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Benzyne Thermochemistry: A Benchmark ab Initio Study

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The thermochemistry of the benzynes has been reinvestigated in a set of benchmark calculations including, e.g., multireference perturbation theory in combination with large basis sets up to correlation consistent polarized valence quadruple ζ followed by basis set extrapolation procedures. The vibrational corrections have been deduced from multiconfiguration self-consistent field (MCSCF) calculations employing average atomic natural orbital basis sets. The quality of the isodesmic reactions has been investigated by analyzing the errors of the utilized methods in predicting the CH bond strengths and energies of the related molecules. It turns out that multireference third order perturbation theory, although occasionally better than second order, suffers from less systematic errors and thus is not as well suited for use in isodesmic reactions as the corresponding second order theory. The present extended calculations show that all the isodesmic reactions used in previous studies of the thermochemistry of the benzynes are adequate. Furthermore, it is demonstrated that multireference second order perturbation theory accurately reproduces the singlet−triplet energy splittings of the benzynes.

1. Introduction

The thermochemistry of the benzynes is a challenging task for theory. Numerous investigations on this issue are reported in the literature.[1−9] The large number of such studies is a reflection on the difficulty of the problem and the development of new tools for theoretical studies. As the biradical character of some of the members in the benzyne series increases, conventional single configuration methods like single and double coupled-cluster theory with triple corrections (CCSD(T)) have been demonstrated to be incapable of describing the relative energies of the ortho, meta, and para species. Furthermore, density functional theory (DFT), which inherently picks up some of the static correlation by including only *local* exchange in the exchange-correlation functional (and not the exact Hartree−Fock exchange), also has shown only poor results in predicting the benzyne thermochemistry.[7,9] The general conclusions of the investigations are that a multiconfigurational treatment including dynamical electron correlation, basis sets of triple-ζ quality, and the use of isodesmic techniques[10] are mandatory for quantitative agreement between experiments and theory. One possible alternative might be multiconfigurational DFT methods, which deal with static correlation effects via a multiconfiguration self-consistent field (MCSCF) procedure, while treating dynamic correlation effects at the level of DFT. Such methods are presently under development,[11,12] and the success or failure of the approach lies in the future. Another avenue would be the use of Brueckner orbitals in connection with the single-reference coupled-cluster approach (BCC). Cramer[13] has in a recent study of aryne biradicals demonstrated that the use of BCCD(T) vs CCSD(T) represents a considerable improvement/difference in some particular cases. The observed difference between CC and BCC is usually in the literature argued to be due to the ability of Brueckner's approach to include some of the static correlation effects in the reference function. However, no study has yet been published which supports that BCC in general is better than standard CC approach in case of a significant multiconfigurational character of the wave function.

One of the recent theoretical studies on the benzyne thermochemistry[8] has questioned the experimental results of Roth et al.[14] and Wenthold and co-workers,[15,16] yet this was recently demonstrated by Cramer et al.[9] to be based on the use of incorrect multireference second order perturbation theory (CASPT2) energies. The CASPT2 prediction of the enthalpy of formation of *p*-benzyne in combination with an atomic natural orbital (ANO) type basis set and vibrational corrections based on DFT (BPW91/cc-pVDZ) force constants resulted in 138.2 kcal/mol,[9] a result in excellent agreement with experiment.[14,16] The study of Cramer et al., however, ignored the known systematic error of the CASPT2[g0][17] method which correlates to the number of unpaired electrons. The error in correlation energy is proportional to 3−4 kcal/mol per unpaired electron, an error empirically corrected for in the work by Lindh and Persson[6] and analytically corrected in later works by the use of the CASPT2 with a g1 corrected zero Hamiltonian.[18] Recent developments in integral direct electron correlation methods[19] and combined developments in hardware capacity and conventional methods[20] enable calculations of the benzynes with substantially larger basis sets (quadruple ζ quality and higher). This, in turn, now allows the use of basis set extrapolation techniques to explore the one-particle basis set limit for the various relevant reaction energies. The previously used vibrational information has been based on either a combination of theoretical and experimental results[8] or DFT frequencies.[9] Frequency calculations on the benzene molecule in particular have demonstrated that a multiconfigurational treatment is necessary for quantitative agreement with experiment.[21] Recently developed algorithms for calculations of multiconfigurational self-consistent field second derivatives for large one- and

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N-particle basis sets[20] allow for better and more consistent estimates of the vibrational contributions to the thermochemistry of the singlet and triplet benzynes.

In this study the systematic error of the CASPT2[g0] method, the effect of basis set extrapolation, and the quality of vibrational corrections have been addressed, benefiting from the new technical developments in multiconfigurational ab initio theory, as mentioned above. Studies of biradical chemistry are also attracting more and more attention as ab initio theory is used to provide theoretical information on femtosecond laser experiments of fast reactions, for example, the photoinduced dissociation of tetramethylene.[22] For that purpose it is of importance to use such benchmark systems to calibrate the methods. In this respect the present calculations on the thermodynamics of the benzynes are also of interest.

