

# Problematic *p*-benzyne: Orbital instabilities, biradical character, and broken symmetry

T. Daniel Crawford<sup>a)</sup>

*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24060*

Elfi Kraka

*Department of Theoretical Chemistry, Göteborg University, Reutersgatan 2, S-41320 Göteborg, Sweden*

John F. Stanton

*Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712*

Dieter Cremer<sup>a)</sup>

*Department of Theoretical Chemistry, Göteborg University, Reutersgatan 2, S-41320 Göteborg, Sweden*

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The equilibrium geometry, harmonic vibrational frequencies, and infrared transition intensities of *p*-benzyne were calculated at the MBPT(2), SDQ-MBPT(4), CCSD, and CCSD(T) levels of theory using different reference wave functions obtained from restricted and unrestricted Hartree-Fock (RHF and UHF), restricted Brueckner (RB) orbital, and Generalized Valence Bond (GVB) theory. RHF erroneously describes *p*-benzyne as a closed-shell singlet rather than a singlet biradical, which leads to orbital near-instabilities in connection with the mixing of orbital pairs  $b_{1u}-a_g$  (HOMO-LUMO),  $b_{2g}-a_g$  (HOMO-1-LUMO), and  $b_{1g}-a_g$  (HOMO-2-LUMO). Vibrational modes of the corresponding symmetries cause method-dependent anomalous increases (unreasonable force constants and infrared intensities) or decreases in the energy (breaking of the  $D_{2h}$  symmetry of the molecular framework of *p*-benzyne). This basic failure of the RHF starting function is reduced by adding dynamic electron correlation. However RHF-MBPT(2), RHF-SDQ-MBPT(4), RHF-CCSD, RB-CCD, and RHF-CCSD(T) descriptions of *p*-benzyne are still unreliable as best documented by the properties of the  $b_{1u}$ -,  $b_{2g}$ -, and  $b_{1g}$ -symmetrical vibrational modes. The first reliable spin-restricted description is provided when using Brueckner orbitals at the RB-CCD(T) level. GVB leads to exaggerated biradical character that is reduced at the GVB-MP2 level of theory. The best results are obtained with a UHF reference wave function, provided a sufficient account of dynamic electron correlation is included. At the UHF-CCSD level, the triplet contaminant is completely annihilated. UHF-CCSD(T) gives a reliable account of the infrared spectrum apart from a CCH bending vibrational mode, which is still in disagreement with experiment. © 2001 American Institute of Physics. [DOI: 10.1063/1.1373433]

## I. INTRODUCTION

Singlet biradicals such as 1,4-didehydrobenzene (commonly known as *p*-benzyne)<sup>1,2</sup> have attracted considerable attention in the last 10 years due to their potential role as antitumor agents.<sup>3-12</sup> Naturally occurring enediynes can dock into the minor groove of DNA and, if properly triggered, can undergo a Bergman cyclization reaction<sup>13-19</sup> to produce *p*-benzyne or one of its derivatives.<sup>3-12</sup> Contrary to doublet radicals, which attack biochemical compounds in an unselective manner, biradical *p*-benzyne abstracts H atoms from well-defined positions in DNA,<sup>20-23</sup> leading to a cleavage of the DNA strands and the death of the parent cell.<sup>3-12</sup> Based on the reactivity of biradicals such as *p*-benzyne it is possible to design enediyne drugs with high antitumor or anticancer activity.<sup>24</sup>

The properties of *p*-benzyne, in particular its stereoselectivity, are a result of the fact that its ground state state is a singlet (*S*) rather than a triplet (*T*).<sup>1,2,13-19,25,26</sup> Since singlet

biradicals are difficult to detect and analyze by experimental means,<sup>1,2,20-23,25,26</sup> most of their properties have been determined by quantum chemical calculations, which have become an indispensable tool in this connection.<sup>1,24,27-46</sup> High-level theoretical investigations of *p*-benzyne have been carried out with wave-function-based theories such as coupled cluster (CC),<sup>47-53</sup> while work on the larger, derivative enediyne systems is increasingly carried out with density functional theory (DFT).<sup>54-62</sup> However, because of the inherent multiconfigurational character of biradical systems such as *p*-benzyne, both CC and DFT face considerable challenges in predicting their properties.<sup>63</sup>

Single determinant approaches [e.g., Hartree-Fock (HF), or correlation methods based on a HF reference] can often fail to describe biradicals correctly. Consistently reliable descriptions can only be obtained with multireference approaches such as MRCI<sup>64</sup> or MRCC,<sup>65</sup> orbital-optimized methods such as VOO-CCD<sup>66,67</sup> or VOO-CCD(2),<sup>68</sup> or, alternatively, a single-determinant method recovering high amounts of dynamic electron correlation (depending on the system in question). A method such as CCSD(T)

<sup>a)</sup>Authors to whom correspondence should be addressed.

(the CC single- and double-excitation approach, including a perturbative correction for triple excitations)<sup>52,69</sup> will compensate under certain circumstances for most of the deficiencies of a single-determinant reference and may therefore provide a reasonable account of the properties of biradicals.<sup>24,27,28,36–38,41</sup> In this way, the rather high computational expense and the often ad hoc choices of active spaces associated with multireference approaches can be avoided. Nevertheless, considerable care has to be taken when systems such as *p*-benzyne are described using standard single-determinant methods.

Quantum chemical calculations often suffer from a phenomenon known commonly as spatial symmetry breaking, in which, in the absence of appropriate constraints, the model electronic wave function fails to transform as an irreducible representation of the molecular point group.<sup>70–75</sup> In conventional *ab initio* calculations, these problems are manifested within the molecular orbitals themselves, and their chemical origins can often be explained in valence-bond terms as a competition between orbital size effects and resonance interactions.<sup>76–78</sup> Infamous examples of symmetry breaking include NO<sub>3</sub>,<sup>79–83</sup> the allyl radical,<sup>73,84</sup> and the formylxyl radical.<sup>78,85–89</sup> A close connection exists between symmetry-breaking, molecular orbital near-instabilities, and qualitatively incorrect predictions of molecular properties such as equilibrium structures, harmonic vibrational frequencies, electric polarizabilities, and infrared transition intensities. Several recent studies have explained how such instabilities can lead even highly correlated methods such as CC theory to yield nonsensical results for such properties.<sup>89–91</sup>

The objectives of this work are threefold. First, we show that a restricted HF (RHF) description of *p*-benzyne suffers from orbital near-instabilities that lead to serious flaws in correlation-corrected methods based on this reference function. We investigate how dynamic electron correlation effects can compensate for the deficiencies of the reference wave function and how this influences the calculated properties. Second, we contrast RHF based descriptions of *p*-benzyne with those obtained from a restricted Brueckner (RB) orbital or a spin unrestricted HF (UHF) reference function. The latter are generally considered to be inadequate because of spin contamination inherent in the UHF reference.<sup>92–100</sup> However, in the case of *p*-benzyne, we show correlation-corrected UHF methods provide highly reliable results that can be used for the analysis of the experimental data. Accordingly, the third objective of this work is to critically reanalyze the measured infrared (IR) spectrum.<sup>1</sup> In this regard, we also consider previous CCSD(T) studies of the Bergman reaction and evaluate their reliability.

For the RHF- and UHF-based MBPT(2), SDQ-MBPT(4), CCSD, and CCSD(T) methods, harmonic vibrational frequencies were computed using analytic second derivatives,<sup>101–103</sup> while for the Brueckner-based methods, vibrational frequencies were computed using finite differences of either analytic first derivatives<sup>53,104</sup> or energies. All CC and MBPT calculations reported in this work were carried out with the ACESII program system<sup>105</sup> and all GVB calculations with the COLOGNE 99 program system.<sup>106</sup> (See EPAPS, Ref. 127.)

## II. THE ELECTRONIC STRUCTURE OF *p*-BENZYNE: BASIC REQUIREMENTS FOR A WAVE-FUNCTION-BASED DESCRIPTION

The peculiar electronic nature of *p*-benzyne results from the fact that the singly occupied orbitals on carbon atoms one and four form symmetric and an antisymmetric combinations by through-space interactions ( $a_g$  below  $b_{1u}$ ), which are nearly degenerate. These orbitals can interact with  $\sigma(\text{CC})$  and  $\sigma^*(\text{CC})$  orbitals (Fig. 1), which leads to a stabilization of the  $b_{1u}$  MO, but a destabilization of the  $a_g$  MO [Fig. 1(a)] so that the energy of the former drops below that of the latter. This well-known through-bond interaction<sup>1,24,27,28,45,107,108</sup> between the unpaired electrons at C1 and C4 has two important consequences: (a) The unpaired electrons become more coupled and consequently, the biradical character of *p*-benzyne is reduced. (b) The (H)CC(H) bonds C1–C2, C3–C4, C4–C5, C6–C1 are shortened while the CC(H) bonds C2–C3 and C5–C6 are lengthened [Fig. 1(d)].

Since the HOMO–LUMO gap is still relatively small, it is possible that both the  $b_{1u}$ -symmetric HOMO and the  $a_g$ -symmetric LUMO are important for a correct description of the <sup>1</sup>A<sub>g</sub> ground state of *p*-benzyne. Hence, the RHF ground state electronic configuration ( $\cdots b_{1u}^2 a_g^0$ ) can mix in the exact wave function with the doubly excited singlet configuration ( $\cdots b_{1u}^0 a_g^2$ ) thus lending the <sup>1</sup>A<sub>g</sub> ground state biradical character due to the fact that one electron is preferentially at C1, the other at C4. This must not be confused with the excited open-shell singlet and triplet biradical states of *p*-benzyne (with the electron configuration  $\cdots b_{1u}^1 a_g^1$ ), which possess 100% biradical character.

