical trapping experiments in solution suggest singlet ground states for both **2** (<sup>1</sup>A<sub>1</sub>) and **3** (<sup>1</sup>A<sub>g</sub>) and a biradical (as opposed to a closed-shell bicyclic structure for **3**).<sup>40</sup> Scheiner, Schaefer, and Liu used CISD methods with a polarized, double- $\zeta$  basis set to investigate the structure, the vibrational spectrum, and the singlet-triplet splitting for **1**.<sup>36</sup> They calculated a singlet-triplet gap of 33.3 kcal/mol and attributed the 4.4 kcal/mol difference from the experimental value to basis set limitations. Semiempirical molecular orbital calculations for **1-3** have led to various conflicting conclusions regarding the preferred structures (open-shell biradical vs closed-shell bicyclic) and relative stabilities of the three isomers.<sup>33</sup> *Ab initio* molecular orbital calculations for **2** and **3** were carried out by Noell and Newton.<sup>34</sup> They used a GVB(1/2)-PP method with limited geometry optimization and a relatively small 4-31G basis set and found singlet biradical ground states for **2** and **3** lying 14.5 and 23.3 kcal/mol,

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respectively, higher in energy than that of singlet 1. The singlet-triplet gaps at this level of theory were predicted to be 28.1, 12.2, and 1.4 kcal/mol for 1, 2, and 3, respectively. Recently, Sutter and Ha carried out CASSCF and multireference CI calculations to predict vertical excitation energies for the singlet and triplet states of 1.<sup>38</sup>

Measurements of the absolute heats of formation of *o*-, *m*-, and *p*-benzynes were described in a recent report from this laboratory.<sup>45</sup> The values of  $106 \pm 3$ ,  $116 \pm 3$ , and  $128 \pm 3$  kcal/mol for 1, 2, and 3, respectively, were determined from the measured onsets for collision-induced dissociation (CID) of the corresponding chlorophenyl anion isomers in a flowing afterglow-triple quadrupole instrument. The measured heat of formation for 1 is in excellent agreement with recent measurements by different experimental methods,<sup>46</sup> and the apparent stability ordering  $\Delta H_f(1) < \Delta H_f(2) < \Delta H_f(3)$  is consistent with the earlier *ab initio* calculations by Noell and Newton.<sup>34</sup> However, the heats of formation for 2 and 3, when compared with the value derived from a simple bond-energy additivity calculation for didehydrobenzene ( $140 \pm 3$  kcal/mol, *vide infra*), imply stabilization energies of 24 kcal/mol for 2 and 12 kcal/mol for 3—somewhat larger than might have otherwise been expected for 1,3- and 1,4-biradicals.

The goal of the present work is to evaluate the performance of various levels of *ab initio* theory for calculating the geometric and electronic structures, the state splittings, and the absolute energetics for the three benzynes and to use the most reliable method possible to assess the experimental thermochemistry. It will be shown here that while high-level calculations support the reported heat of formation for 1, they provide compelling evidence that the measured values for 2 and 3 are both too low by as much as 10 kcal/mol. These same conclusions were reached simultaneously and independently by Nicolaidis and Borden, as described in the preceding paper in this issue.<sup>47</sup> The discrepancy between experiment and theory led us to a critical reevaluation of the measurements. In a forthcoming paper, we will present a complete description of the benzyne thermochemical measurements along with the revised values for  $\Delta H_f(2)$  and  $\Delta H_f(3)$  that are consistent with the calculations described herein.<sup>48</sup>

### Computational Details

The geometries of 1, 2, and 3 were optimized with  $C_{2v}$ ,  $C_{2v}$ , and  $D_{2h}$  symmetry constraints, respectively, using two different MCSCF active orbital spaces. The smaller of these, MCSCF(2,2), has two active electrons in the two nonbonding  $\sigma$  orbitals, which is equivalent to TSCF for the singlet states and ROHF for the triplet states. The larger active space, MCSCF(8,8), has eight active electrons distributed among all symmetry-allowed configurations involving the two nonbonding  $\sigma$  orbitals and the six  $\pi$  and  $\pi^*$  orbitals. Three different basis sets were employed for the geometry optimizations: 3-21G, 6-31G\*, and 6-311G\*\*.<sup>49</sup> The 6-31G\* basis set includes a set of six d-type polarization functions for carbon, and the 6-311G\*\* basis set includes six d-functions for carbon and a set of three p-type polarization functions for hydrogen. The MCSCF(2,2) optimizations were carried out using the 3-21G, 6-31G\*, and 6-311G\*\* basis sets, whereas only the 3-21G basis set was used for the MCSCF(8,8) optimizations. Optimized geometries for benzene ( $D_{6h}$ ) and the phenyl radical ( $C_{2v}$ ) were obtained at the HF or ROHF levels with the 3-21G, 6-31G\*, and 6-311G\*\* basis sets and at the MCSCF(6,6) and MCSCF(7,7) levels, respectively, with the 3-21G basis set. The active spaces used in the latter calculations allow correlation between all valence  $\pi$  and nonbonding  $\sigma$  electrons and are analogous to the larger active

spaces used for 1, 2, and 3. To simplify the presentation and discussion of the theoretical results, the geometries obtained at the MCSCF(2,2)/3-21G level are labeled A, the MCSCF(2,2)/6-31G\* geometries are labeled B, the MCSCF(2,2)/6-311G\*\* geometries are labeled C, and the MCSCF( $n,n$ )/3-21G ( $n = 8, 7, \text{ or } 6$ ) geometries are labeled D. Harmonic vibrational frequencies were computed for 1–3 at the MCSCF(2,2)/6-31G\* level, for benzene at the HF/6-31G\* level, and for the phenyl radical at the ROHF/6-31G\* level. All structures were verified to be energy minima in the given symmetries by the absence of any negative eigenvalues in the hessian matrix. Zero-point energies (ZPE) were derived from the computed frequencies after scaling by a factor of 0.89.<sup>50</sup>

Total energies for 1–3, benzene, and the phenyl radical were also computed at the appropriate large active space MCSCF( $n,n$ )/6-31G\* ( $n = 8, 7, \text{ or } 6$ ) and CISD/6-31G\* levels using the B geometries. Identical calculations were performed on all species at the D geometries using the Dunning correlation-consistent [9s4p1d/3s2p1d] basis set for carbon<sup>51</sup> and the Dunning double- $\zeta$  [4s/2s] basis set for hydrogen.<sup>52</sup> This basis set is designated pVDZ, although it lacks polarization functions on the hydrogen atoms. The CI calculations used the natural orbitals resolved from the appropriate MCSCF( $n,n$ ) calculations. Using a single reference configuration for the triplet state and two reference configurations for the singlet state, all symmetry-allowed single and double excitations from the reference configurations were included, except for those from the non valence molecular orbitals (frozen-core approximation). In order to account for potential size-consistency problems with the CISD calculations,<sup>15</sup> the Davidson correction (DV2)<sup>53,54</sup> for quadruple excitations was applied to all CISD energies.

Finally, a correlation-consistent CI (CCCI) method similar to that described by Carter and Goddard<sup>27</sup> was also used to calculate total energies for 1–3, benzene, and the phenyl radical. Using the resolved natural orbitals generated by MCSCF(2,2)/6-31G\* calculations, we first performed a limited CI calculation which included all symmetry-allowed configurations involving the six  $\pi$  and  $\pi^*$  orbitals and, for 1–3 and the phenyl radical, the nonbonding  $\sigma$  orbitals. The procedure used in this work differs somewhat from the restricted CI (RCI) approach described by Carter and Goddard in ref 27 in that each of the electrons in the active space are allowed to populate any molecular orbital in the active space rather than being restricted to pairwise excitations among the two GVB-paired molecular orbitals assigned to those particular electrons. The only difference between this limited CI and the MCSCF( $n,n$ ) procedures is that the orbitals remain unchanged in the former, whereas they are self-consistently reoptimized during the latter. In addition to the limited CI, correlation of the nonbonding  $\sigma$  electrons is included by allowing all single and double excitations of these electrons from the MCSCF(2,2) reference configurations (singles only for the phenyl radical) to all of the virtual orbitals. The potential problems with this approach have been discussed by Shin et al.<sup>28</sup> CCCI energies were computed with several basis sets: 6-31G\*, 6-311G\*\*, the correlation-consistent pVDZ basis set<sup>51</sup> (including polarization functions on all atoms), and a valence triple- $\zeta$  polarized basis set (pVTZ), which employs a [10s6p1d/5s3p1d] contraction on carbon and a [5s1p/3s1p] contraction on hydrogen.<sup>52</sup> The CCCI calculations used either the B, C, or D molecular geometries.