2. Methods

The molecular species[23] of *o*-, *m*-, and *p*-benzyne, benzene, phenyl radical, methane, methyl radical, and hydrogen were studied by using second and third order Møller−Plesset perturbation theory (MP2 and MP3), multireference second order perturbation theory (CASPT2[g0][17] and CASRS2[24]), multireference second order perturbation theory with a g1 corrected zero Hamiltonian (CASPT2[g1]),[18] multireference third order perturbation theory (CASRS3),[25] multireference configuration interaction (MRCI), Davidson corrected multireference configuration interaction (MRCI(Q)), single and double coupled-cluster theory (CCSD), and single and double coupled-cluster theory with perturbational triple corrections (CCSD(T)), all in combination with the average atomic natural orbitals (ANO)[26] basis sets in C[14s9p4d]/(5s4p2d)//H[8s4p]/(3s2p) contraction (denoted aANO(1)), and C[14s9p4d3f]/(5s4p3d1f)//H[8s4p3d]/(3s2p1d) contraction (denoted aANO(2)), respectively, as well as the Dunning correlation consistent sets cc-pVDZ, cc-pVTZ, and cc-pVQZ.[27,28] The real spherical harmonics were used throughout. With some of the larger basis sets used here state-of-the-art correlation methods were employed in combination with basis set sizes exceeding 500 contracted functions. The ab initio calculations were extrapolated to the complete basis set limit (CBL) using the extrapolation schemes (for details see refs 29−31)

$$E(X) = E_\infty + AX^{-3} + BX^{-5} \tag{1}$$

$$E(X) = E_\infty + A(X + 1/2)^{-\alpha} \tag{2}$$

$$E(X) = E_\infty + AX^{-3} \tag{3}$$

and

$$E(X) = E_\infty + AX^{-5} \tag{4}$$

denoted CBL(1), CBL(2), CBL(3), and CBL(4), respectively. X denotes the so-called cardinal number ($X = 2, 3, 4$ for cc-pVXZ, $X = D, T, Q$). For CBL(3) and CBL(4), the notation is augmented such that, e.g., CBL(3:3,4) indicates that the two CBL(3) parameters were derived from the energies of cardinal numbers 3 and 4.

The structures and vibrational harmonic frequencies used in this work were obtained at the level of the complete active space self-consistent field theory (CASSCF) employing an aANO(1) basis set[8,9] (for auxiliary data cf. ref 23). The active orbital space in the CASSCF wave function included all valence π-orbitals and the valence σ-orbitals at each dehydrocarbon. Each of these orbitals contains one single electron giving for benzene, phenyl radical, and the benzynes CASSCF model spaces which are denoted as CAS(6,6), CAS(7,7) and CAS(8,8), respectively. In the case of the isodesmic reactions the constraint was applied that the union of the active spaces of the reactants and products should be the same. The CASSCF procedure was followed by CASPT2, CASRS2, and CASRS3 calculations to include dynamical correlation. The carbon 1s core orbitals were not correlated in this step. The CASPT2 and the CASRS2 methods are essentially identical, both being multiconfigurational reference second order perturbation methods. However, whereas the CASPT2 has a contracted reference, the CASRS2 method decontracts the reference when treating the singly external excitations. This difference is more of a technical nature, and the methods are expected in general to give very similar results. The CASRS3 is a third order extension of the CASRS2 method.

TABLE 1: Collected Standard Enthalpies at 298 K in kcal/mol of the Species Used in This Study

species	$\Delta H_{f,298}$	reference
benzene	19.7 ± 0.2	38
phenyl radical	81.2 ± 0.6	37
o-benzyne	106.6 ± 3.0	16
m-benzyne	121.9 ± 3.1	16, 37
p-benzyne	137.8 ± 2.9	16, 37
	138.0 ± 1.0	14
methane	−17.83 ± 0.07	39, 40
methyl radical	35.0 ± 0.1	41
acetylene	54.35 ± 0.19	39, 40
ethylene	12.52 ± 0.12	39, 40
atomic hydrogen	52.102	

The experimentally deduced enthalpies used in the study (identical with those used in ref 9) are all collected in Table 1. The latest versions of the MOLCAS 4.1[32] and MOLPRO 98[33] quantum chemistry program packages were used for all calculations.

3. Results and Discussion

The discussion here will first assess the accuracy of the methods used in the study by considering the related issues of the zero point energy (ZPE) correction, the singlet−triplet energy splittings, and the C−H bond strength and energies of some relevant species. This is followed by an investigation of the isodesmic reactions used in the study. The quality of these isodesmic reactions is demonstrated to be related to the errors in the predicted C−H bond strength at various levels of approximation. This all then leads to the conclusions with respect to the thermochemistry of the singlet and triplet benzynes.