Even if the two unpaired electrons are well separated, they can interact via spin polarization, which can be explained by using the intraatomic Hund rule and electron coupling in bond pairs. As indicated in Fig. 1(c) spin polarization implies that electrons at C4 possess spin opposite to those at C1. If electrons at C1 have  $\alpha$  spin, in a singlet state stabilizing  $\beta$ – $\beta$  interactions will be encountered at C4 while in a triplet state destabilizing  $\beta$ – $\alpha$  interactions must occur at C4. Hence, spin polarization is another reason why the singlet state of *p*-benzyne is more stable than its lowest triplet state.

Approximations in wave-function-based methods used to describe *p*-benzyne can lead to erroneous descriptions of the properties of the biradical. In a two-configuration description, such as that provided by a GVB wave function,<sup>109</sup> the natural orbitals  $\varphi_a$  and  $\varphi_b$  [similar to  $\psi_a$  and  $\psi_b$  in Fig. 1(b)] are used to form the GVB pair orbitals, which are closely related to the  $b_{1u}$ -HOMO and the  $a_g$ -LUMO of the RHF description (cf. Fig. 2). The first GVB pair orbital is occupied by 1.18 electrons, the second by 0.82 electrons according to the calculated natural orbital occupation numbers (NOON).<sup>110</sup> The similarity of the NOON values is consociate with a low overlap between  $\varphi_a$  and  $\varphi_b$  (0.090) and a strong biradical character of 82%. The partial occupation of both the GVB orbitals and the resulting high biradical character imply that the CC(H) and (H)CC(H) bonds adjust in length relative to their RHF counterparts (from 1.328 and 1.489 to 1.370 and 1.401 Å, respectively; cf. Table I). There-

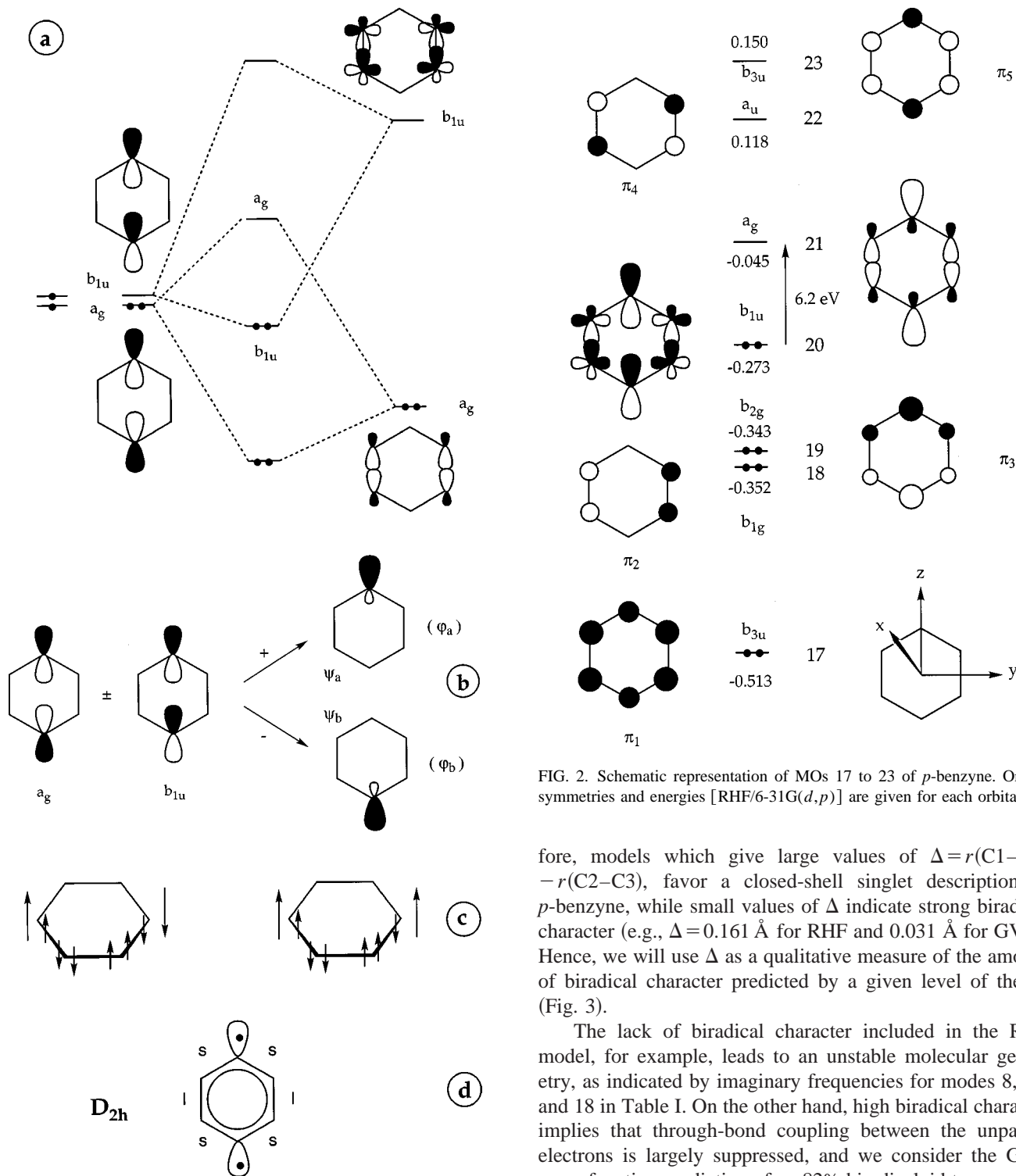


FIG. 1. (a) Schematic representation of orbital mixings leading to through-bond interactions and spin coupling between the single electrons of *p*-benzyne. (b) HOMO–LUMO mixing leading to the orbitals  $\psi_a$  and  $\psi_b$  used in the UHF description. The GVB natural orbitals  $\varphi_a$  and  $\varphi_b$  resemble  $\psi_a$  and  $\psi_b$ . (c) Schematic representation of spin polarization in the singlet and the triplet state of *p*-benzyne using the intraatomic Hund rule and pair coupling of bonding electrons. (d) Distortion of the  $C_6$  hexagon caused by through bond interactions between the single electrons. Symbols l and s denote a lengthening and a shortening of the CC bonds, respectively.

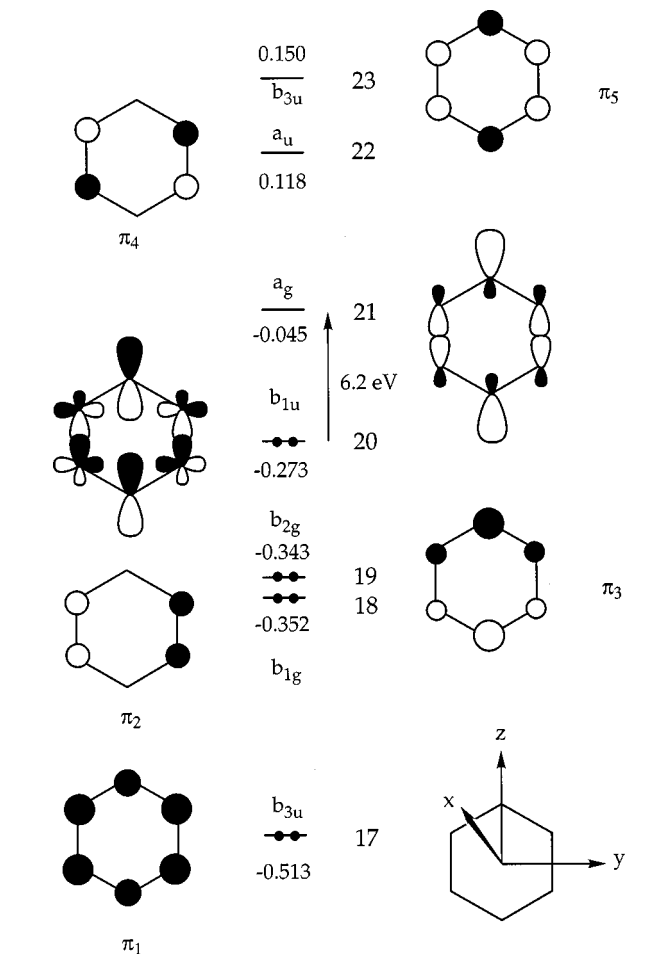


FIG. 2. Schematic representation of MOs 17 to 23 of *p*-benzyne. Orbital symmetries and energies [RHF/6-31G(*d,p*)] are given for each orbital.

fore, models which give large values of  $\Delta = r(C1-C2) - r(C2-C3)$ , favor a closed-shell singlet description of *p*-benzyne, while small values of  $\Delta$  indicate strong biradical character (e.g.,  $\Delta = 0.161 \text{ \AA}$  for RHF and  $0.031 \text{ \AA}$  for GVB). Hence, we will use  $\Delta$  as a qualitative measure of the amount of biradical character predicted by a given level of theory (Fig. 3).