In the following tabulations and discussions, we use the standard notation for specifying a particular calculation.<sup>15</sup> A "/" separates the computational method used from the basis set employed, while a "/" separates the combination used to compute the total energy from that used to optimize the molecular geometry. For example, a calculation where the CCCI method was used with the pVTZ basis set to compute the total energy for an optimized geometry derived from a MCSCF(8,8) calculation employing the 3-21G basis set is labeled CCCI/pVTZ//MCSCF(8,8)/3-21G or, in accordance with the simplified descriptors defined above, CCCI/pVTZ//D.

The GAUSSIAN90<sup>55</sup> and -92<sup>56</sup> programs were used for all geometry optimizations. The larger active space MCSCF single-point energies were computed using either the GAMESS,<sup>57</sup> COLUMBUS,<sup>58</sup> or MOLPRO<sup>59</sup> codes, whereas all CISD-derived energies were obtained using the MOLPRO program. All CCCI calculations employed the MELDF<sup>60</sup> suite of programs.

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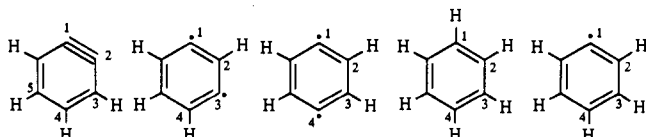
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## Results

The aim of these calculations is to evaluate the performance of different levels of theory so that reliable predictions of singlet–triplet splittings, relative energies, and absolute heats of formation for the benzyne can be made for comparison with the available experimental data. The size of the systems under examination necessarily limits the size of the basis sets that can be practically employed, and it is recognized that this could limit the accuracy of the calculations. Some of the problems and pitfalls associated with each method will be addressed in the Discussion section.

The C–C bond lengths obtained from the various geometry optimizations for 1–3, benzene, and the phenyl radical are summarized in Table I. The numbering schemes used are indicated below.



Also included are the distances between the radical sites in *m*- and *p*-benzyne as well as the corresponding distances in benzene and the phenyl radical for comparison. The vibrational frequencies and zero-point vibrational energies (ZPE) of all species were computed at the MCSCF(2,2)/6-31G\*, HF/6-31G\*, or ROHF/6-31G\* level and are available as supplementary material.<sup>61</sup> No negative force constants were found for the planar structures of the indicated symmetries, verifying them as true minima on the corresponding potential energy surfaces.

Total energies for the singlet and triplet states of 1–3 computed at the various levels of theory are summarized in Tables II–IV, and Table V lists the energies calculated for benzene and the phenyl radical at these same levels of theory. The singlet–triplet energy gaps  $\Delta E_{ST}$  for 1–3, defined according to eq 1,

$$\Delta E_{ST} = (E_{\text{tot}} + \text{ZPE})_{\text{triplet}} - (E_{\text{tot}} + \text{ZPE})_{\text{singlet}} \quad (1)$$

are also given in Tables II–IV for each of the computational levels. Note that a positive value for  $\Delta E_{ST}$  indicates that the singlet state is lower in energy than the triplet state. Also, the singlet–triplet splittings calculated for identical benzyne structures with the same basis sets using the MOLPRO code, which employs an internally-contracted CI list,<sup>59</sup> and with the MELDF program, which uses uncontracted CI,<sup>60</sup> were found to be the same within 0.3 kcal/mol.

In order to derive the absolute heats of formation for the benzyne from the calculated total energies, it is necessary to compute the energy change for an isodesmic reaction<sup>15</sup> involving

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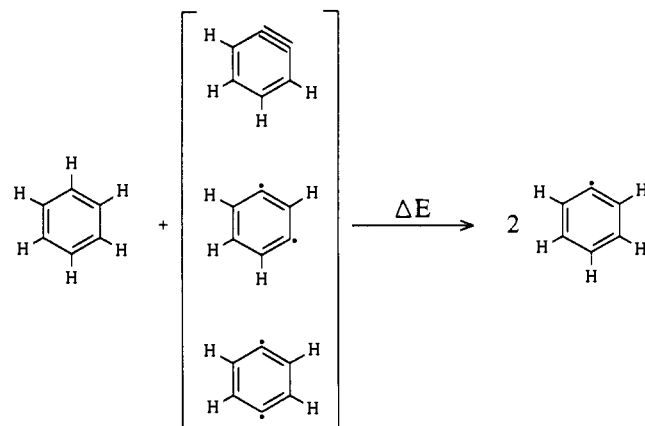
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(60) Developed at the University of Washington by L. McMurchie, S. Elbert, S. Langhoff, E. R. Davidson, D. Feller, and D. Rawlings.

(61) See Supplementary Material Available paragraph for ordering information.

## Scheme I



the benzyne, in which the experimental heats of formation for the other products and reactants are known. For this purpose, we use the hypothetical hydrogen-atom transfer to 1, 2, or 3 from benzene to form two phenyl radicals (Scheme I) and define the energy change for this reaction as the *biradical separation energy* (BSE). The BSE value provides a direct measure of the stabilization or destabilization involved when two radical centers are present in the same molecule, i.e., it indicates the difference between the true heat of formation for benzyne and that predicted by simple bond-energy additivity models (*vide infra*).<sup>62</sup> A positive value indicates that the biradical is stabilized, and a negative value indicates it is destabilized, with respect to a "noninteracting" biradical model. The calculated biradical separation energies, which include the appropriate  $\Delta ZPE$  and 298 K temperature corrections, are listed in Table VI for the singlet and triplet states of the three benzyne. The calculated BSE values may be combined with  $\Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_6) = 19.8 \pm 0.1 \text{ kcal/mol}$ <sup>63</sup> and  $\Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_5) = 80 \pm 2 \text{ kcal/mol}$  according to eq 2 to derive

$$\Delta H_{f,298}^{\circ}(1, 2, \text{ or } 3) =$$

$$2\Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_5) - \Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_6) - \text{BSE}(1, 2, \text{ or } 3) \quad (2)$$

the standard heats of formation of 1–3. The value used here for the heat of formation of the phenyl radical is based upon a benzene C–H bond enthalpy at 298 K of  $112 \pm 2 \text{ kcal/mol}$ .<sup>64</sup> The heats of formation for the benzyne calculated with eq 2 can thus be directly compared to the values obtained from experiment. The derived heats of formation for the singlet ground states of 1–3 are listed in Table VII along with the experimental values from ref 45. These data can be used to evaluate bond additivity models for benzyne thermochemistry and, when combined with the  $\Delta E_{ST}$  values, permit an examination of the proposed relationship between the heats of formation and singlet–triplet splittings of benzyne.<sup>70</sup>

## Discussion

The computational results listed in Tables I–VII permit a systematic evaluation of the effects of the basis set and the level

(62) This definition for a stabilization energy is analogous to the divalent state stabilization energy (DSSE) originally defined by Walsh for silylenes (Walsh, R. *Acc. Chem. Res.* 1981, 14, 246) and recently employed by Grev et al. (Grev, R. S.; Schaefer, H. F., III; Baines, K. M. *J. Am. Chem. Soc.* 1990, 112, 9458). We thank Professor Leo Radom for recommending this isodesmic reaction for use in evaluating benzyne thermochemistry.

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(64) The magnitude of the C–H bond strength in benzene has been somewhat controversial.<sup>65,66</sup> The value used in this work ( $\text{DH}_{298}[\text{C}_6\text{H}_5\text{--H}] = 112 \pm 2 \text{ kcal/mol}$ ) is derived from the gas-phase acidity of benzene ( $\Delta H_{\text{acid}}(\text{C}_6\text{H}_6)$ ), the electron affinity of the phenyl radical ( $\text{EA}(\text{C}_6\text{H}_5)$ ), and the ionization potential of hydrogen (IP(H)) according to the relation:<sup>67</sup>  $\text{DH}[\text{C}_6\text{H}_5\text{--H}] = \Delta H_{\text{acid}}(\text{C}_6\text{H}_6) + \text{EA}(\text{C}_6\text{H}_5) - \text{IP}(\text{H})$  and using the data  $\Delta H_{\text{acid}}(\text{C}_6\text{H}_6) = 400.7 \pm 2.0 \text{ kcal/mol}$ ,<sup>68</sup>  $\text{EA}(\text{C}_6\text{H}_5) = 25.3 \pm 0.1 \text{ kcal/mol}$ ,<sup>69</sup> and  $\text{IP}(\text{H}) = 313.6 \text{ kcal/mol}$ .<sup>3</sup>

(65) (a) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* 1982, 33, 493. (b) Robaugh, D.; Tsang, W. *J. Phys. Chem.* 1986, 90, 5363.