3.1. Vibrational Corrections. The CASSCF/aANO(1) ZPE and temperature corrections to the enthalpy at 298 K due to vibrational, translational, and rotational motions together with the corresponding BPW91/cc-pVDZ values by Cramer and coworkers[9] are collected in Table 2. The CASSCF method is known to predict force constants that are too low, a trend which originates from the fact that CASSCF overemphasizes the antibonding configurations.[34] However, in these particular calculations only the π-space is correlated and the CASSCF treatment of the π-space is counterbalanced by the HF-like treatment of the σ-space. This warrants rather accurate prediction of the force constants at the CASSCF/aANO(1) level of theory, with the exception of the pure H−C stretching modes which will be too stiff. One interesting point to note in the comparison of CASSCF vs BPW91 is the uBPW91 ZPE of 44.88 kcal/mol for the singlet state *p*-benzyne. The single-configuration uBPW91 model with the possibility of different α and β electron densities improves the modeling of singlet biradical states at

TABLE 2: Calculated ZPE and Temperature Corrections to the Enthalpy at 298 K in kcal/mol Computed at the BPW91/cc-pVDZ and CASSCF/aANO(1) Levels of Theory

		rBPW91/cc-pVDZ		CASSCF/aANO(1)	
molecule	spin	ZPE	H298-H0	ZPE	H298-H0
o-benzyne	0	45.82	3.48	49.27	3.25
	1	45.35[a]	3.44[a]	48.90	3.23
m-benzyne	0	44.74	3.71	48.56	3.28
	1	45.22[a]	3.44[a]	48.69	3.25
p-benzyne	0	44.09	3.57	48.49	3.24
	0	44.88[a]	3.44[a]		
	1	45.28	3.43	48.64	3.25
benzene	0	61.43	3.42	65.50	3.27
phenyl radical	1/2	53.29[a]	3.42[a]	57.11	3.25
methane	0	27.30	2.40	29.43	2.38
methyl radical	1/2	18.08[a]	2.54[a]	19.07	2.73
ethylene	0	31.07	2.52	33.05	2.50
acetylene	0	16.45	2.41	16.48	2.49
hydrogen atom	1/2	0.0	1.77	0.0	1.77

[a] uBPW91/cc-pDVZ.

the expense of not providing a spin eigenfunction. However, because of considerable spin contamination in this particular case ($S^2 = 0.86$), Cramer et al. rather used the 44.09 kcal/mol value from the restricted BPW91 model. The ZPE correction to the singlet−triplet energy splitting of *p*-benzyne is computed to 1.05 and 0.39 kcal/mol using the restricted and the unrestricted BPW91 procedure, respectively. A rather small discrepancy at first glance, however, it corresponds to 21% of the singlet−triplet energy splitting. The ZPE correction yielded by the CASSCF/aANO(1) approach is 0.16 kcal/mol. Moreover, a comparison of the BPW91 vs CASSCF ZPE values for the ring systems reveals that the CASSCF results are higher by 3.36−3.82 kcal/mol with a single exception—for the singlet *p*-benzyne the difference is 4.40 kcal/mol. However, using the unrestricted DFT result instead, it is only 3.61 kcal/mol, i.e., in the range of the other results. Considering that the difference in both the geometrical structure and the wave function between the singlet and triplet states is small for the para species as compared to the ortho one, would expect the smallest correction for the former. However, the DFT corrections of Cramer and co-workers are 1.05 and −0.51 kcal/mol, respectively, whereas the CASSCF corrections are 0.16 and −0.39 kcal/mol. It is evident that the multiconfigurational approach is the most consistent way to proceed for the benzynes. The method, in contrast to DFT, allows for an accurate modeling of closed shell, open shell, and biradical systems while still providing a proper spin eigenfunction. All these properties are of importance in computing accurate singlet−triplet energy splitting for the benzynes.

3.2. Benzyne Singlet−Triplet Splitting. The singlet−triplet (S−T) energy splitting was identified by Cramer et al. as an indicator of the performance of the methods employed in the studies on biradicals. The same view is shared here, including also CASPT2[g1], CASRS2, and CASRS3 results and complete basis set extrapolations in the comparison. The results are collected in Table 3. For example, the CASPT2[g1]/CBL(2) results are 36.3 (37.5 ± 0.3), 20.5 (21.0 ± 0.3), and 2.8 (3.8 ± 0.3 or 2.1 ± 0.4) kcal/mol for the singlet−triplet energy splitting of *o*-, *m*-, and *p*-benzyne, respectively, with experimental values by Wenthold et al.[35] in parenthesis. The overall conclusions from these computations are that basis set extrapolation is a prerequisite for quantitative agreement (±1 kcal/mol) with experiment. The CASPT2[g1]/CBL(2) result of 2.8 kcal/mol also shows that once the g1 corrected zero order Hamiltonian is used, it is no longer true that the singlet−triplet energy splitting of *p*-benzyne is overestimated by more than 50%, as stated by Cramer et al.[9] Three differences in comparison to the study of Cramer and co-workers on the S−T energy splitting are worthwhile to note: (i) the correction of the systematic error of the CASPT2 method for unpaired electrons is significant for the accuracy;[18] (ii) saturated basis sets and basis set extrapolation are required; (iii) the zero point energy corrections (as discussed in the previous subsection) at the BPW91/cc-pVDZ and uBPW91/cc-pVDZ levels of approximation deviate from the balanced CASSCF/aANO(1) vibrational corrections by about 1 kcal/mol in the case of the splitting of the *p*-benzyne. In comparison to the “extrapolated” CCSD(T)/cc-pVTZ results of Cramer et al., which after vibrational correction at the CASSCF/aANO(1) level of theory compile the singlet−triplet energy splitting to 35.4, 20.6, and 1.4 kcal/mol, respectively (with the original BPW91 vibrational correction the S−T splitting was estimated to be 35.3, 20.7, and 2.3 kcal/mol, respectively), the CASPT2[g1] method is marginally better. Finally, it is noted that the CASPT2[g1]/CBL(2), CASRS3/CBL(2), and the CCSD(T)/cc-pVDZ results for the singlet−triplet energy splitting of 2.8, 2.2, and 1.4 kcal/mol, respectively, indicate that the alternative experimental value of the singlet−triplet energy splitting of the *p*-benzyne of 2.1 ± 0.4 kcal/mol which “cannot be ruled out but is considered unlikely” according to Wenthold and co-workers[35] might have to be reconsidered. This point is further supported by the “extrapolated” BCCD(T)/cc-pVTZ results by Cramer[13] which, after including the CASSCF/aANO(1) vibrational corrections, yield an S−T splitting of 2.1 kcal/mol.