The lack of biradical character included in the RHF model, for example, leads to an unstable molecular geometry, as indicated by imaginary frequencies for modes 8, 10, and 18 in Table I. On the other hand, high biradical character implies that through-bond coupling between the unpaired electrons is largely suppressed, and we consider the GVB wave function prediction of an 82% biradicaloid to represent an upper limit for pure-singlet wave functions. As indicated in Table I, the  $D_{2h}$ -symmetrical equilibrium geometry of *p*-benzyne is stable at the GVB level.

Alternatively, one could choose to use a broken-symmetry unrestricted HF (BS-UHF) wave function to describe *p*-benzyne.<sup>70–75</sup> Such a wave function is constructed by mixing HOMO  $\psi_{b_{1u}}$  and LUMO  $\psi_{a_g}$  to give the new orbitals,

$$\psi_a = \cos \theta \psi_{b_{1u}} + \sin \theta \psi_{a_g}, \quad (1)$$

$$\psi_b = -\sin \theta \psi_{b_{1u}} + \cos \theta \psi_{a_g}. \quad (2)$$

TABLE I. Geometrical parameters, harmonic vibrational frequencies, and IR intensities for the  $^1A_g$  ground state of *p*-benzyne as obtained by various methods and the 6-31G(*d,p*) basis set.<sup>a</sup>

Parameter	MBPT(2)			SDQ-MBPT(4)			CCSD			CCSD(T)				
	RHF	UHF	GVB	RHF	UHF	GVB	RHF	UHF	RHF	UHF	RB-CCD <sup>b</sup>	RHF	UHF	RB-CCD(T) <sup>b</sup>
$r(C_1-C_2)$	1.328	1.391	1.370	1.381	1.361	1.368	1.361	1.371	1.360	1.378	1.360	1.382	1.379	1.383
$r(C_2-C_3)$	1.489	1.411	1.401	1.421	1.385	1.433	1.444	1.396	1.449	1.410	1.447	1.426	1.416	1.424
$\Delta$	0.161	0.020	0.031	0.040	0.024	0.065	0.083	0.025	0.089	0.032	0.087	0.044	0.037	0.041
$\omega_1(a_g)$	3414	3370	3379	3289	3304	3298	3298	3292	3299	3278	3300	3264	3258	3263
$\omega_2(a_g)$	1379	1538	1646	1327	1653	1356	1338	1589	1344	1531	1337	1342	1498	1338
$\omega_3(a_g)$	1256	1194	1250	1185	1220	1207	1194	1207	1193	1192	1194	1174	1183	1173
$\omega_4(a_g)$	980	993	1116	1026	1067	1027	1025	1052	1017	1047	1021	1018	1044	1017
$\omega_5(a_g)$	775	630	662	698	652	648	699	639	696	625	694	608	620	598
$\omega_6(a_u)$	1004	965	1080	927	1077	925	937	1028	923	959	923	913	938	915
$\omega_7(a_u)$	489	390	464	454	458	440	454	432	447	408	446	417	407	415
$\omega_8(b_{1g})$	961 <i>i</i>	806	897	2790	903	708	891	858	426	794	582	349	771	770
$\omega_9(b_{2g})$	946	943	1042	843	1031	877	842	986	860	919	863	832	897	833
$\omega_{10}(b_{2g})$	310 <i>i</i>	673	715	23161	696	518	1179	670	504	606	519	5612 <i>i</i>	577	596
$\omega_{11}(b_{3g})$	3396	3353	3362	3280	3291	3292	3285	3276	3285	3263	3286	3250	3242	3234
$\omega_{12}(b_{3g})$	1869	1624	1785	1678	1808	1686	1737	1735	1728	1694	1729	1657	1683	1624
$\omega_{13}(b_{3g})$	1335	1369	1397	1292	1341	1302	1299	1336	1297	1323	1299	1301	1309	1258
$\omega_{14}(b_{3g})$	592	625	640	566	610	578	572	606	576	594	577	586	584	594
$\omega_{15}(b_{1u})$	3391	3353	3361	3249	3288	3282	3272	3275	3283	3262	3283	3238	3241	3246
$\omega_{16}(b_{1u})$	1504	1559	1604	1470	1552	1475	1480	1533	1486	1506	1487	1482	1489	1494
$\omega_{17}(b_{1u})$	1164	1074	1124	1068	1116	1090	1094	1095	1106	1074	1098	1058	1067	1049
$\omega_{18}(b_{1u})$	621 <i>i</i>	1024	1050	5788	972	952	2698 <i>i</i>	977	1032	967	911	3739 <i>i</i>	953	999
$\omega_{19}(b_{2u})$	3415	3368	3378	3290	3305	3293	3298	3291	3299	3277	3300	3263	3257	3245
$\omega_{20}(b_{2u})$	1546	1411	1457	1597	1474	1489	1432	1438	1435	1400	1437	1388	1391	1380
$\omega_{21}(b_{2u})$	1144	1388	1297	1345	1260	1267	1199	1257	1168	1264	1173	1275	1256	1276
$\omega_{22}(b_{2u})$	306	1117	1097	1104	1114	1084	1020	1102	955	1088	965	1068	1079	1060
$\omega_{23}(b_{3u})$	812	786	853	771	861	746	767	830	755	781	756	750	766	751
$\omega_{24}(b_{3u})$	519	443	492	469	492	456	475	474	469	445	469	443	439	442
$I_{15}(b_{1u})$	31	10	6	X <sup>c</sup>	1	...	767	3	0	4	1	1107	4	...
$I_{16}(b_{1u})$	23	9	10	30	10	...	29	9	8	6	0	10	5	...
$I_{17}(b_{1u})$	18	2	11	18	18	...	41	12	2	9	23	19	10	...
$I_{18}(b_{1u})$	X <sup>c</sup>	7	5	X <sup>c</sup>	3	...	X <sup>c</sup>	5	28	7	68	X <sup>c</sup>	10	...
$I_{19}(b_{2u})$	6	30	18	2	5	...	1	12	0	13	1	10	12	...
$I_{20}(b_{2u})$	15	8	8	3	5	...	5	6	5	6	5	3	6	...
$I_{21}(b_{2u})$	21	0	0	4	0	...	7	0	10	0	10	3	1	...
$I_{22}(b_{2u})$	6	1	0	3	9	...	1	6	0	4	0	2	3	...
$I_{23}(b_{3u})$	95	74	79	74	73	...	77	69	77	65	77	69	65	...
$I_{24}(b_{3u})$	34	9	14	13	14	...	16	12	15	11	15	10	12	...
$\langle \xi^2 \rangle$	0.0	1.83	0.0	0.0	1.53	0.0	0.0	...	0.0	0.980	...	0.0	0.881	...
HOMO <sup>d</sup>	2.000	1.068	1.179	1.641	1.123	...	1.691	1.117	1.687	1.108	1.677	1.305	...	...
LUMO <sup>e</sup>	0	0.932	0.821	0.355	0.860	...	0.294	0.868	0.308	0.877	0.320	0.683	...	...

<sup>a</sup>Bond lengths and difference  $\Delta = r(C_2-C_3) - r(C_1-C_2)$  in Å, frequencies in  $\text{cm}^{-1}$ , IR intensities in  $\text{km/mol}$ .<sup>b</sup>All Brueckner orbitals are spin restricted.<sup>c</sup>Computed intensity exceeds 5000  $\text{km/mol}$ .<sup>d</sup>Natural orbital occupation number of the  $b_{1u}$ -symmetric HOMO.<sup>e</sup>Natural orbital occupation number of the  $a_g$ -symmetric LUMO.

Such a mixing leads to orbitals  $\psi_a$  and  $\psi_b$  which transform as irreducible representations of the  $C_{2v}$  point group, rather than those of the higher-symmetry  $D_{2h}$  group associated with the molecular geometry. These broken-symmetry orbitals [Fig. 1(b)] are largely localized and resemble the natural orbitals  $\varphi_a$  and  $\varphi_b$  of the GVB calculation.<sup>111</sup> The open-shell

part of the BS-UHF wave function is constructed from these orbitals,

$$\Phi_{\text{open}}^{\text{BS-UHF}} = |\psi_a \overline{\psi_b}\rangle. \quad (3)$$