Table I. Optimized C–C Bond Lengths (Å) for 1–3, Benzene, and the Phenyl Radical

compound	method	state	C <sub>1</sub> –C <sub>2</sub>	C <sub>2</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>4</sub>	C <sub>4</sub> –C <sub>5</sub>	C*–C* <sup>a</sup>
1, C <sub>2v</sub>	MCSCF(2,2)/3-21G (A)	T	1.3895	1.3717	1.3941	1.3832	1.3895
		S	1.2609	1.3823	1.3919	1.4026	1.2609
	MCSCF(2,2)/6-31G* (B)	T	1.3864	1.3722	1.3946	1.3841	1.3864
		S	1.2605	1.3828	1.3894	1.4042	1.2605
	MCSCF(2,2)/6-311G** (C)	T	1.3865	1.3709	1.3942	1.3827	1.3865
		S	1.2545	1.3828	1.3880	1.4044	1.2545
	MCSCF(8,8)/3-21G (D)	T	1.4045	1.3836	1.4056	1.3947	1.4045
		S	1.2602	1.4025	1.3965	1.4218	1.2602
2, C <sub>2v</sub>	MCSCF(2,2)/3-21G (A)	T	1.3759	1.3739	1.3739	1.3919	2.3265
		S	1.3772	1.3725	1.3725	1.3903	2.2420
	MCSCF(2,2)/6-31G* (B)	T	1.3763	1.3743	1.3743	1.3920	2.3235
		S	1.3713	1.3728	1.3728	1.3897	2.1981
	MCSCF(2,2)/6-311G** (C)	T	1.3753	1.3732	1.3732	1.3914	2.3200
		S	1.3705	1.3715	1.3715	1.3888	2.1901
	MCSCF(8,8)/3-21G (D)	T	1.3882	1.3877	1.3877	1.4023	2.3536
		S	1.3880	1.3839	1.3839	1.4005	2.2508
3, D <sub>2h</sub>	MCSCF(2,2)/3-21G (A)	T	1.3742	1.3937			2.6539
		S	1.3686	1.4034			2.6780
	MCSCF(2,2)/6-31G* (B)	T	1.3744	1.3935			2.6499
		S	1.3705	1.4012			2.6758
	MCSCF(2,2)/6-311G** (C)	T	1.3744	1.3935			2.6498
		S	1.3689	1.4009			2.6722
	MCSCF(8,8)/3-21G (D)	T	1.3873	1.4037			2.6827
		S	1.3811	1.4145			2.7115
benzene, D <sub>6h</sub>	HF/3-21G (A)	S	1.3846			2.3982	2.7692
	HF/6-31G* (B)	S	1.3862			2.4009	2.7723
	HF/6-311G** (C)	S	1.3854			2.3996	2.7708
	MCSCF(6,6)/3-21G (D)	S	1.3953			2.4167	2.7905
phenyl radical, C <sub>2v</sub>	exp <sup>b</sup>	S	1.397			2.419	2.794
	ROHF/3-21G (A)	D	1.3714	1.3898	1.3866	2.3560	2.7128
	ROHF/6-31G* (B)	D	1.3725	1.3903	1.3877	2.3560	2.7128
	ROHF/6-311G** (C)	D	1.3713	1.3897	1.3868	2.3535	2.7100
	MCSCF(7,7)/3-21G (D)	D	1.3843	1.4000	1.3978	2.3798	2.7386

<sup>a</sup> Distance between the dehydrocarbon atoms. <sup>b</sup> Reference 71.

of electron correlation on the geometries, the state splittings, and both the relative and absolute energies of the three benzyne isomers. The experimental bench marks used for comparison are the measured singlet–triplet splitting for *o*-benzyne (37.7 ± 0.6 kcal/mol)<sup>5</sup>, the recently-redetermined heat of formation for *o*-benzyne (105 ± 3<sup>46a</sup> and 105 ± 5<sup>46b</sup> kcal/mol—obtained from two independent methods), and the accurately-known geometry of benzene.<sup>71</sup> On the basis of these comparisons, we will select the most credible theoretical model and then use the computed heats of formation for 1–3 to assess the experimental thermochemistry derived from CID threshold measurements carried out in this laboratory.<sup>45</sup>

**Geometries.** The C–C bond lengths obtained from the various optimization procedures are summarized in Table I. For the triplet states of 1–3, the MCSCF(2,2)/3-21G-optimized geometries (method A) are nearly identical to those obtained from either the MCSCF(2,2)/6-31G\* (B) or MCSCF(2,2)/6-311G\*\* (C) procedures. The largest difference in the bond lengths for the three sets of geometries for the triplet benzyne is 0.003 Å. This is also evident for the computed geometries of benzene and the phenyl radical obtained at these same three levels of theory, i.e., the largest differences in the bond lengths are only 0.002 and 0.001 Å, respectively. Moreover, the distances between the two radical sites in the triplet states of 1–3 are also relatively insensitive to the choice of basis set used for the MCSCF(2,2) optimizations. The largest difference in the calculated distances between the dehydrocarbon atoms occurs with 2, in which the C<sub>1</sub>–C<sub>3</sub> distance is found to be 0.007 Å longer with the relatively small 3-21G

basis set than with the extended 6-311G\*\* basis set. Thus, the optimized geometries for the triplet states of 1–3, benzene, and the phenyl radical obtained at this level of theory are not greatly affected by the number of Gaussian functions used for each Slater-type orbital, by the addition of polarization functions on either the carbon or hydrogen atoms, or by additional valence-shell splitting.

Somewhat larger variations in the MCSCF(2,2)-derived geometries for the singlet states of 1–3 are apparent. For example, for singlet 1, method C gives a C<sub>1</sub>–C<sub>2</sub> bond length that is 0.006 Å shorter than that obtained with method A and 0.006 Å shorter than that obtained with method B. Likewise, for singlet 2, the C<sub>1</sub>–C<sub>2</sub> (and C<sub>2</sub>–C<sub>3</sub>) bond lengths are similar with methods B and C but *ca.* 0.007 Å longer with method A. As a result, the distance between the two radical centers for singlet 2 is 0.044–0.052 Å (2%) shorter with the larger basis sets. For singlet 3, the geometries obtained with the three methods are quite similar, e.g., the largest difference in the calculated bond lengths is 0.003 Å. Accordingly, the calculated C<sub>1</sub>–C<sub>4</sub> distances for singlet 3 are also comparable for the various optimizations—the largest difference being 0.006 Å (only 0.2%) for 3-21G vs 6-311G\*\*. The shorter C<sub>1</sub>–C<sub>2</sub> bond length obtained for singlet 1 with method C undoubtedly results from the improved description of the outer valence region with the larger, more flexible basis set which, in turn, leads to better overlap between the adjacent  $\sigma$  orbitals. Similarly, because of the relatively small separation of the radical centers in singlet 2 (*ca.* 2.2 Å), the use of a larger basis set with polarization functions is also important for properly describing the weak C<sub>1</sub>–C<sub>3</sub> bonding interaction in this molecule.<sup>34</sup> The relative insensitivity to basis set quality of the computed geometry for singlet 3 is a result of the larger separation between the radical centers (*ca.* 2.7 Å) and the absence of a direct C<sub>1</sub>–C<sub>4</sub> bonding interaction.

The geometries for 1–3, the phenyl radical, and benzene obtained from the larger active space MCSCF(*n,n*)/3-21G optimizations (*n* = 8, 7, or 6; method D) are significantly different

(66) A value of 111 ± 2 kcal/mol has been recently recommended in: Ellison, G. B.; Gutman, D.; Berkowitz, J. *Ann. Rev. Phys. Chem.*, in press. We thank Professor Ellison for a preprint of this comprehensive review.

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(68) Meot-Ner, M.; Kafafi, S. A. *J. Am. Chem. Soc.* 1988, 110, 6297.

(69) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* 1992, 117, 601.

(70) Zhang, X.; Chen, P. *J. Am. Chem. Soc.* 1992, 114, 3147.