3.3. The C−H Bond Strengths and Energies. An accurate theoretical prediction of the energy of the C−H bond in benzene is a nontrivial task as demonstrated by, e.g., Ochterski and co-workers.[36] In their study on complete basis set model chemistry employing various extrapolation schemes, the dissociation energy of a C−H bond in benzene was estimated to 113.1 ± 0.2 kcal/mol at the CBS-Q level of approximation, a result in agreement with the most recent experiment[37] (112.0 ± 0.6 kcal/mol). The C−H bond strengths of benzene and other species are included here to assess the accuracy of the methods employed in this study. Furthermore, from these results the expected quality of the isodesmic reactions relevant for the thermochemistry of the benzynes can be assessed. In the present work the C−H bond strengths and energies of the following reactions

$$CH_4 \rightarrow CH_3 + H \tag{5}$$

$$C_2H_4 \rightarrow C_2H_2 + 2H \tag{6}$$

$$C_6H_6 \rightarrow C_6H_5 + H \tag{7}$$

$$C_6H_5 \rightarrow p\text{-}C_6H_4 + H \tag{8}$$

$$C_6H_5 \rightarrow m\text{-}C_6H_4 + H \tag{9}$$

and

$$C_6H_5 \rightarrow o\text{-}C_6H_4 + H \tag{10}$$

were investigated. The isodesmic reactions discussed in the subsequent section (see reactions 11−14) can all be constructed from these parent reactions, and the idea of the isodesmic reaction is that the errors in the C−H bond energies or strengths should cancel. The calculated C−H bond energies and strengths at 298 K for a number of methods and basis sets are compiled in Tables 4 and 5. The computed CASRS3/CBL(2) results (experimental result in parenthesis) for reactions 5−10 are 103.6 (104.9 ± 0.1), 142.8 (146.0 ± 0.2), 113.4 (113.6 ± 0.6), 112.1

TABLE 3: Calculated Singlet−Triplet Splittings in kcal/mol at 298 K for *o*-, *m*-, and *p*-Benzyne at the CASPT2 and CASRS3 Levels of Approximation

molecule	basis set	CASPT2[g0]	CASPT2[g1]	CASRS2	CASRS3	expt
o-benzyne						37.7 ± 0.7[a] 37.5 ± 0.3[b]
	aANO(1)	32.7(32.6)[c]	34.0			
	cc-pVDZ	30.1	31.0	30.6	31.7	
	cc-pVTZ	33.2	34.6	33.8	35.2	
	cc-pVQZ	34.1	35.6	34.6	36.2	
	CBL(1)	34.8	36.4	35.3	37.0	
	CBL(2)	34.8	36.3	35.3	37.0	
	CBL(3:3,4)	34.7	36.3	35.3	37.0	
	CBL(4:3,4)	34.4	35.9	34.9	36.5	
m-benzyne						21.0 ± 0.3[b]
	aANO(1)	18.6(19.0)[c]	19.0			
	cc-pVDZ	17.6	17.8	18.1	16.8	
	cc-pVTZ	19.1	19.6	19.6	18.2	
	cc-pVQZ	19.6	20.1	20.0	18.5	
	CBL(1)	19.9	20.5	20.3	18.7	
	CBL(2)	19.8	20.5	20.3	18.7	
	CBL(3:3,4)	19.8	20.5	20.3	18.7	
	CBL(4:3,4)	19.7	20.3	20.2	18.6	
p-benzyne						3.8 ± 0.5[b] 2.1 ± 0.4[d]
	aANO(1)	4.8(5.8)[c]	3.3			
	aANO(2)	4.7	3.1			
	cc-pVDZ	4.9	2.9	5.1	2.5	
	cc-pVTZ	4.7	3.2	4.9	2.3	
	cc-pVQZ	4.7	3.1	4.8	2.2	
	CBL(1)	4.7	3.0	4.8	2.2	
	CBL(2)	4.7	2.8	4.8	2.2	
	CBL(3:3,4)	4.7	3.1	4.8	2.2	
	CBL(4:3,4)	4.7	3.1	4.8	2.2	

[a] Reference 42. [b] Reference 35. [c] Reference 9. [d] Alternative value by ref 35.