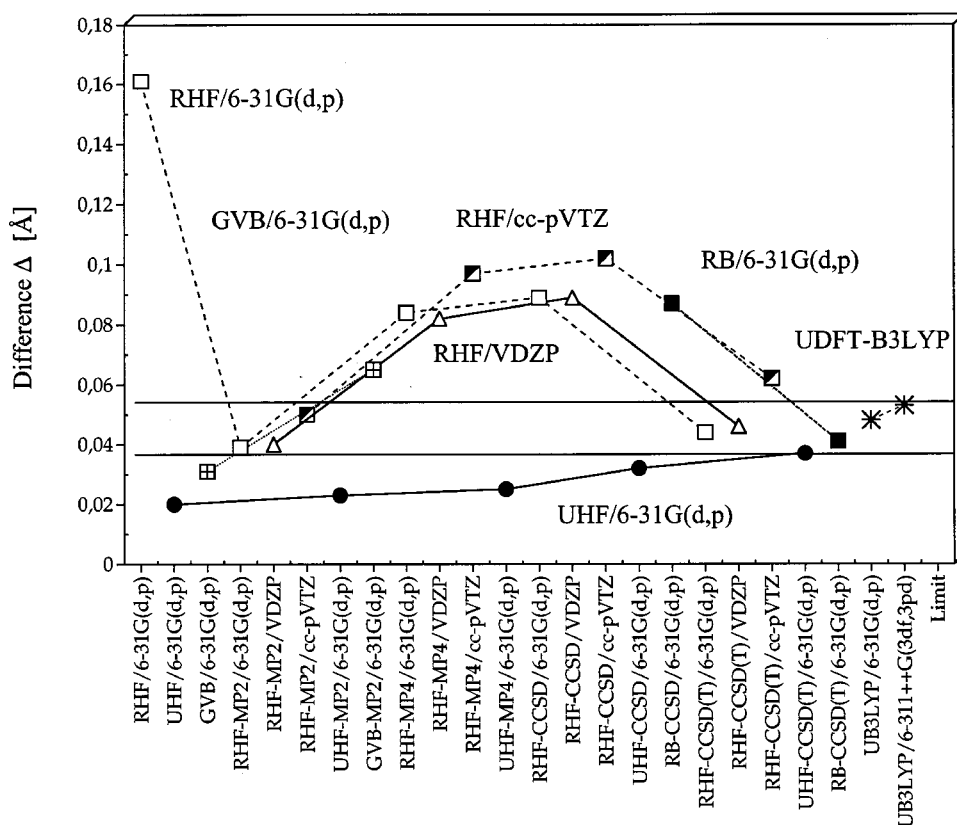


FIG. 3. Changes in the bond length difference  $\Delta$  in dependence of reference function, method, and basis set. The limiting value (denoted by the upper horizontal line) is given for the estimated UHF-CCSD(T)/cc-pVTZ result.

Hence, the  $\Phi_{\text{open}}^{\text{BS-UHF}}$  wave function can be rewritten as a mixture of singlet and triplet states (and thus with broken spin symmetry) as

$$\Phi_{\text{open}}^{\text{BS-UHF}} = \cos^2 \theta |\psi_{b_{1u}} \overline{\psi_{b_{1u}}}\rangle - \sin^2 \theta |\psi_{a_g} \overline{\psi_{a_g}}\rangle + \sqrt{2} \cos \theta \sin \theta |\psi_{b_{1u}} \overline{\psi_{a_g}}\rangle^T, \quad (4)$$

where a bar over the orbital symbol indicates  $\beta$ -spin and the triplet function ( $M_S=0$ ) is given by

$$|\psi_{b_{1u}} \overline{\psi_{a_g}}\rangle^T = \frac{1}{\sqrt{2}} (|\psi_{b_{1u}} \overline{\psi_{a_g}}\rangle - |\psi_{a_g} \overline{\psi_{b_{1u}}}\rangle). \quad (5)$$

Hence, the BS-UHF wave function mimics the GVB wave function at the price of triplet contamination. The biradical character of the BS-UHF wave function can be calculated from the optimized rotational angle  $\theta$  or from the NOON values, which both suggest 93% biradical character. However, this is the total biradical character for both the singlet state and the triplet contaminant. The calculated spin-squared expectation value,  $\langle \hat{S}^2 \rangle$ , of 1.83 suggests that actually more than one triplet contaminant plays a role in the UHF reference (see Sec. IV) thus increasing the biradical character to an unreasonable value. This is confirmed by the fact that the CC(H) and (H)CC(H) bond lengths are nearly equivalent at 1.391 and 1.411 Å,  $\Delta = 0.020$  Å (cf. Table I and Fig. 3). In addition, the calculated UHF geometry is a minimum, i.e., all vibrational frequencies are real.

In summary, each of the three reference wave functions has deficiencies. GVB and UHF appear to exaggerate the biradical character of *p*-benzyne, while RHF erroneously in-

cludes no biradical component. In addition, UHF involves a substantial admixture of triplet contamination. Furthermore, the failure to predict a correct symmetry of the molecular framework of *p*-benzyne suggests that the inadequacies of the RHF wave function may be the most serious.

### III. CORRELATION-CORRECTED DESCRIPTIONS OF *p*-BENZYNE

A reliable description of *p*-benzyne, as measured by calculated geometries, vibrational frequencies, and IR intensities (see Table I), can potentially be determined from inadequate RHF, UHF, or GVB reference wave functions through the systematic inclusion of greater and greater levels of dynamic electron correlation. Concomitantly, the true biradical character of *p*-benzyne can be obtained and the triplet contaminations of UHF-based descriptions vanish. We have investigated this issue by using several levels of theory with two different basis sets: the 6-31G(*d,p*) basis set<sup>112</sup> for comparison to previous ab initio studies, as well as Dunning's correlation-consistent polarized-valence triple-zeta (cc-pVTZ)<sup>113</sup> basis set to test the effects of varying/increasing the number of basis functions.

#### A. GVB descriptions

At the GVB-MP2 level of theory, the most important correlation contributions result from double excitations involving the  $b_{1u}$  (HOMO) and  $a_g$  (LUMO) orbitals and the  $a_u$  orbital (LUMO+1) (Fig. 2). This leads to a substantial lowering of the GVB biradical character as documented by a lengthening of the (H)CC(H) bonds (from 1.401 to 1.433 Å),

while the CC(H) bonds become only slightly shorter (the  $a_u$  orbital is nonbonding with regard to these bonds, cf. Fig. 2). The value of  $\Delta$  increases for GVB-MP2 to 0.065 Å corresponding to a reduction of the biradical character to about 60%. As in the case of the GVB reference, the GVB-MP2 equilibrium geometry is stable.

## B. RHF descriptions

Inclusion of pair correlation effects as described by double excitations represents an important correction to the RHF reference wave function. At the RHF-MBPT(2) level, the major contribution comes from the  $b_{1u} \rightarrow a_g$  excitation ( $T_2 = 0.335$ ),<sup>114</sup> which leads to a shortening of the (H)CC(H) and a lengthening of the CC(H) bonds. The value of  $\Delta$  in this case is reduced from 0.161 to 0.039 Å. According to the RHF-MBPT(2) NOON values, the  $a_g$ -LUMO is occupied by 0.355 electrons while the population of the  $b_{1u}$ -HOMO is reduced from 2.0 to 1.641, suggesting that the biradical character increases to about 36%.

While the equilibrium geometry at the RHF-MBPT(2) level is an energy minimum as indicated by the presence of only stable vibrational modes, several of the frequencies are clearly nonsensical: (a) the RHF-MBPT(2) prediction for  $\omega_8(b_{1g})$  of 2790 cm<sup>-1</sup> is substantially different from its UHF, GVB, UHF-MBPT(2), and GVB-MBPT(2) counterparts, all of which are similar to one another at around 800 cm<sup>-1</sup>; (b) the RHF-MBPT(2) values for  $\omega_{10}(b_{2g})$  and  $\omega_{18}(b_{1u})$  are also unreasonably large indicating a resistance of the molecule to change orbital contributions to the wave function of certain symmetry; (c) the IR transition intensities of  $\omega_{15}(b_{1u})$  and  $\omega_{18}(b_{1u})$  are larger than 5000 km/mol, a result of artifactual orbital contributions which will be discussed later.

At the RHF-SDQ-MBPT(4) level, the exaggeration of the electron-pair correlation effects typical of RHF-MBPT(2) is corrected somewhat by the inclusion of disconnected quadruple-excitation effects. Although the calculated equilibrium geometry is unstable, as indicated by the imaginary vibrational frequency for  $\omega_{18}(b_{1u})$ , the magnitudes of the frequencies are somewhat better behaved than their RHF-MBPT(2) analogs; (a) the value of  $\omega_8(b_{1g})$  is now normal; (b) the value of  $\omega_{10}(b_{2g})$  is twice as large as the corresponding UHF-MBPT(2) value; (c) the intensities of modes 15 and 18 are still too large. Since RHF-SDQ-MBPT(4) recovers more dynamic electron correlation, it also should provide a slightly better representation of the biradical character of *p*-benzyne despite the RHF starting function. At the same time, effects of the RHF-MBPT(2) double excitations are reduced at the RHF-SDQ-MBPT(4) level by double-double coupling and disconnected quadruple excitations. For example, the dominant  $b_{1u} \rightarrow a_g$  double excitation is now accompanied by a  $b_{2g} \rightarrow a_u$  double excitation thus reducing the effect of the former. This is clearly reflected by the fact that (a) the population of the  $a_g$  NOON LUMO is decreased from 0.355 (MBPT(2)) to 0.294 (Table I) and (b) the value of  $\Delta$  is increased to 0.084 Å (Table I, Fig. 3).

According to the calculated vibrational frequencies and intensities, the electronic structure of *p*-benzyne at the RHF-CCSD level appears to be both stable and no longer elec-

tronically distorted despite the use of the RHF reference function. In view of the fact that RHF-CCSD includes all infinite order correlation effects in the single- and double-excitation space, this seems to be reasonable. However, comparison to the UHF-based CC results, which converge in a systematic manner (*vide infra*), reveals that frequency  $\omega_8(b_{1g})$  is too low by more than 300 cm<sup>-1</sup> and the value of  $\omega_{10}(b_{2g})$  by about 100 cm<sup>-1</sup>. For  $\omega_{15}(b_{1u})$  the calculated intensity is too small and for  $\omega_{18}(b_{1u})$  both frequency and intensity are too large. Further, the value of  $\Delta$  is similar to the corresponding RHF-SDQ-MBPT(4) value. The use of restricted-Brueckner orbitals as a reference determinant for the CCSD wave function leads to similar results as RHF-CCSD.