(71) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* 1976, 30, 243.

from the MCSCF(2,2) geometries described above (methods A, B, and C). For example, the C–C bond lengths obtained with method D are on the average 0.01–0.03 Å longer than those obtained with the MCSCF(2,2) calculations using any of the basis sets. With the exception of singlet 1, the distances between the dehydrocarbon atoms obtained with method D are also consistently greater than those obtained with methods A, B, or C. These effects are to be expected because the larger active space includes configurations that arise from excitations into the virtual  $\pi^*$  orbitals. The partial occupation of the antibonding  $\pi^*$  orbitals (and the accompanying depopulation of the  $\pi$  and  $\sigma$  orbitals) naturally results in longer C–C bond lengths.

The optimized geometry for benzene obtained with method D is in excellent agreement with the experimentally-determined structure of this molecule,<sup>71</sup> i.e., the calculated and experimental C–C bond lengths differ by only 0.002 Å ( $D_{6h}$  symmetry). The apparent success with this method compared with methods A, B, or C suggests that the inclusion of the  $\pi$  and  $\pi^*$  orbitals in the active space for MCSCF geometry optimizations for benzene and, presumably, benzene derivatives and other unsaturated molecules is important. These results suggest that accurate geometries can be obtained, even with relatively small basis sets (such as 3-21G), as long as the full  $\pi$  space is included in the MCSCF optimizations. Similar conclusions were reached in recent MCSCF studies by Jordan and co-workers of the structures of tetramethyleneethane and cyclopentadienyltrimethylenemethane.<sup>24</sup> On the basis of the good performance of the MCSCF(6,6)/3-21G procedure for benzene, we will assume that the corresponding MCSCF( $n,n$ )/3-21G (method D)-derived geometries for 1–3 and the phenyl radical are the most accurate.

A comparison of the structures of 1–3, the phenyl radical, and benzene obtained by method D reveals several notable trends. First, the geometries of both the singlet and triplet states of the benzyne differ significantly from those of benzene and the phenyl radical. Both singlet and triplet 1 have alternating C–C bond lengths, with half longer and half shorter than the C–C bonds in benzene. The bond alternation is opposite in the singlet and triplet states, which naturally arises from the long  $C_1$ – $C_2$  bond in the triplet (1.405 Å) and the short acetylene-like bond in the singlet (1.260 Å;  $r(\text{HC}\equiv\text{CH}) = 1.204 \text{ \AA}^{72}$ ). The  $C_1$ – $C_2$  bond length in the phenyl radical is also longer than that for singlet 1 and shorter than that for triplet 1. The geometries of singlet and triplet 2 are similar except for the 0.1 Å shorter  $C_1$ – $C_3$  distance (and the accompanying bond angle differences) for the singlet state. However, both the singlet and triplet states of 2 have shorter  $C_1$ – $C_3$  distances than the corresponding distances in benzene and the phenyl radical, so the smaller distance in the singlet cannot be entirely due to  $C_1$ – $C_3$  bonding. Rather, it is a consequence of the natural tendency for the CCC bond angles at the dehydrocarbon atoms to expand as the s-character in the CC bonds increases, thus forcing them closer together. This effect is also evident for 3, in which the distance between radical centers in both the singlet and triplet states is shorter than the corresponding  $C_1$ – $C_4$  distance in benzene and the phenyl radical. As with 2, the computed structures for singlet and triplet 3 are comparable. However, unlike 2 (and 1), the distance between the dehydrocarbon atoms in 3 ( $C_1$ – $C_4$ ) is nearly 0.03 Å shorter in the triplet state than in the singlet state. This is a consequence of the fact that, for *p*-benzyne, the antisymmetric combination of the  $\sigma$  nonbonding orbitals ( $\Phi_A$ ) is actually lower in energy than the symmetric combination ( $\Phi_S$ ), while the reverse is true for the *ortho* and *meta* isomers,<sup>31</sup> as shown in Figure 1. The conjugation elements in 3 that are responsible for lowering  $\Phi_A$  are the  $\sigma^*$  orbitals of the adjacent  $C_2$ – $C_3$  and  $C_5$ – $C_6$  bonds.<sup>31</sup> Therefore, in the singlet state of 3, donation by  $\Phi_A$  into the adjacent  $\sigma^*$  orbitals and depletion of the corresponding  $\sigma$  orbitals by  $\Phi_S$  lead to increases in the  $C_2$ – $C_3$  and  $C_5$ – $C_6$  bond lengths and a corresponding increase in the  $C_1$ – $C_4$  distance. For triplet 3, the

**Table II.** MCSCF, CISD, and CCCI Energies (au) for the Singlet and Triplet States of 1

level	geom-etry	$E(\text{triplet})$	$E(\text{singlet})$	$\Delta E_{\text{ST}}^{a,b}$
MCSCF(2,2)/3-21G	A	-228.11011	-228.15780	29.5
MCSCF(8,8)/3-21G	A	-228.19129	-228.24806	35.2
MCSCF(2,2)/6-31G*	B	-229.39176	-229.43607	27.4
MCSCF(2,2)/6-311G**	C	-229.43904	-229.48523	28.6
MCSCF(8,8)/3-21G	D	-228.19214	-228.24896	35.3
MCSCF(8,8)/6-31G*	B	-229.47042	-229.52417	33.3
MCSCF(8,8)/pVDZ	D	-229.48532	-229.53955	33.6
CISD/6-31G*	B	-230.00649	-230.05793	31.9
CISD + DV2/6-31G*	B	-230.12420	-230.17775	33.2
CISD/pVDZ	D	-230.01918	-230.06960	31.2
CISD + DV2/pVDZ	D	-230.14167	-230.19382	32.3
CCCI/6-31G*	B	-229.45314	-229.50942	34.9
CCCI/pVDZ	B	-229.47403	-229.53080	35.2
CCCI/6-311G**	C	-229.50182	-229.56050	36.4
CCCI/pVTZ	C	-229.51613	-229.57549	36.8
CCCI/pVTZ	D	-229.51594	-229.57532	36.9
exp <sup>d</sup>				37.7 ± 0.6
ZPE (kcal/mol) <sup>c</sup>		45.1	45.5	

<sup>a</sup> In kcal/mol; a positive value indicates that the singlet state is below the triplet state. <sup>b</sup> Corrected for the zero-point energy difference. <sup>c</sup> Computed from the scaled vibrational frequencies obtained with method B. <sup>d</sup> Reference 5.

**Table III.** MCSCF, CISD, and CCCI Energies (au) for the Singlet and Triplet States of 2

level	geom-etry	$E(\text{triplet})$	$E(\text{singlet})$	$\Delta E_{\text{ST}}^{a,b}$
MCSCF(2,2)/3-21G	A	-228.11564	-228.13237	10.8
MCSCF(8,8)/3-21G	A	-228.19649	-228.21587	12.5
MCSCF(2,2)/6-31G*	B	-229.39571	-229.41601	13.0
MCSCF(2,2)/6-311G**	C	-229.44322	-229.46363	13.1
MCSCF(8,8)/3-21G	D	-228.19740	-228.21660	12.3
MCSCF(8,8)/6-31G*	B	-229.47420	-229.49817	15.3
MCSCF(8,8)/pVDZ	D	-229.48916	-229.51295	15.2
CISD/6-31G*	B	-230.01148	-230.03646	16.0
CISD + DV2/6-31G*	B	-230.12957	-230.15568	16.7
CISD/pVDZ	D	-230.02377	-230.04840	15.8
CISD + DV2/pVDZ	D	-230.14652	-230.17222	16.4
CCCI/6-31G*	B	-229.45612	-229.48349	17.5
CCCI/pVDZ	B	-229.47693	-229.50476	17.8
CCCI/6-311G**	C	-229.50495	-229.53277	17.8
CCCI/pVTZ	C	-229.51950	-229.54748	17.9
CCCI/pVTZ	D	-229.51928	-229.54613	17.1
ZPE (kcal/mol) <sup>c</sup>		45.0	44.7	

<sup>a</sup> In kcal/mol; a positive value indicates that the singlet state is below the triplet state. <sup>b</sup> Corrected for the zero-point energy difference. <sup>c</sup> Computed from the scaled vibrational frequencies obtained with method B.