(108.9 ± 1.2), 97.1 (92.8 ± 3.2), and 82.2 (77.5 ± 3.1) kcal/mol, respectively. All results are close to the experimental values at this level of approximation, with the possible exception of the two later reactions; however, these have a significantly larger experimental error bar. Note that the CASPT2 and CASRS2 almost always underestimate the C−H bond energy; for example, for the CASPT2[g1]/CBL(2) the deviations are −2.6, −4.5, −4.1, −1.1, −2.1, and +1.7 kcal/mol, respectively, for reactions 5, 6, 7, 8, 9, and 10. The only exception is again observed for one of the reactions with the largest experimental error bar. The CASRS3/CBL(2) values, however, are more randomly scattered around the experimental findings, −1.3, −3.2, −0.1, 3.2, 4.3, and 4.7 kcal/mol, respectively. Hence, the reaction energies of the isodesmic reactions at the CASPT2 and CASRS2 levels of theory will be of better accuracy than the corresponding computed C−H bond energies. For the CASRS3 approximation, on the other hand, the lack of systematic errors disqualifies it from improving its accuracy due to cancellation of errors by virtue of isodesmic reactions. Actually, it is expected that the computed reaction energies of the isodesmic reactions at the CASRS2/CASPT2 level due to favorable cancellation of systematic errors will be better than those computed at the CASRS3 level of theory. A comparison of the distinct basis set extrapolation schemes reveals no significant differences: all yield very similar results, hence anyone can be used equally well. However, it is evident that the quality of the one-particle basis set and the CBS extrapolation affect the results significantly: CBS extrapolation improved the predicted bond strengths by up to 2 kcal/mol, relative to the corresponding cc-pVTZ results. We also note that there is good agreement between the CASRS3 and the CCSD(T) results (cf. Tables 4 and 5). Furthermore, it is observed that the size-inconsistency error of the MRCI can be significant, 3.3−6.0 kcal/mol, as indicated from a comparison of MRCI to MRCI(Q) (cf. Table 5). Finally, the correction for the known systematic error of the CASPT2-[g0] approximation as introduced by the CASPT2[g1] approach is usually rather small, as expected. Yet, if some of the species involved have a pronounced biradical character as in reaction 8, the corrections can be as large as 2.9 kcal/mol. In such cases the CASPT2[g1] approach should be employed. To conclude this section, the CASRS3 method in conjunction with large basis sets and basis set extrapolation predict the hydrogen−carbon bonding close to chemical accuracy. However, the errors of the CASRS3 method turn out to be less systematic than for second order multireference perturbation methods (CASRS2 and CASPT2), and it is anticipated that the latter will provide more accurate reaction energies of isodesmic reactions. Judging from the observed systematic errors in the computed C−H bond energies at the CASPT2[g1]/CBL(2) level of theory, the accuracy of the reaction energies of the isodesmic reactions due to favorable cancellation of errors is expected to be in the range of 1−3 kcal/mol.

3.4. Assessment of Several Isodesmic Reactions. In prior investigations the enthalpy of formation for the *p*-benzyne has been deduced by utilizing the following three reactions:

$$p\text{-}C_6H_4 \rightarrow o\text{-}C_6H_4 \tag{11}$$

$$C_6H_6 + 2CH_3 \rightarrow p\text{-}C_6H_4 + 2CH_4 \tag{12}$$

$$C_6H_6 + p\text{-}C_6H_4 \rightarrow 2C_6H_5 \tag{13}$$

In order to determine the enthalpy of formation of *o*-benzyne, the reaction

$$C_6H_6 + C_2H_2 \rightarrow o\text{-}C_6H_4 + C_2H_4 \tag{14}$$

has been employed. Reaction 11 was used in direct estimates, whereas reactions 12−14 were used in so-called isodesmic

TABLE 4: Calculated C−H Bond Strength in Methane,[a] C−H Bond Energies[a] in Ethylene[b] Abstracting Two Hydrogens, and C−H Bond Strength in Benzene[c] in kcal/mol at 298 K for a Number of Methods and One-Particle Basis Sets