The inclusion of triple-excitation contributions at the RHF-CCSD(T) level dramatically resuscitates the erroneous orbital contributions which plagued the RHF-MBPT(2) and RHF-SDQ-MBPT(4) levels of theory: (a) Both the  $\omega_{10}(b_{2g})$  and  $\omega_{18}(b_{1u})$  are imaginary; (b) the intensities of modes 18( $b_{1u}$ ) and 15( $b_{1u}$ ) are very large; (c) the value of  $\omega_8(b_{1g})$  is too small by several hundred cm<sup>-1</sup>. NOON values suggest an increase of the biradical character at the RHF-CCSD(T) level to 69%; however, this value is misleading insofar as it also includes effects from dynamic electron correlation involving three-, disconnected four- or even higher electron excitations.<sup>115</sup>

At the RB-CCD(T) level of theory, the deficiencies of the restricted starting function appear to be substantially offset. The  $\Delta$  value of 0.041 Å (Table I) is halfway between the corresponding RHF-CCSD(T) and UHF-CCSD(T) values. Agreement between calculated and experimental frequencies is satisfactory and close to the UHF-CCSD(T) description (*vide infra*). Although we were unable to obtain IR intensities at this level of theory, we conclude that RB-CCD(T) includes a sufficient amount of dynamic electron correlation effects to offer a reliable description for *p*-benzyne and its analogues. The same conclusion has been drawn by other authors.<sup>24,27,28,41,45</sup>

It is also worth noting that the  $\mathcal{T}_1$  diagnostic,<sup>116</sup> a common measure of the quality of the reference wave function for describing multiconfigurational effects in CC calculations, is  $\approx 0.016$  for RHF-CCSD and RHF-CCSD(T). This value is below the proposed cutoff of 0.02 above which CC results are generally considered suspect. In the case of *p*-benzyne, however, the most important single excitation wave function amplitudes that could potentially contribute heavily to the  $\mathcal{T}_1$  diagnostic—in particular, those excitations between the HOMO, HOMO-1, HOMO-2, and the LUMO—are constrained by symmetry to be identically zero. Therefore, while the true biradical character of *p*-benzyne clearly compromises the quality of the RHF reference wave function, the  $\mathcal{T}_1$  diagnostic offers no warning of potential problems.<sup>117</sup> Hence, *p*-benzyne represents a failure of the  $\mathcal{T}_1$  diagnostic for identifying certain types of inadequacies of the reference determinant.

## C. Basis set effects

In order to test the adequacy of the 6-31G(*d,p*) basis for a reasonable description of electron correlation effects in

TABLE II. Geometrical parameters, harmonic vibrational frequencies, and IR intensities for the  $^1A_g$  ground state of *p*-benzynes as obtained by various methods based on a RHF reference function and the cc-pVTZ basis set.<sup>a</sup>

Parameter	MBPT(2)	SDQ-MBPT(4)	CCSD	CCSD(T)
$r(C_1-C_2)$	1.370	1.347	1.346	1.366
$r(C_2-C_3)$	1.420	1.444	1.448	1.428
$\Delta$	0.050	0.097	0.102	0.062
$\omega_1 (a_g)$	3257	3274	3278	3240
$\omega_2 (a_g)$	1290	1306	1314	1292
$\omega_3 (a_g)$	1162	1179	1180	1161
$\omega_4 (a_g)$	1019	1016	1009	1015
$\omega_5 (a_g)$	690	704	705	640
$\omega_6 (a_u)$	958	967	957	949
$\omega_7 (a_u)$	465	465	462	439
$\omega_8 (b_{1g})$	2780	675	360	427
$\omega_9 (b_{2g})$	912	927	910	903
$\omega_{10} (b_{2g})$	9862	690	520	2035i
$\omega_{11} (b_{3g})$	3240	3254	3257	3220
$\omega_{12} (b_{3g})$	1657	1732	1726	1653
$\omega_{13} (b_{3g})$	1258	1272	1270	1270
$\omega_{14} (b_{3g})$	546	556	561	569
$\omega_{15} (b_{1u})$	3216 (4575)	3244 (590)	3256 (0)	3211 (583)
$\omega_{16} (b_{1u})$	1435 (48)	1452 (51)	1459 (1)	1449 (25)
$\omega_{17} (b_{1u})$	1051 (25)	1084 (52)	1088 (29)	1052 (30)
$\omega_{18} (b_{1u})$	5838 (X <sup>b</sup> )	2652i (X <sup>b</sup> )	923 (25)	2891i (X <sup>b</sup> )
$\omega_{19} (b_{2u})$	3256 (0)	3273 (1)	3277 (2)	3239 (1)
$\omega_{20} (b_{2u})$	1592 (2)	1434 (3)	1437 (3)	1392 (2)
$\omega_{21} (b_{2u})$	1304 (5)	1151 (11)	1136 (13)	1218 (6)
$\omega_{22} (b_{2u})$	1084 (4)	967 (0)	903 (0)	1037 (2)
$\omega_{23} (b_{3u})$	782 (86)	784 (84)	777 (85)	769 (82)
$\omega_{24} (b_{3u})$	477 (19)	486 (24)	482 (24)	461 (16)

<sup>a</sup>Bond lengths and difference  $\Delta = r(C_2-C_3) - r(C_1-C_2)$  in Å, frequencies in  $\text{cm}^{-1}$ , IR intensities in  $\text{km/mol}$ .

<sup>b</sup>Computed intensity exceeds 5000  $\text{km/mol}$ .

*p*-benzynes, we examined the effect of improving the basis to the cc-pVTZ level with the RHF-MBPT(2), RHF-SDQ-MBPT(4), RHF-CCSD, and RHF-CCSD(T) levels of theory. None of these calculations led to a significant improvement in calculated geometries, vibrational frequencies or IR intensities, and the essential deficiencies observed at the 6-31G(*d,p*) level remained. Small changes in the values of  $\Delta$  suggest even a reduction of the biradical character (Fig. 3). The more flexible cc-pVTZ basis set increases (a) the overlap between the interacting orbitals (Fig. 1) and, therefore, the coupling between the unpaired electrons in the reference wave function and (b) dynamic electron correlation effects at the MBPT and CC levels of theory. Hence, there is no chance of curing the starting wave function at a given level of theory by simply improving the basis set. On the other hand, it is reasonable to expect that once the basic failure of the restricted description is compensated by adding a sufficient amount of dynamic electron correlation any larger basis set will lead to more accurate properties of *p*-benzynes.

#### D. UHF descriptions

By adding dynamic electron correlation to a UHF description of *p*-benzynes, the calculated properties

smoothly change and seem to converge in each case to a limiting value. The values of the CC(H) and (H)CC(H) bond lengths are estimated to be 1.363 and 1.418 Å at the UHF-CCSD(T)/cc-pVTZ level of theory,<sup>118</sup> thus yielding a  $\Delta$  of 0.055 Å (Fig. 3). These values are close to the UB3LYP/6-311++G(3*df*,3*pd*) results of Cremer and co-workers (1.366, 1.419, 0.053 Å, Fig. 3).<sup>1</sup> In addition, the GVB-MP2 (1.368, 1.433, 0.065, Table I), RHF-CCSD(T)/cc-pVTZ (1.366, 1.428, 0.062, Table II), and estimated UHF-CCSD(T)/cc-pVTZ results (1.363, 1.418, 0.055 Å) (Ref. 118) are in the range of estimated limiting values. This indicates that even RHF-CCSD(T), despite the instability of the calculated geometry, can provide a reasonable energy and geometrical parameters.

The NOON values (Table I) suggest that the high biradical character of the UHF reference function is reduced by adding dynamic electron correlation. This is reasonable because the addition of dynamic correlation effects leads to a suppression of triplet contamination, which artificially enhances the biradical character. We note in this connection that the expectation value  $\langle \hat{S}^2 \rangle$  itself is no longer at this level of theory a reliable parameter to reflect the degree of spin contamination.<sup>119</sup> A better indicator of spin contamination at the UHF-CCSD level is the energy-related term of  $\langle \hat{S}^2 \rangle$  described by He and Cremer,<sup>119</sup> which is close to zero indicating that the (*S*+1) contaminants are annihilated. This is in line with the fact that the UHF-CCSD energy is identical with that of spin-projected CCSD based on the use of the *S*+1 projection operator as was first observed by Schlegel.<sup>94</sup> Hence, the UHF-CCSD and UHF-CCSD(T) levels of theory provide reasonable descriptions of the biradical character of *p*-benzynes where the latter is more reliable in view of the higher amount of dynamic electron correlation effects covered. Therefore, the UHF-CCSD(T) description of *p*-benzynes should be considered to be the most reliable obtained in this work.

#### IV. ORBITAL INSTABILITY EFFECTS IN *p*-BENZYNES

The orbital instability effects alluded to above are the result of near-degeneracies among electronic configurations of different symmetry, leading to energetic competition among solutions to the HF equations. Although this competition cannot directly affect properties such as the energy or geometry, it can dramatically distort second- and higher-order properties (e.g., harmonic vibrational frequencies or IR intensities) through the first-derivative of the wave function, which allows configurations of different symmetry to mix.