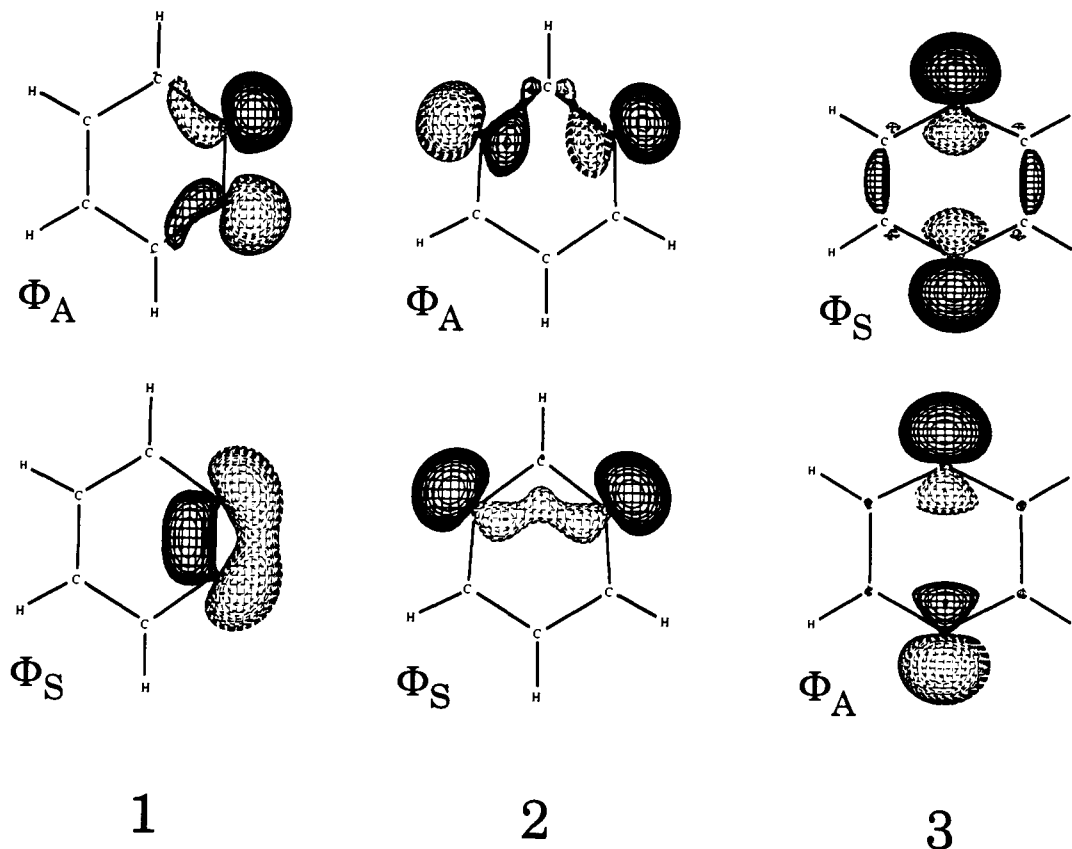
decreased occupation of  $\Phi_A$  and the increased occupation of  $\Phi_S$  lead to a shorter  $C_1$ – $C_4$  distance.

Finally, it is instructive to consider the "biradical character" of the three isomeric benzyne singlet states. A useful index can be derived from the ratio of the squares of the CI coefficients for the electron configurations involving double occupation of either the symmetric ( $C_S$ ) or the antisymmetric ( $C_A$ ) nonbonding orbital.<sup>73</sup> For a "pure" biradical, both configurations are equally populated, so the coefficients are equal and  $C_S^2/C_A^2 = 1.0$ . Using the CI coefficients obtained from the MCSCF(8,8)/3-21G wave functions, we find  $C_S^2/C_A^2 = 11.1$  for singlet 1, 4.3 for singlet 2, and 0.6 for singlet 3. The ratio is <1 for 3 because  $\Phi_A$  is lower in energy than  $\Phi_S$ . From these indices, it is clear that *p*-benzyne has the most biradical character, while *o*-benzyne has the least.

**Absolute Energies and Singlet–Triplet Splittings.** The total energies and singlet–triplet splittings obtained from the MCSCF, CISD, and CCCI calculations for 1–3 are summarized in Tables II–IV. All levels of theory employed in this work predict singlet ground states for the three benzyne isomers. This is consistent

(72) Helcher, J. L. In *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; J. Wiley and Sons: New York, 1978; Chapter 2.

(73) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; McGraw-Hill: New York, 1989; p 258.



**Figure 1.** Plots of the highest-occupied and lowest-unoccupied molecular orbitals of the singlet states of **1**, **2**, and **3** obtained from the MCSCF(2,2)/6-31G\* wave functions.<sup>78</sup> For **1** and **2**, the symmetric combination of  $\sigma$  orbitals  $\Phi_S$  is lower in energy than the antisymmetric combination  $\Phi_A$ , whereas for **3**,  $\Phi_A$  is below  $\Phi_S$ .

**Table IV.** MCSCF, CISD, and CCCI Energies (au) for the Singlet and Triplet States of **3**

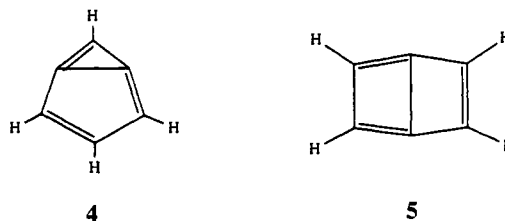
level	geom-etry	$E(\text{triplet})$	$E(\text{singlet})$	$\Delta E_{ST}^{a,b}$
MCSCF(2,2)/3-21G	A	-228.11765	-228.11978	1.1
MCSCF(8,8)/3-21G	A	-228.19765	-228.20311	3.2
MCSCF(2,2)/6-31G*	B	-229.39810	-229.39914	0.5
MCSCF(2,2)/6-311G**	C	-229.44518	-229.44640	0.6
MCSCF(8,8)/3-21G	D	-228.19850	-228.20398	3.2
MCSCF(8,8)/6-31G*	B	-229.47583	-229.48001	2.4
MCSCF(8,8)/pVDZ	D	-229.49075	-229.49507	2.5
CISD/6-31G*	B	-230.01409	-230.01692	1.6
CISD + DV2/6-31G*	B	-230.13194	-230.13597	2.3
CISD/pVDZ	D	-230.02647	-230.02960	1.8
CISD + DV2/pVDZ	D	-230.14898	-230.15336	2.5
CCCI/6-31G*	B	-229.45805	-229.46156	2.0
CCCI/pVDZ	B	-229.47876	-229.48259	2.2
CCCI/6-311G**	C	-229.50674	-229.51058	2.2
CCCI/pVTZ	C	-229.52131	-229.52505	2.1
CCCI/pVTZ	D	-229.52112	-229.52492	2.2
ZPE (kcal/mol) <sup>c</sup>		45.0	45.2	

<sup>a</sup> In kcal/mol; a positive value indicates that the singlet state is below the triplet state. <sup>b</sup> Corrected for the zero-point energy difference. <sup>c</sup> Computed from the scaled vibrational frequencies obtained from method B.

with the original predictions based on extended Hückel calculations by Hoffmann *et al.*<sup>31</sup> and with the *ab initio* calculations reported by Noell and Newton<sup>34</sup> and Schaefer and co-workers.<sup>36</sup> It is also consistent with an abundance of experimental evidence in the case of **1**.<sup>30</sup> The calculated stability ordering of the singlet states of the three benzyne isomers is also found to be the same at all levels of theory used in this work, i.e.,  $E(\text{ortho}) < E(\text{meta}) < E(\text{para})$ . This is in agreement with the earlier *ab initio* results of Noell and Newton<sup>34</sup> and with the experimental thermochemistry obtained from the CID threshold measurements.<sup>45</sup> That the *meta* isomer is lower in energy than the *para* isomer also finds support from the report by Bergman and co-workers<sup>40d</sup> that silylated

*p*-benzyne derivatives undergo thermal, silotropic rearrangement to the corresponding *m*-benzyne isomers. For the benzyne triplet states, the calculated relative stability order is reversed,  $E(\text{para}) < E(\text{meta}) < E(\text{ortho})$ .