	basis sets								
methods	aANO(1)	aANO(2)	cc-pVDZ	cc-pVTZ	cc-pVQZ	CBL(1)	CBL(2)	CBL(3:3,4)	CBL(4:3,4)
				Methane					
RSCF	79.7	79.8	79.5	80.0	79.9	79.8	79.8	79.9	79.9
MP2[g0]	97.2	98.9	96.2	99.2	100.0	100.5	100.4	100.5	100.2
MP2[g1]	98.9	100.7	97.6	100.9	101.8	102.4	102.3	102.4	102.0
MP3	99.6		98.5	101.5	102.2	102.7	102.6	102.8	102.4
CISD	98.5		97.5	100.3	100.9	101.4	101.3	101.4	101.1
CISD(Q)	100.6		99.4	102.6	103.3	103.8	103.7	103.8	103.5
CASRS2	98.8		97.7	100.7	101.5	101.8	101.6	101.8	101.5
CASRS3	100.5		99.1	102.4	103.1	103.6	103.6	103.6	103.3
				Ethylene					
MP2			134.3	137.9	138.8	139.4	139.2	139.4	139.0
MP3			142.5	145.9	146.4	146.7	146.4	146.8	146.6
CASSCF	96.2	95.8	96.2	95.7	95.7	95.7	95.7	95.6	95.6
CASPT2[g0]	137.2	139.6	136.2	139.7	140.7	141.5	141.5	141.4	141.0
CASPT2[g1]	137.2	139.7	136.2	139.8	140.8	141.6	141.5	141.5	141.1
CASRS2			136.2	140.0	140.9	141.7	141.6	141.6	141.2
CASRS3			139.4	142.2	142.6	142.9	142.8	143.0	142.8
RCCSD			142.5	145.7	146.3	146.7	146.5	146.8	146.5
RCCSD(T)			141.7	144.8	145.4	145.8	145.7	145.9	145.6
				Benzene					
CASSCF	88.8	88.8	87.9	88.7	88.8	88.8	88.7	88.8	88.8
CASPT2[g0]	105.5	107.2	103.4	107.2	108.2	108.9	108.6	108.9	108.5
CASPT2[g1]	106.2	108.0	103.8	108.0	109.0	109.8	109.5	109.7	109.3
CASRS2	105.0		103.0	106.8	107.8	108.4	108.2	108.4	108.0
CASRS3	110.5		108.3	112.3	113.1	113.7	113.4	113.7	113.4
MRCI	104.0		102.4	105.0					
MRCI(Q)	108.1		106.2	109.7					
RCCSD	110.0			111.7					
UCCSD	109.6			111.4					
RCCSD(T)	110.0			112.0					
UCCSD(T)	109.9			111.7					

[a] Experimental value: 104.9 ± 0.1 kcal/mol. [b] Experimental value: 146.0 ± 0.2 kcal/mol. [c] Experimental value: 113.6 ± 0.6 kcal/mol.

investigations. For an ideal isodesmic reaction the predicted enthalpy of reaction should be independent of the method employed. This criterion is used here to assess the quality of the reactions and the suitability for accurate predictions of the thermochemistry of the benzynes. In particular the CASRS2 and CASRS3 results are used to assess the quality of the proposed isodesmic reactions. The quality of the employed experimental enthalpies of formation will of course affect the accuracy with which the desired ΔH_f is computed as well. The computed enthalpies of reactions for reactions 11−14 are collected in Table 6. For all the reactions, it is noted that extrapolation to CBL after the cc-pVQZ basis set does not change the computed values in any significant way. Actually, the cc-pVTZ results are not very far off from the cc-pVQZ results, either. The largest discrepancy of 0.4 kcal/mol is noted for reaction 12, while for the three other reactions the differences decrease to 0.1 kcal/mol. Hence, with respect to the one-particle basis set all four reactions exhibit favorable cancellation of errors, a property expected for isodesmic reactions. For the treatment of the *N*-particle space, however, significant differences are noted. In particular, it is noted that reactions 12 and 14 behave especially badly. The differences in the CASRS2/CBL(2) and CASRS3/CBL(2) predicted enthalpies of reaction for reactions 11−14 are computed to 5.0, 8.8, −2.7, and 7.0 kcal/mol, respectively. The problem of reaction 12 has earlier, but in another context, been discussed by Cramer and coworkers,[9] who tagged it as a “flawed” isodesmic reaction. In their study they attribute the problem to the fact that the dehydrocarbons have different hybridization in methane, benzene, methyl radical, and *p*-benzyne. In this reaction the methane and methylene radical are treated in a single reference framework (SCF, MP2, and MP3), whereas the benzene and *p*-benzyne have a multiconfigurational reference (CASSCF, CASRS2, and CASRS3). In this sense the treatment of the “radical” orbitals will not be similar and large fluctuations in the computed values could be expected as the level of perturbation goes beyond second order. Cramer et al. employed reaction 14 as an isodesmic reaction in the determination of the enthalpy of formation of *o*-benzyne. However, judging from the results presented here, this reaction seems to have problems similar to those of reaction 12, which they disqualified. In reaction 14 we have again the problem of mixing species for which single reference perturbation theory works excellently (see reaction 6) with species for which a multireference treatment is required. The remaining reactions, 11 and 13, do not suffer from the mixture of single configurational and multiconfigurational reference treatments. However, one should expect that reaction 11 is the poorest isodesmic reaction due to the disparity of unpaired electrons in the reaction on the left and the right hand side. Indeed, reaction 11 in comparison to reaction 13 exhibits a variation in the computed heat of reaction which is almost twice as large. Furthermore, the size of the related reaction energy itself could serve as an indicator also for the quality of the corresponding isodesmic reaction. As anticipated, reaction 13 has the lowest reaction energy. The quality of the reactions, based on the difference CASRS3 vs CASRS2, from the best to the worst is 13, 11, 14, and 12. With respect to the basis set extrapolation schemes, it seems that CBL(2) is slightly better than the others, yet the differences from the other schemes are marginal (less than 0.4 kcal/mol).