Another, closely related perspective on the instability problem can be gained from the the second-order Jahn-Teller effect (SOJT),<sup>120</sup> where a given electronic state of one symmetry interacts with another state of different symmetry along a particular vibrational mode. A Taylor expansion of the molecular Hamiltonian in a given vibrational mode,  $Q_\mu$ , leads to the second-order energy expression,

$$E_{\mu}(2) = \frac{1}{2} \left\langle \Phi_0 \left| \frac{\partial^2 H}{\partial Q_{\mu}^2} \right| \Phi_0 \right\rangle Q_{\mu}^2 + \sum_k \frac{\left| \left\langle \Phi_0 \left| \frac{\partial H}{\partial Q_{\mu}} \right| \Phi_k \right\rangle \right|^2}{E_0 - E_k} Q_{\mu}^2, \quad (6)$$

where  $\Phi_0$  and  $\Phi_k$ , respectively, represent the electronic state of interest (in this case, the ground  $^1A_g$  state of *p*-benzyne) and a perturbing state. The first term in Eq. (6) involves the diagonal contribution to the quadratic force constant in the absence of the state interaction, and the second term the magnitude of the interaction. The second term will be non-zero only if the direct product of the irreducible representations of  $\partial H/\partial Q_{\mu}$ ,  $\Phi_0$ , and  $\Phi_k$  contains the totally symmetric representation of the molecular point group. If the perturbing state,  $\Phi_k$ , lies higher in energy than  $\Phi_0$ , then the second term in Eq. (6) will be negative and, depending on its magnitude, may cause an energy lowering upon distortion of the molecular geometry along the symmetry-breaking mode  $Q_{\mu}$ . If either the two electronic states are close in energy or the nonadiabatic coupling matrix element in the numerator is substantial, then this term will be large and the resulting SOJT interaction will be significant.

To understand the anomalies in RHF frequencies and intensities in Table I within the framework of Eq. (6), we may take  $\Phi_0$  to be the HF wave function for the  $^1A_g$  ground state of *p*-benzyne and  $\Phi_k$  to be any of the electronic configurations obtained by exciting an electron from the HOMO ( $b_{1u}$ ), HOMO-1 ( $b_{2g}$ ), or HOMO-2 ( $b_{1g}$ ) orbitals into the LUMO ( $a_g$ ) (but without subsequent relaxation of the molecular orbitals). The denominator in the second term therefore becomes the corresponding orbital energy difference, and  $Q_{\mu}$  an appropriate vibrational mode for mixing the two orbitals of interest. A measure of the importance of these mixings is given by the eigenvalues of the molecular orbital Hessian<sup>90</sup>—the second derivative of the HF energy with respect to orbital rotations—whose inverse implicitly appears in the second term of Eq. (6).<sup>90</sup> Strongly positive orbital Hessian eigenvalues indicate a highly stable HF wave function, while a strongly negative eigenvalue indicates that a lower-energy (possibly symmetry-broken) solution to the HF equations exists. In the case of *p*-benzyne, however, a more subtle problem arises, insofar as the signs of the Hessian eigenvalues are much less important than their magnitudes. As discussed in detail in Ref. 90, a near-zero eigenvalue can lead to nonsensical vibrational frequencies and IR intensities (cf. Table I), even for highly correlated wave functions.

In a similar manner, Eq. (6) may be used to understand the anomalous CC frequencies and intensities by taking  $\Phi_0$  to be the appropriate correlated wave function,  $\Phi_k$  to be an excited state wave function (specifically a solution of the applicable equation-of-motion CC equations), and the denominator of the second term the difference in the energies of the two states. However, unlike the HF case, in which the response of the molecular orbitals alone determines the importance of the  $\partial H/\partial Q_{\mu}$  term, in CC theory, the response of both the molecular orbitals and the cluster amplitudes influences the strength of the SOJT interaction. Nonetheless, it is

TABLE III. Stability analyses of the RHF/6-31G(*d,p*) description of the  $^1A_g$  ground state of *p*-benzyne.<sup>a</sup>

Symmetry	Largest orbital components	Eigenvalue ( $E_h$ )
Spatial-symmetry instabilities		
$B_{1u}$	$b_{1u}-a_g$ (20–21)	0.0213
$B_{2g}$	$b_{2g}-a_g$ (19–21)	0.0062
$B_{1g}$	$b_{1g}-a_g$ (18–21)	0.0368
Singlet instabilities		
$B_{2g}$	$b_{2g}-a_g$ (19–21)	0.0118
	$b_{1u}-b_{3u}$ (20–23)	
$B_{1g}$	$b_{1g}-a_g$ (18–21)	0.0461
	$b_{1u}-a_u$ (20–22)	
Triplet instabilities		
$B_{1u}$	$b_{1u}-a_g$ (20–21)	−0.2782
$B_{2g}$	$b_{2g}-a_g$ (19–21)	−0.0626
	$b_{1u}-a_{3u}$ (20–23)	
$B_{1g}$	$b_{1g}-a_g$ (18–21)	0.0354
	$b_{1u}-a_u$ (20–22)	
$B_{1u}$	$b_{1g}-a_u$ (18–22)	0.0479
	$b_{2g}-b_{3u}$ (19–23)	

<sup>a</sup>The symmetry notation and the numbering of the MOs is explained in Fig. 2. All orbital Hessian eigenvalues were calculated at the RHF-CCSD(T)/6-31G(*d,p*) geometry.

the molecular orbital response—as measured by the eigenvalues of the molecular orbital Hessian—which leads to the clearly incorrect CC vibrational frequencies observed in Table I.<sup>121</sup>

For *p*-benzyne, three orbital near-instabilities plague the RHF-based MBPT and CC methods (Table III). The first involves the interaction between the  $a_g$ -symmetrical LUMO and the  $b_{1u}$ -symmetrical HOMO. The energy difference between the two is only  $\approx 6.2$  eV (Fig. 2) and the associated eigenvalue of the HF molecular orbital Hessian is  $0.0213 E_h$  (Table III). As discussed in Sec. III, this instability has a pronounced effect on the RHF-based MBPT(2), SDQ-MBPT(4), and CCSD(T) harmonic vibrational frequencies in the  $b_{1u}$ -symmetry block.

The second important orbital instability in *p*-benzyne involves rotation between the  $a_g$  LUMO and the  $b_{2g}$  HOMO-1 (orbital energy difference:  $\approx 8.2$  eV, Fig. 1). The corresponding eigenvalue of the molecular orbital Hessian is only  $0.0062 E_h$ , suggesting a strong interaction between the two orbitals upon distortions of the molecular framework of appropriate symmetry. This problem is manifested in the  $b_{2g}$  harmonic vibrational frequencies at certain levels of theory, particularly RHF-MBPT(2) and RHF-CCSD(T) (see Sec. III).

The third orbital instability again involves the  $a_g$  LUMO and the  $b_{1g}$  HOMO-2 (Fig. 1). The harmonic vibrational frequency distortions caused by this instability are more subtle than their  $b_{1u}$  and  $b_{2g}$  counterparts, and would appear to be nonexistent at several levels of theory without a direct comparison to the UHF-based results (see Sec. III). The eigenvalue of the molecular orbital Hessian for this interaction is only  $0.0368 E_h$ , a value small enough to lend skepticism for the accuracy of results associated with the  $b_{1g}$  vibrational mode.

In Fig. 4, the  $b_{1u}$ -,  $b_{2g}$ -, and  $b_{1g}$ -symmetrical normal



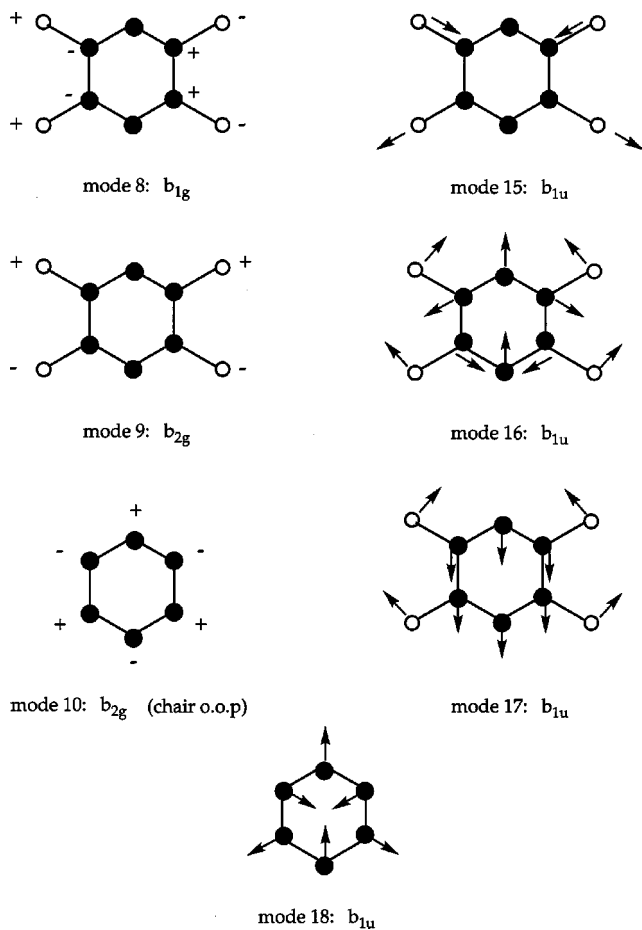


FIG. 4. Schematic representation of vibrational normal modes of  $b_{1u}$ -,  $b_{2g}$ -, and  $b_{1g}$ -symmetry. For those modes which preferentially involve the  $C_6$ -framework, H atoms are not shown.