Both of the stability orderings indicated above can be easily understood in terms of the nature and magnitude of the interaction between the radical sites in the three isomers. In **1** and **2**, direct overlap of the nominally nonbonding  $\sigma$  orbitals is possible, albeit only weakly so in **2** via the smaller rear lobes.<sup>31,34</sup> Thus, for singlet **1**, a "partial" triple bond is formed, while for singlet **2**, a weak 1,3-bond is present (*cf.* Figure 1). However, *m*-benzyne is *not* realistically considered to have a bicyclic structure. We find the total energy of planar bicyclo[3.1.0]hexa-1,3,5-triene, **4**, to be 15 kcal/mol higher than that of singlet **2** at the MCSCF(2,2)/6-31G\*//RHF/6-31G\* level of theory. Moreover, structure **4** is unlikely to represent a real minimum, since attempts to optimize the geometry at the MCSCF(2,2)/6-31G\* level of theory lead to ring opening and formation of **2**. Similarly, planar bicyclo[2.2.0]hexa-1,3,5-triene, **5**, is found to be 59 kcal/mol higher in energy than singlet **3** at the MCSCF(2,2)/6-31G\*//RHF/6-31G\* level of theory. Nonplanar structures for **4** and **5** are significantly higher in energy and unstable with respect to



reversion to planarity. The relative instabilities of the closed-shell, bicyclic isomers of **2** and **3** were reported previously by Noell and Newton<sup>34</sup> and verified at higher levels of theory by

Table V. HF, ROHF, MCSCF, CISD, and CCCI Energies (au) for Benzene and the Phenyl Radical

level <sup>a</sup>	geom-etry	<i>E</i> (benzene)	<i>E</i> (phenyl radical)
(RO)HF/3-21G	A	-229.41945	-228.76898
MCSCF( <i>n,n</i> )/3-21G	A	-229.49353	-228.84618
(RO)HF/6-31G*	B	-230.70314	-230.05092
(RO)HF/6-311G**	C	-230.75437	-230.10027
MCSCF( <i>n,n</i> )/3-21G	D	-229.49419	-228.84695
MCSCF( <i>n,n</i> )/6-31G*	B	-230.77585	-230.12629
MCSCF( <i>n,n</i> )/pVDZ	D	-230.78911	-230.14040
CISD/6-31G*	B	-231.35373	-230.68442
CISD + DV2/6-31G*	B	-231.48050	-230.80686
CISD/pVDZ	D	-231.36573	-230.69664
CISD + DV2/pVDZ	D	-231.49717	-230.82374
CCCI/6-31G*	B	-230.75901	-230.10879
CCCI/pVDZ	B	-230.78022	-230.12976
CCCI/6-311G**	C	-230.81134	-230.15932
CCCI/pVTZ	C	-230.82639	-230.17412
CCCI/pVTZ	D	-230.82640	-230.17403
ZPE (kcal/mol) <sup>b</sup>		60.1	52.5

<sup>a</sup> Hartree-Fock or MCSCF(6,6) procedures used for benzene; restricted open-shell Hartree-Fock or MCSCF(7,7) procedures used for the phenyl radical. <sup>b</sup> Computed from the scaled vibrational frequencies obtained with method B.

Nicolaides and Borden.<sup>47</sup> For *p*-benzyne, the distance between the radical sites (*ca.* 2.7 Å) is too large for direct overlap and only weak through-bond coupling<sup>31</sup> is available for stabilization of the singlet state of this molecule. In contrast, direct overlap is destabilizing in triplet 1 and triplet 2 since the relatively higher-lying antisymmetric (antibonding) combination of the nonbonding  $\sigma$  orbitals ( $\Phi_A$ ) is singly occupied (Figure 1). This "overlap repulsion"<sup>74</sup> is greatest in triplet 1, smaller in triplet 2, and essentially absent in triplet 3, thus giving rise to the reversed stability ordering compared to that of the singlet states. The geometric distortions relative to benzene for both the singlet and triplet states of 1-3 are consistent with this description of the bonding in these systems.

We now consider the calculated singlet-triplet splittings for 1-3 and the performance of the different computational methods in deriving these quantities. Schaefer and co-workers previously demonstrated the inadequacy of a single-configuration, zeroth-order description for the singlet state of *o*-benzyne.<sup>36</sup> A single-determinant (HF) treatment yields a triplet ground state for 1 and a singlet-triplet splitting at the CISD/pVDZ level (17 kcal/mol) that is well below the experimentally-determined value of  $37.7 \pm 0.6$  kcal/mol.<sup>5</sup> The serious shortcomings of single-determinant treatments for the singlet states of 2 and 3 were also evident in preliminary calculations carried out in the present work. For this reason, all energetics presented here involving singlet-state species are derived from a two-configuration reference.

While basis set quality has relatively small effects on the calculated geometries of 1-3, the absolute energies and the singlet-triplet splittings are significantly affected by both the basis set and computational methodology employed. At the MCSCF(2,2) level, the singlet-triplet splittings in 1-3 increase by 1.2, 0.1, and 0.1 kcal/mol, respectively, as the basis set is improved from 6-31G\* to 6-311G\*\* due to differential stabilization of the singlet states. A much larger relative stabilization of the singlet states occurs when electron correlation is better described in the MCSCF(8,8) calculations. The singlet-triplet splittings for 1 and 2 increase by 15-18% at the MCSCF(8,8) level compared to the MCSCF(2,2) level with all of the basis sets employed, while for 3, much larger changes are evident (60-80%). The MCSCF(8,8) calculations using the comparably-sized 6-31G\* and pVDZ basis sets give essentially identical results. The larger splittings for 1 and 3 (but not 2) obtained with the MCSCF(8,8)/3-21G procedure compared to those from the MCSCF(8,8)/6-31G\*

or MCSCF(8,8)/pVDZ calculations are most likely artifacts of the deficiencies of the smaller basis set.

Further improvement in the representation of electron correlation by means of CISD calculations gives mixed results. For 1 and 3, the CISD/6-31G\* and CISD/pVDZ calculations show differential stabilization of the triplet states, i.e., the singlet-triplet splittings are smaller by 0.6-2.4 kcal/mol compared to the corresponding MCSCF(8,8) results. In contrast, the CISD procedure leads to an *increased* singlet-triplet splitting for 2 by 0.6 kcal/mol. The Davidson correction stabilizes the singlet state relative to the triplet state in all three isomers. As a result, the splittings for 1 and 3 obtained from the MCSCF(8,8) and CISD + DV2 calculations are nearly the same, while for 2, the CISD + DV2 value is >1 kcal/mol larger than the MCSCF(8,8) result. It is also noteworthy that the singlet-triplet splittings for 1-3 are relatively unaffected by the choice of basis set (6-31G\* vs pVDZ) or by the choice of geometry (B vs D) in the CISD calculations.

The singlet-triplet splitting calculated for 1 at the CISD + DV2 level is still 4-5 kcal/mol below the experimentally-determined value. A possible reason for this (other than basis set limitations<sup>36</sup>) is that the CISD method may suffer from a natural "triplet bias" in that more than twice as many configurations and a larger maximum number of open-shell electrons per configuration are generated for the triplet state compared to the singlet state, thus leading to greater stabilization of the former.<sup>27,28</sup> The MCSCF calculations treat electron correlation in a more balanced manner. For example, in the MCSCF(8,8) calculations, the numbers of configurations contributing to the triplet state compared to those contributing to the singlet state (T/S) are 596/480 for 1, 604/480 for 2, and 300/264 for 3. In contrast, the ratios are 654 009/319 001 for 1, 654 327/319 399 for 2, and 327 039/160 069 for 3 at the CISD level.

The CCCI method described by Carter and Goddard specifically addresses some of the inherent inconsistencies in the CISD method. This is accomplished by applying a CI-contraction scheme that leads to balanced (albeit considerably smaller) correlation spaces for singlet and triplet states in which the maximum number of open-shell electrons per configuration is exactly the same, such as it would be in a full CI calculation.<sup>27</sup> Application of CCCI calculations to 1-3 using various different basis sets leads to systematically larger singlet-triplet splittings, indicating a differential stabilization of the singlet state in all three isomers. The increase in  $\Delta E_{ST}$  is largest for 1 (3.1-5.6 kcal/mol) and smallest for 3 (0.2-0.6 kcal/mol) compared to the CISD/6-31G\* and CISD/pVDZ values (before the DV2 correction). An evaluation of the basis set dependence for the CCCI results is obscured by the slight differences in the geometries used, although the effects appear to be relatively minor. The CCCI wave functions are well balanced, e.g., with the pVTZ basis set, the triplet/singlet configuration ratios are 2999/2945 for 1, 2935/3017 for 2, and 1521/1546 for 3. The ratios obtained with the other basis sets are similar.