3.5. Benzyne Thermochemistry. The study of the C−H bond energy of benzene definitely demonstrates the need for highly

TABLE 5: Calculated C−H Bond Strength in the Phenyl Radical at the para,[a] meta,[b] and ortho[c] Position in kcal/mol at 298 K for a Number of Methods and One-Particle Basis Sets

	basis sets								
methods	aANO(1)	aANO(2)	cc-pVDZ	cc-pVTZ	cc-pVQZ	CBL(1)	CBL(2)	CBL(3:3,4)	CBL(4:3,4)
				para					
CASSCF	86.4	86.5	85.5	86.4	86.5	86.4	86.4	86.5	86.5
CASPT2[g0]	101.8	103.5	99.5	103.5	104.5	105.2	104.9	105.2	104.8
CASPT2[g1]	104.1	106.1	102.2	106.0	107.0	107.9	107.8	107.8	107.4
CASRS2	101.1		98.9	102.9	103.8	104.5	104.2	104.5	104.1
CASRS3	109.1		106.6	110.9	111.8	112.4	112.1	112.5	112.1
MRCI	101.4		99.6	102.6					
MRCI(Q)	105.1		103.0	106.8					
RCCSD	129.2			131.6					
UCCSD	129.6			132.0					
RCCSD(T)	106.5			108.8					
UCCSD(T)	106.8			109.2					
				meta					
CASSCF	74.6	74.5	74.1	74.4	74.4	74.4	74.3	74.4	74.4
CASPT2[g0]	89.3	90.3	88.1	90.8	91.1	91.5	90.6	91.4	91.1
CASPT2[g1]	89.5	90.5	88.3	91.0	91.3	91.4	90.7	91.5	91.4
CASRS2			87.1	89.5	90.1	90.5	90.3	90.5	90.3
CASRS3			93.7	96.4	97.0	97.4	97.1	97.4	97.2
MRCI			86.6	88.2					
MRCI(Q)			89.9	92.0					
				ortho					
CASSCF	57.9	57.7	58.6	57.8	57.7	57.5	57.5	57.6	57.6
CASPT2[g0]	79.1	80.1	79.0	80.3	80.5	80.6	80.3	80.6	80.5
CASPT2[g1]	78.7	79.6	78.8	79.9	80.0	80.1	79.8	80.1	80.1
CASRS2			78.1	79.3	79.5	79.5	79.3	79.6	79.5
CASRS3			81.9	82.8	82.7	82.6	82.2	82.7	82.7
MRCI			73.5	72.4					
MRCI(Q)			78.1	78.4					

[a] Experimental value: 108.9 ± 1.2 kcal/mol. [b] Experimental value: 92.8 ± 3.2 kcal/mol. [c] Experimental value: 77.5 ± 3.1 kcal/mol.

correlated methods with systematic errors in conjunction with isodesmic reactions. Furthermore, the previous section illustrates the possible problems of several isodesmic reactions in cases of a method like CASRS3 which apparently has a sizable nonsystematic error. In addition, the study of the singlet−triplet energy splittings demonstrates the reliability of the CASPT2[g1] approximation. On the basis of the computed deviations from experiment for the hydrogen abstraction reactions introduced before, we regard the CASPT2[g1]/CBL(2) results as the most reliable ones having an accuracy of ±2 kcal/mol. The computed CASPT2[g1]/CLB(2) results (experimental prediction in parenthesis) for reactions 13, 11, 14, and 12 are 1.6 ± 2.0 (4.7 ± 1.6), −28.1 ± 2.0 (−31.4 ± 3.2), 47.6 ± 2.0 (45.1 ± 3.0), and 12.7 ± 2.0 (12.6 ± 1.0) kcal/mol, respectively. Considering the theoretical and experimental error bars, excellent agreement is observed. The corresponding predicted values by Cramer et al. at the CASPT2[g0]/aANO(1) level were 4.4, −23.5, 46.2, and 10.8 kcal/mol. After inclusion of the g1 correction in the CASPT2 approach, no data support the critics against the use of reaction 12 to determine the enthalpy of formation of *p*-benzyne or the use of reaction 11 to determine the difference in enthalpy of formation of *p*- and *o*-benzyne. Rather, reaction 12 supports the two independent experimental studies by Roth et al.[14] and Wenthold and co-workers[15,16] which predict the enthalpy of formation of *p*-benzyne to be 138.0 ± 1.0 and 137.8 ± 2.9 kcal/mol, respectively. The present theoretical prediction of the enthalpy of formation of *p*-benzyne is 138.0 and 141.4 kcal/mol by reactions 12 and 13, respectively, while for *o*-benzyne it is computed to be 108.8 kcal/mol using reaction 14.

It is remarkable that even for the best isodesmic reaction 13 the difference in the predicted reaction energy between CASPT2[g0] and CASPT2[g1] amounts to 2 kcal/mol (or 50−100% of the reaction energy). This is the largest correction of all four reactions apart from reaction 11, which illustrates convincingly the importance of the g1 correction. It seems that by introducing g1 an important (although systematic) error is removed, which is ill balanced in all four isodesmic reactions.