modes of *p*-benzyne are shown schematically. Those modes that lead to a pronounced change in the carbon framework (i.e., the folding mode  $\omega_8$ , the chair mode  $\omega_{10}$ , and the deformation mode  $\omega_{18}$ ), in particular with regard to the C1–C4 distance and the overlap between the  $b_{1u}$ -HOMO and  $\sigma^*$ (CC) orbitals [Fig. 1(a)], should be the most sensitive with regard to a geometry-dependent orbital mixing. As is evident from Table I, this is clearly the case. Furthermore, those normal modes that preferentially involve movements of the H atoms, on the other hand (e.g., modes 9, 15, 16, and 17, as shown in Fig. 4), are less affected by orbital mixing, and should therefore be less influenced by the orbital near-instability effects. Nevertheless, the orbital mixings still have some impact on these modes, as indicated by anomalous IR intensities. It should be noted however, for *p*-benzyne, the effects expressed within the framework of Eq. (6) depend on the erroneous description of the interaction of  $\Phi_0$  and approximate excited state wave functions,  $\Phi_k$ , upon perturbation of the molecular framework. While the mathematical analysis is indeed that of SOJT interactions, this effect is clearly artifactual in *p*-benzyne and must not be confused with true SOJT phenomena.

It should also be noted that the RHF wave function contains two triplet instabilities, with eigenvalues of  $-0.278$  and  $-0.063 E_h$  (Table III) involving the HOMO, LUMO, and

LUMO+2. These instabilities [perhaps along with higher odd- $(2S+1)$  spin states] are responsible for the large  $\langle \hat{S}^2 \rangle$  value of the UHF reference function. Since two additional eigenvalues of the triplet stability matrix have very small values (0.035 and 0.048  $E_h$ , Table III), additional triplet contaminations can be expected from the corresponding orbital combinations. Hence, the stability analyses carried out in this work demonstrate that the problem of correctly describing the  $^1A_g$  ground state of *p*-benzyne with a HF starting function does not just depend on a HOMO–LUMO instability, but involves the frontier orbitals 18 to 23 shown in Fig. 2.

## V. COMPARISON WITH EXPERIMENT

Among the many methods examined here, the molecular properties of *p*-benzyne are best described by CC methods based on a UHF reference wave function. This becomes obvious when comparing the calculated and measured IR spectra<sup>1</sup> of *p*-benzyne (Table IV). For the harmonic vibrational frequencies, an optimal scale factor (Table IV) was determined utilizing the set of seven measured frequencies. In most cases, the new scale factors compare well with those normally used for a given method/basis set combination.<sup>122,123</sup> Scaled and measured frequencies differ on the average by more than 20  $\text{cm}^{-1}$  when a method with little electron correlation [e.g., UHF, GVB, GVB-MBPT(2), MBPT(2), MPBT(4), Table IV] or a method based on a restricted reference function (RHF-CCSD, RB-CCD) is used. A satisfactory agreement is only obtained for UHF-CCSD (mean deviation, 16.7  $\text{cm}^{-1}$ ), RB-CCD(T) (16.2  $\text{cm}^{-1}$ ), and UHF-CCSD(T) (15.4  $\text{cm}^{-1}$ , Table IV), which are comparable with the accuracy of the previously published UB3LYP frequencies [6-31G(*d,p*) 12.6; 6-311++G(3*df*,3*pd*): 16.9  $\text{cm}^{-1}$ , Ref. 1 and Table IV]. Two important conclusions can be drawn from the data collected in Table IV:

(a) Restricted and unrestricted wave-function-based methods seem to converge together to the same limit, particularly at the RB-CC and UHF-CC levels of theory. Noteworthy is the fact that the UHF-CCSD(T) and RB-CCD(T) results agree well with the broken-symmetry UB3LYP results published in Ref. 1. Since it appears that UDFT is able to reliably describe biradicals such as *p*-benzyne,<sup>124</sup> the agreement among RB-CCD(T), UHF-CCSD(T), and UB3LYP is another indication that at this level of theory the biradical character of *p*-benzyne and its molecular properties can be adequately described. (b) At all levels of theory that lead to a mean deviation smaller than 20  $\text{cm}^{-1}$  the value of the frequency  $\omega_{17}(b_{1u})$  is found to be close to or slightly larger than 1000  $\text{cm}^{-1}$  while the experimental value is 976 or 980  $\text{cm}^{-1}$ .<sup>1</sup> Although affected by the  $a_g$ - $b_{1u}$  orbital instability, this CCH bending mode (cf. Fig. 3) is less sensitive to the orbital instability effects described earlier. The fact that even after scaling all unrestricted methods (including UB3LYP) as well as RB-CCD(T) fail to reproduce this frequency with an accuracy better than 20  $\text{cm}^{-1}$  suggests that either anharmonic effects are not properly accounted by the scaling factors or the experimental frequency may be associated with a compound other than *p*-benzyne. A UHF-

TABLE IV. Comparison of experimental and scaled harmonic vibrational frequencies for the  $^1A_g$  ground state of *p*-benzynes as obtained by various methods and basis sets.<sup>a</sup>

No.	Method/basis set	$\omega_{16}(b_{1u})$	$\omega_{17}(b_{1u})$	$\omega_{18}(b_{1u})$	$\omega_{20}(b_{2u})$	$\omega_{21}(b_{3u})$	$\omega_{23}(b_{3u})$	$\omega_{24}(b_{3u})$	Scale factor <sup>b</sup>	Mean dev. <sup>c</sup>	ZPE <sup>d</sup>	ZPE scaled <sup>d</sup>
1	RHF/6-31G( <i>d,p</i> )	1349	1044	557 <i>i</i>	1387	1026	728	466	0.897 <sup>e</sup>		iF	iF
2	UHF/6-31G( <i>d,p</i> )	1429	984	939	1294	1273	721	406	0.9169	27	48.6	44.6
3	GVB(1)/6-31G( <i>d,p</i> )	1412	989	924	1282	1141	751	433	0.8844	25	50.2	44.4
4	RHF-MBPT(2)/6-31G( <i>d,p</i> )	1377	1001	5423	1496	1260	722	439	0.937 <sup>e</sup>	683	89.6	84.0
5	RHF-MBPT(2)/VDZP	1332	970	5907	1490	1224	689	429	0.937 <sup>e</sup>	754	130.8	122.6
6	RHF-MBPT(2)/cc-pVTZ	1363	998	5546	1512	1239	743	453	0.950 <sup>e</sup>	706	70.2	66.7
7	UHF-MBPT(2)/6-31G( <i>d,p</i> )	1397	1004	875	1327	1134	775	443	0.9008	31	49.4	44.5
8	GVB(1)-MBPT(2)/6-31G( <i>d,p</i> )	1386	1025	895	1400	1191	701	429	0.9397	28 (21)	47.2	44.4
9	RHF-MBPT(4)/6-31G( <i>d,p</i> )	1421	1050	2590 <i>i</i>	1375	1150	736	456	0.96 <sup>e</sup>		iF	iF
10	RHF-MBPT(4)/VDZP	1380	1021	2802 <i>i</i>	1346	1128	708	444	0.96 <sup>e</sup>		iF	iF
11	RHF-MBPT(4)/cc-pVTZ	1394	1041	2546 <i>i</i>	1377	1105	753	467	0.96 <sup>e</sup>		iF	iF
12	UHF-MBPT(4)/6-31G( <i>d,p</i> )	1406	1004	896	1319	1153	761	435	0.9169	23 (21)	48.6	44.6
13	RHF-CCSD/6-31G( <i>d,p</i> )	1392	1036	967	1345	1095	707	439	0.9371	38 (34)	46.6	43.7
14	RHF-CCSD/VDZP	1390	1035	968	1354	1098	700	441	0.9627	40 (36)	45.6	43.9
15	RHF-CCSD/cc-pVTZ	1391	1037	880	1370	1083	741	459	0.9532	46 (42)	46.1	43.9
16	UHF-CCSD/6-31G( <i>d,p</i> )	1419	1012	911	1319	1191	736	419	0.9423	17 (12)	47.6	44.9
17	RB-CCD/6-31G( <i>d,p</i> )	1418	1047	869	1371	1119	721	447	0.9538	39	46.7	44.5
18	RHF-CCSD(T)/6-31G( <i>d,p</i> )	1423	1016	3589 <i>i</i>	1332	1224	720	425	0.96 <sup>e</sup>		iF	iF
19	RHF-CCSD(T)/VDZP	1381	990	3784 <i>i</i>	1312	1200	691	418	0.96 <sup>e</sup>		iF	iF
20	RHF-CCSD(T)/cc-pVTZ	1391	1010	2775 <i>i</i>	1336	1169	738	443	0.96 <sup>e</sup>		iF	iF
21	UHF-CCSD(T)/6-31G( <i>d,p</i> )	1419	1017	908	1325	1197	730	418	0.9529	15 (10)	47.1	44.9
22	RB-CCD(T)/6-31G( <i>d,p</i> )	1418	996	948	1310	1211	713	419	0.9490	16	46.6	44.2
23	BS-UB3LYP/6-31G( <i>d,p</i> )	1397	1010	900	1344	1203	725	426	0.9579	13 (9)	46.5	44.6
24	BS-UB3LYP/6-311++G(3 <i>df</i> ,3 <i>pd</i> )	1394	1012	892	1344	1190	733	430	0.9665	17 (14)	46.2	44.7
25	Experiment <sup>f</sup>	1403	976	918	1331	1207	721	435				44.6 <sup>g</sup>

<sup>a</sup>Vibrational frequencies and mean deviations in  $\text{cm}^{-1}$ , zero point energy (ZPE) in kcal/mol.<sup>b</sup>Scale factors were determined to give the best agreement between theory and experiment.<sup>c</sup>Mean deviations in parentheses were obtained by deleting  $\omega_{17}(b_{1u})$ .<sup>d</sup>Symbol ‘‘iF’’ denotes that the ZPE value could not be calculated because of imaginary frequencies.<sup>e</sup>Scale factors taken from the literature: MBPT(2) from Ref. 122; CCSD(T) from Ref. 123.<sup>f</sup>From Ref. 1.<sup>g</sup>Limit value obtained as an average of the ZPE values for entries 21, 22, 23, and 24.