At the CCCI/pVTZ//D level, the calculated  $\Delta E_{ST}$  value for 1, after correction for the 0.4 kcal/mol difference in zero-point energies, is 36.8 kcal/mol—only 0.9 kcal/mol lower than the experimentally-determined splitting.<sup>5</sup> The calculated splittings for 2 and 3 at this level are 17.2 and 2.2 kcal/mol, respectively. However, these results should be interpreted with some degree of caution since the numbers of configurations used to estimate the correlation energy for 1-3 represent only a small fraction (0.4-1%) of those generated in the CISD calculations. Moreover, it has been argued that the CCCI method may also have an inherent bias—in this case, one that favors singlet states,<sup>28,75</sup> that is, the CCCI method when used in conjunction with a "complete" basis set could actually *overestimate*  $\Delta E_{ST}$  for open-shell systems with singlet ground states. A plausible means to overcome this bias would be to include additional configurations in the CI

(74) (a) Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* 1973, 95, 6649. (b) Borden, W. T. *Modern Molecular Orbital Theory for Organic Chemists*, Prentice-Hall: Englewood Cliffs, NJ, 1975; p 11.

(75) This is still a matter of some debate, cf. ref 27d and Khodabandeh, S.; Carter, E. A. *J. Phys. Chem.* 1993, 97, 4360.



**Table VI.** Biradical Separation Energies (kcal/mol) for 1, 2, and 3<sup>a,b</sup>

level	geom- etry	1		2		3	
		T	S	T	S	T	S
MCSCF(2,2)/3-21G	A	-5.4	24.1	-1.9	8.9	-0.6	0.5
MCSCF(8,8)/3-21G	A	-4.8	30.3	-1.5	10.9	-0.8	2.5
MCSCF(2,2)/6-31G*	B	-4.5	22.9	-1.9	11.1	-0.4	0.1
MCSCF(2,2)/6-311G**	C	-4.6	24.0	-1.9	11.2	-0.6	0.2
MCSCF(8,8)/3-21G	D	-4.9	30.4	-1.5	10.8	-0.8	2.5
MCSCF(8,8)/6-31G*	B	-4.1	29.2	-1.6	13.7	-0.6	1.9
MCSCF(8,8)/pVDZ	D	-4.1	29.5	-1.6	13.5	-0.6	1.8
CISD/6-31G*	B	-5.5	26.3	-2.3	13.6	-0.7	0.8
CISD + DV2/6-31G*	B	-5.8	27.4	-2.3	14.3	-0.8	1.4
CISD/pVDZ	D	-5.4	25.8	-2.4	13.3	-0.7	1.1
CISD + DV2/pVDZ	D	-5.5	26.8	-2.4	13.9	-0.9	1.6
CCCI/6-31G*	B	-3.5	31.4	-1.6	15.8	-0.3	1.7
CCCI/pVDZ	B	-3.4	31.8	-1.5	16.2	-0.4	1.8
CCCI/6-311G**	C	-3.6	32.8	-1.5	16.2	-0.4	1.9
CCCI/pVTZ	C	-3.7	33.1	-1.5	16.3	-0.4	1.7
CCCI/pVTZ	D	-3.7	33.1	-1.5	15.6	-0.4	1.7

<sup>a</sup> Biradical separation energy defined in Scheme I; see text. <sup>b</sup> Corrected for the zero-point energy difference and temperature (298 K).

calculation derived from all symmetry-allowed single excitations out of all valence orbitals, as is done in the related DCCI method.<sup>28</sup> Nevertheless, in view of the fact that the computed singlet-triplet splitting for 1 is still lower than the experimental value and that the CCCI results for 2 and 3 are nearly identical to the results obtained from the potentially "triplet-biased" CISD method, it seems unlikely that the differential stabilization of the singlet states is very large. We therefore conclude that the singlet-triplet splittings for 1-3 calculated at the CCCI/pVTZ//D level are realistic estimates of the actual values. Thus, the following values are assigned,  $\Delta E_{ST}(1) = 36 \pm 2$  kcal/mol,  $\Delta E_{ST}(2) = 17 \pm 1$  kcal/mol, and  $\Delta E_{ST}(3) = 2.2 \pm 0.5$  kcal/mol, where the estimated uncertainties are intended to partially reflect the CISD + DV2 results and to accommodate a potential singlet bias in the CCCI calculations.

**Biradical Separation Energies and Heats of Formation.** The biradical separation energies (BSE) listed in Table VI provide a direct measure of the energetic effects of having two radical sites in the same vs separate benzene molecules. They can also be used in conjunction with the experimental heats of formation for benzene and the phenyl radical according to eq 2 to derive estimates of the absolute heats of formation of 1-3 for comparison with the experimentally-determined values<sup>45,46</sup> as well as with the values predicted from promotion energy models.<sup>70</sup> With the larger active space MCSCF calculations and the CCCI calculations carried out with the larger basis sets, the ranges of triplet BSE values (in kcal/mol; corrected for zero-point energy differences and temperature) are  $-3.8 \pm 0.3$  for 1,  $-1.5 \pm 0.1$  for 2, and  $-0.4 \pm 0.2$  for 3. At these same levels of theory, the average singlet BSE values are  $31 \pm 2$ ,  $15.0 \pm 1.7$ , and  $1.9 \pm 0.1$  for 1, 2, and 3, respectively. The BSE results from the CISD calculations differ somewhat in that the triplet states all appear to be ca. 50% (0.3-1.5 kcal/mol) less stable compared to the bond additivity estimate, whereas the singlet states all appear to be about 10% (0.1-4 kcal/mol) more stable. Nevertheless, the BSE values all generally indicate that hydrogen-atom transfer from benzene to 1-3 is endothermic for the singlet states and slightly exothermic for the triplet states, that is, relative to the phenyl radical, two radical sites in the same molecule are stabilized if they are singlet coupled but destabilized if they are triplet coupled. In other words, the second C-H bond strength in benzene is weaker than the first if a singlet benzyne is formed but stronger if a triplet benzyne is produced.

The relative destabilization of the triplet-state benzynes can be understood in terms of the overlap-repulsion<sup>74</sup> effects that give rise to the isomer stability ordering  $E(3) < E(2) < E(1)$ . It is a natural consequence of the unsymmetrical splitting of the two nonbonding  $\sigma$  orbitals ( $\Phi_S$  and  $\Phi_A$ ) with respect to the nominal

$\sigma$  nonbonding energy level associated with the phenyl radical (Figure 1). Single occupancy of the higher-lying  $\Phi_A$  orbitals in the triplet states of 1 and 2 is destabilizing relative to that in the phenyl radical; the energy penalty is largest for 1 for which the 1,2-antibonding interaction is greatest and smaller for 2 where the 1,3-overlap is much weaker. The triplet state of 3 is only slightly destabilized compared to two separate phenyl radicals (ca. 0.4 kcal/mol), presumably due to the ring-strain ( $\sigma$ ) effects and, perhaps, the disruption of  $\pi$  overlap caused by geometric distortions relative to those in benzene. Note that these effects should also be present in 1 and 2.

The availability of a consistent set of BSE values for the benzynes allows us to evaluate the valence-electron-promotion-energy model proposed by Chen<sup>70,76</sup> for the thermochemistry of biradicals possessing singlet ground states. This zeroth-order model equates the energy of the triplet state with that derived from a simple bond-strength additivity calculation, while the singlet ground state is presumed to be lower in energy by an amount equal to the singlet-triplet splitting. Thus, for the benzynes, the implicit assumption is that the triplet BSE values should all equal zero. For triplet 2 and triplet 3, this assumption appears to be justified since the average BSE values are relatively small. However, the calculations suggest that this assumption is in error by 4-5 kcal/mol for triplet 1. As a result, any estimate of the absolute heat of formation for singlet 1, based on correcting the bond-energy additivity estimate by the corresponding  $\Delta E_{ST}$  value, would be too high (too positive) by about 4-5 kcal/mol.<sup>70</sup> Thus, useful promotion-energy models for biradical thermochemistry must take into account the possible destabilization of the triplet states via overlap repulsion.<sup>74</sup> The energy of the triplet state can be equated with the bond-strength additivity estimate only when the radical sites are relatively remote and noninteracting.<sup>77</sup>

The absolute heats of formation for the singlet ground states of 1-3 have been computed from the corresponding singlet BSE values listed in Table VI and the experimental heats of formation for benzene and the phenyl radical according to eq 2. The heats of formation thus derived are listed in Table VII along with the experimentally-determined heats of formation for the three benzynes.<sup>45</sup> For comparison, the heat of formation of a "generic" didehydrobenzene,  $C_6H_4$ , can be obtained from the simple bond-strength additivity relationship shown in eq 3.

$$\Delta H_{f,298}^\circ(C_6H_4) = \Delta H_{f,298}^\circ(C_6H_6) + 2DH_{298}^\circ[C_6H_5-H] - 2\Delta H_{f,298}^\circ(H) \quad (3)$$

Using  $\Delta H_{f,298}^\circ(C_6H_6) = 19.8 \pm 0.1$  kcal/mol,<sup>63</sup>  $\Delta H_{f,298}^\circ(H) = 52.1 \pm 0.0$  kcal/mol,<sup>63</sup> and  $DH_{298}^\circ[C_6H_5-H] = 112 \pm 2$  kcal/mol,<sup>64</sup> we obtain a value of  $140 \pm 3$  kcal/mol, where the uncertainty is the square root of the sum of the squares of the component uncertainties.