CCSD(T) determination of this vibrational frequency using larger basis sets would be valuable in resolving this discrepancy.

Since biradical *p*-benzynes is an intermediate of the Bergman reaction, the calculation of the energetics of this reaction depends critically on a correct account of the properties of *p*-benzynes.<sup>24,27–46</sup> Clearly, energy and geometry are not directly affected by orbital near-instabilities within the reference wave function and, therefore, useful energetics may be obtained with a restricted reference function provided three-electron correlation effects are included in the calculation. However, the stationary points calculated along the reaction path have to be characterized with the help of the vibrational frequencies and, of similar importance, the calculated energy differences must be converted to enthalpy differences at 298 K in order to be directly compared with the experimental thermochemical data.<sup>26</sup> This latter point is rather critical in view of the discussion presented in Sec. III and has been solved in different ways.

In Ref. 27, Kraka and Cremer used RHF-CCSD(T) together with the 6-31G(*d,p*) basis to examine the reaction path and activation energy of the Bergman cyclization. Since RHF-CCSD(T) leads to anomalous vibrational frequencies, those authors instead utilized GVB/6-31G(*d,p*) vibrational data (together with a scaling factor of 0.89) to estimate the zero-point energy (ZPE) of *p*-benzynes to be 44.6 kcal/mol.<sup>125</sup>

Other authors have found the ZPE of *p*-benzynes to be in the range of 48.1 kcal/mol (Ref. 126) to 43.8 kcal/mol,<sup>39</sup> where criticism was raised that the reaction and activation enthalpies published by Kraka and Cremer<sup>27,28</sup> might be flawed by an inaccurate ZPE value for *p*-benzynes. The values for ZPE obtained in this work are scaled to be in line with experimental frequencies (Table IV) and clearly support a ZPE value of 44.6 kcal/mol in agreement with Ref. 27. Hence, the enthalpy differences reported by Kraka and Cremer agree well with the experimentally determined activation barrier and reaction enthalpy published by Roth and co-workers.<sup>26</sup>

## VI. CONCLUSIONS

(1) CC methods based on a UHF reference function and including triple excitation effects provide a reliable account of the properties of biradical *p*-benzynes. The problem of spin contamination is not pendant because the triplet contaminants  $S+1$  are completely annihilated by the infinite-order effects in the single- and double-excitation space of CCSD and any higher CC method. However, correlation-corrected UHF methods that do not include all correlation effects in the single and double space cannot provide reliable results for *p*-benzynes because of the unusually large spin contamination resulting from two rather than just one triplet state.

(2) The description of *p*-benzynes based on spin-restricted electron correlation methods suffers from orbital near-instabilities involving the frontier orbital combinations  $a_g-b_{1u}$ ,  $a_g-b_{2g}$ , and  $a_g-b_{1g}$ . The deleterious effect of these orbital mixings on the harmonic frequencies and IR intensities is clearly revealed through the anomalous  $b_{1u^-}$ ,  $b_{2g^-}$ , and  $b_{1g^-}$ -symmetrical vibrational modes. Among those methods based on the RHF wave function, we find that in the case of biradical *p*-benzynes, the Brueckner-orbital-based RB-CCD(T) is the first method that provides sufficient electron correlation to compensate for the drawbacks of the restricted reference.

(3) In view of (2), results obtained for biradicals with correlated methods based on a restricted reference function should be used with caution. Finite-order MBPT(*n*), with  $n \leq 4$ , should not be trusted in general for such problems. Energies, geometries, and other first order properties obtained with RHF-CCSD(T) may be useful, with the caveat that *p*-benzynes is unstable to certain symmetry-breaking modes at this level of theory. Second order properties can be exquisitely sensitive to changes in the wave function, while first-order properties are completely unaffected, and the eigenvalues of the molecular orbital Hessian often serve as useful diagnostics for problematic orbital effects.

(4) In general, deficiencies of the method in overcoming multireference or orbital instability errors cannot be compensated by the use of larger basis sets.

(5) Both UHF-CCSD(T) and RB-CCD(T) calculations confirm results previously obtained with UB3LYP (Ref. 1) and support arguments that with broken-symmetry UDFC using hybrid functionals, a reasonable description of biradicals such as *p*-benzynes can be obtained.<sup>124</sup>

(6) The analysis of the IR spectrum of *p*-benzynes leads to reasonable agreement between theory and experiment with the exception of vibrational mode 17 (a CCH bending motion). Theory predicts the corresponding frequency to occur between 1010 and 1017  $\text{cm}^{-1}$ . The discrepancy between this result and the measured band at 976  $\text{cm}^{-1}$  suggests that either anharmonic effects are not properly accounted for, the level of electron correlation is still inadequate to correctly describe this vibrational mode, or the experimental frequency may be associated with a compound other than *p*-benzynes.<sup>127</sup>

(7) Calculated ZPE's converge to a value of 44.6 kcal/mol, in agreement with the value first given by Kraka and Cremer.<sup>27,28</sup>

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- <sup>110</sup>The MBPT and CC NOON values reported here were computed using the symmetrized one-electron density matrix, rather than the original non-symmetric form. This approach can lead to nonsensical, negative occupation numbers for high-lying orbitals. However, for those orbitals which contribute most strongly to biradical character, the NOON values give a consistent, qualitative picture of the adequacy or inadequacy of the reference wave function.
- <sup>111</sup>However, it is important to note that the BS-UHF reference function is not completely asymmetric but represents an irreducible representation of a mixed spin-space symmetry group where all reflections at the mirror plane are combined with a simultaneous flip of all spins in the system. Since the BS-UHF wave function belongs to an irreducible representation of an appropriately chosen symmetry group, the breaking of the spin symmetry does not imply a reduction of the molecular symmetry, i.e., the molecule retains its  $D_{2h}$  framework.
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- <sup>115</sup>In previous work (Refs. 27, 28), benzene was used as a reference to convert NOON values into biradical character. However, this will be only useful if trends for closely related compounds are investigated. The RHF-CCSD(T)  $\Delta$  of 0.044 Å (Table I and Fig. 3) suggests that the biradical character is increased in the RHF-CCSD(T) description. However, since  $\Delta$  also reflects the effects of dynamic electron correlation, the increase cannot be quantified.
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- <sup>118</sup>Estimated by adding the changes in bond length between the RCCSD(T)/6-31G(*d,p*) and RCCSD(T)/cc-pVTZ levels of theory to the UHF-CCSD(T)/6-31G(*d,p*) bond lengths.
- <sup>119</sup>Y. He and D. Cremer, *Chem. Phys. Lett.* **324**, 389 (2000).
- <sup>120</sup>I. B. Bersuker, *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry* (Plenum, New York, 1983).
- <sup>121</sup>Unlike CC theory, MBPT includes no direct interaction with excited states through Eq. (6) beyond that already included in the HF reference function. Hence, an instability of the molecular orbitals generally has a

more profound effect on MBPT vibrational frequencies and intensities than on CC properties.

<sup>122</sup>A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).

<sup>123</sup>A. Wu, A. J. Larson, and D. Cremer (to be published).

<sup>124</sup>J. Gräfenstein, M. Filatov, E. Kraka, and D. Cremer, *J. Phys. Chem. A* (submitted).

<sup>125</sup>Kraka and Cremer (Ref. 27) also calculated the ZPE by replacing the  $b_{1u^-}$ ,  $b_{2g^-}$ , and  $b_{1g^-}$ -symmetrical frequencies calculated at the RHF-MBPT(2) level of theory by the corresponding scaled GVB frequencies. This led to a similar ZPE value as obtained directly from GVB. However, the procedure of correcting the frequencies of an unstable description

with those of a stable description is theoretically not sound and, therefore, the corrected MBPT(2) ZPE value was not used in Ref. 27. Hence, the ZPE presented there should have correctly been addressed as GVB rather than MBPT(2) ZPE.

<sup>126</sup>R. Lindh and M. Schütz, *Chem. Phys. Lett.* **258**, 409 (1996).

<sup>127</sup>See EPAPS Document No. E-JCPSA6-114-309124 for a tabulation of energies and Cartesian coordinates for the *p*-benzyne structures discussed here. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for more information.