The large active space, large basis set MCSCF and CISD calculations predict heats of formation of 107-114 kcal/mol for 1, 124-127 kcal/mol for 2, and 138-139 kcal/mol for 3, where the values at the upper end of each range are those derived from the CISD + DV2 results. The CCCI-derived heats of formation are consistently lower than those with all other methods, which may be a reflection of the potential "singlet bias" in this method described earlier. However, the heat of formation for *o*-benzyne derived from the CCCI/pVTZ//D calculation (107 kcal/mol) is in excellent agreement with the three independent experimental

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(77) (a) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 5. (b) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279. (c) Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; J. Wiley and Sons: New York, 1982; Chapter 3.

(78) Jorgensen, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic Press: New York, 1973. Jorgensen, W. L. *QCPE* **1980**, *12*, program 340.

Table VII. Calculated Heats of Formation (kcal/mol) for the Singlet States of 1, 2, and 3<sup>a</sup>

level	geom-etry	1	2	3
MCSCF(2,2)/3-21G	A	116	131	140
MCSCF(8,8)/3-21G	A	110	129	138
MCSCF(2,2)/6-31G*	B	117	129	140
MCSCF(2,2)/6-31G**	C	116	129	140
MCSCF(8,8)/3-21G	D	110	129	138
MCSCF(8,8)/6-31G*	B	111	127	138
MCSCF(8,8)/pVDZ	D	111	127	138
CISD/6-31G*	B	114	127	139
CISD + DV2/6-31G*	B	113	126	139
CISD/pVDZ	D	114	127	139
CISD + DV2/pVDZ	D	113	126	138
CCCI/6-31G*	B	109	124	139
CCCI/pVDZ	B	108	124	138
CCCI/6-311G**	C	107	124	138
CCCI/pVTZ	C	107	124	138
CCCI/pVTZ	D	107	125	138
exp		106 ± 3 <sup>c</sup>	116 ± 3 <sup>c</sup>	128 ± 3 <sup>c</sup>
		105 ± 3 <sup>d</sup>		
		105 ± 5 <sup>e</sup>		
bond additivity <sup>b</sup>		140 ± 3		

<sup>a</sup> Calculated from singlet BSE values (Table VI) using eq 2 and  $\Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_6) = 19.8 \pm 0.1$  kcal/mol and  $\Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_5) = 80 \pm 2$  kcal/mol.<sup>64</sup> <sup>b</sup> Calculated using eq 3 and data indicated in the text. <sup>c</sup> Reference 45. <sup>d</sup> Reference 46a. <sup>e</sup> Reference 46b.

measurements, including the value determined in this laboratory by CID threshold analysis.<sup>45,46</sup> In view of the excellent performance of this same method for predicting the singlet-triplet splitting for *o*-benzyne (cf. Table II), we conclude that CCCI/pVTZ calculations can provide realistic predictions of the thermochemical and electronic properties of benzyne. The heats of formation for 2 and 3 predicted by this method are 125 and 138 kcal/mol, respectively. Given the uncertainty in the experimental value for  $\Delta H_{f,298}^{\circ}(\text{C}_6\text{H}_5)$  of  $\pm 2$  kcal/mol<sup>64</sup> and the probable error in the BSE calculations ( $\pm 2$  kcal/mol estimated), we conservatively assign an uncertainty of  $\pm 3$  kcal/mol to these calculated heats of formation.

Having chosen the CCCI/pVTZ results as the most reliable, we present in Figure 2 a schematic diagram of the theoretically-predicted heats of formation for both the singlet and triplet states of the three benzyne along with the  $140 \pm 3$  kcal/mol value for  $\Delta H_f(\text{C}_6\text{H}_4)$  derived from the bond-strength additivity calculation (eq 3). Also shown are the measured heats of formation for 1–3 from the CID threshold experiments.<sup>45</sup> The discrepancy between the predicted heats of formation for 2 and 3 and the experimental values derived from the CID measurements immediately stands out, i.e., the measured heats of formation for 2 and 3 appear to be 9–10 kcal/mol lower than the CCCI/pVTZ values. Furthermore, although the reported difference between  $\Delta H_f(2)$  and  $\Delta H_f(3)$  ( $12 \pm 4$  kcal/mol) is close to the calculated difference of 13 kcal/mol, the measured differences from  $\Delta H_f(1)$  are both 9–10 kcal/mol larger than the predicted values. We must therefore conclude that the experimentally-determined heats of formation for *m*- and *p*-benzyne are both too low by 9–10 kcal/mol.

The credibility of these calculations, as indicated by their ability to correctly reproduce the absolute heat of formation and singlet-triplet splitting of *o*-benzyne, compelled us to seek an explanation for the apparent failure of the measurements with *m*- and *p*-benzyne but success with the *ortho* isomer using the same experimental method. In a forthcoming paper, we will present an account of this investigation and of the ultimate discovery of the source of the discrepancy.<sup>48</sup> It will be shown that the *m*- and *p*-chlorophenyl anion precursors used for determining  $\Delta H_f(2)$

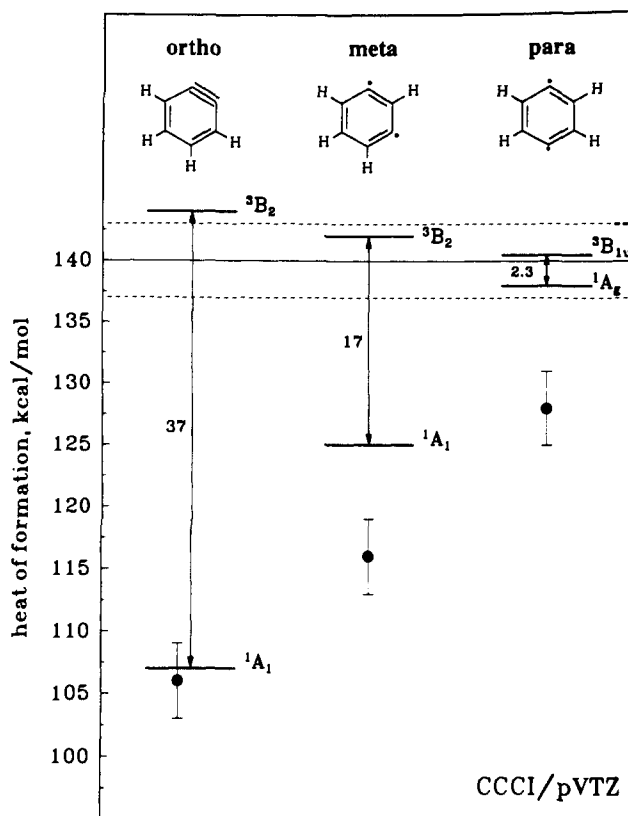


Figure 2. Calculated heats of formation for the singlet and triplet states of *o*-, *m*-, and *p*-benzyne derived from the corresponding BSE values (Scheme I; eq 2) obtained at the CCCI/pVTZ/MCSCF(8,8)/3-21G level of theory. The heat of formation for a dihydrobenzene molecule, based on bond-strength additivity ( $140 \pm 3$  kcal/mol), is indicated by the horizontal and dashed lines, and the experimental heats of formation for each benzyne taken from ref 45 ( $\pm 3$  kcal/mol) are indicated with solid circles.

and  $\Delta H_f(3)$  had undergone partial acid-catalyzed isomerization to the *o*-chlorophenyl anion, thereby leading to reduced CID thresholds and corresponding low values for the benzyne heats of formation. Revised thermochemical measurements will be described for *m*- and *p*-benzyne, free of the contamination problem, which provide a satisfying reconciliation of experiment and theory.

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**Supplementary Material Available:** Calculated harmonic vibrational frequencies (unscaled) for the singlet and triplet states of *o*-, *m*-, and *p*-benzyne, benzene, and the phenyl radical obtained at the MCSCF(2,2), HF, and ROHF levels of theory with a 6-31G\* basis set (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.