At the CASPT2[g1]/CBL(2) level of theory, the isodesmic reactions 12, 13, and 14 (replacing the benzyne species with meta) predict the enthalpy of formation of *m*-benzyne to be 120.7, 124.2, and 119.9 kcal/mol, respectively. This is again in agreement with the experimental finding of 121.9 ± 3.1 kcal/mol.

4. Summary

The thermochemistry of the benzynes was reinvestigated using a variety of different theoretical methods (CASPT2, CASRS2, CASRS3, MRCI, CCSD(T)), together with extended basis sets (up to quadruple-ζ quality). Some of these calculations became feasible only recently, due to progress in the development of integral direct correlation methods.[19] Complete basis set estimates were obtained from these calculations by employing different basis set extrapolation schemes. In order to examine the accuracy of the different methods, the singlet−triplet splittings of *o*-, *m*-, and *p*-benzyne were recomputed, which serves the purpose of a benchmark system for the thermochemistry of the benzynes. The zero point energy corrections were also reexamined at the CASSCF level of theory, using analytical second derivatives implemented recently.[20] The singlet−triplet energy splittings so obtained reveal that both basis set extrapolation and appropriate vibrational corrections are essential for quantitatively correct results. Previous ZPE corrections based on restricted and unrestricted DFT calculations turned out to be slightly hampered due to the use of either a single reference or a spin-contaminated wave function. The resulting imbalance

TABLE 6: Calculated Heats of Reaction in kcal/mol at 298 K for Reactions 11,[a] p-$C_6H_4 \rightarrow o$-C_6H_4; 12,[b] $C_6H_6 + 2CH_3 \rightarrow p$-$C_6H_4 + 2CH_4$; 13,[c] $C_6H_6 + p$-$C_6H_4 \rightarrow 2C_6H_5$; and 14,[d] $C_6H_6 + C_2H_2 \rightarrow o$-$C_6H_4 + C_2H_4$

	basis sets								
methods	aANO(1)	aANO(2)	cc-pVDZ	cc-pVTZ	cc-pVQZ	CBL(1)	CBL(2)	CBL(3:3,4)	CBL(4:3,4)
				Reaction 11					
CASSCF	−28.5	−28.7	−27.0	−28.5	−28.8	−28.9	−28.8	−29.0	−28.9
CASPT2[g0]	−22.7	−23.4	−20.5	−23.2	−24.0	−24.6	−24.6	−24.6	−24.3
CASPT2[g1]	−25.4	−26.4	−23.4	−26.1	−27.0	−27.8	−28.1	−27.7	−27.3
CASRS2			−20.8	−23.6	−24.4	−24.9	−24.9	−24.9	−24.6
CASRS3			−24.8	−28.1	−29.0	−29.8	−29.9	−29.8	−29.4
MRCI			−26.0	−29.1					
MRCI(Q)			−25.0	−28.4					
				Reaction 12					
CASSCF	15.7	15.7	14.4	15.2	15.4	15.6	15.4	15.6	15.5
CASPT2[g0]	12.8	12.9	10.5	12.3	12.7	13.0	12.7	13.0	12.9
CASPT2[g1]	12.6	12.7	10.9	12.1	12.5	12.9	12.7	12.8	12.6
CASRS2	11.7		9.4	11.1	11.6	11.9	11.5	11.9	11.7
CASRS3	20.5		17.9	20.1	20.5	20.7	20.3	20.8	20.6
MRCI	8.3			7.0					
MRCI(Q)	12.1			10.5					
				Reaction 13					
CASSCF	2.3	2.3	2.4	2.3	2.3	2.3	2.3	2.3	2.3
CASPT2[g0]	3.7	3.7	3.9	3.7	3.7	3.7	3.8	3.7	3.7
CASPT2[g1]	2.0	1.9	1.7	2.0	2.0	1.9	1.6	1.9	1.9
CASRS2	4.0		3.6	3.9	3.9	3.9	4.0	3.9	3.9
CASRS3	1.3		1.6	1.4	1.3	1.3	1.3	1.3	1.3
MRCI	2.6		2.8	2.6					
MRCI(Q)	3.0		3.2	3.0					
RCCSD(T)	3.7			3.2					
UCCSD(T)	3.0			2.5					
				Reaction 14					
CASSCF	50.5	50.4	49.9	50.5	50.4	50.2	50.0	50.3	50.3
CASPT2[g0]	47.4	47.4	46.2	47.6	47.7	47.8	47.3	47.8	47.8
CASPT2[g1]	47.6	47.7	46.4	47.8	48.0	48.1	47.6	48.1	48.1
CASRS2			44.8	46.1	46.3	46.3	45.9	46.4	46.3
CASRS3			50.8	52.9	53.2	53.3	52.9	53.4	53.3

[a] Experimental value: −31.4 ± 3.2 kcal/mol. [b] Experimental value: 12.6 ± 1.0 kcal/mol. [c] Experimental value: 4.7 ± 1.6 kcal/mol. [d] Experimental value: 45.1 ± 3.0 kcal/mol.

in the ZPEs, although small, inflicted a significant relative error on the predicted singlet−triplet energy splittings.

Furthermore, the known systematic error of the CASPT2 method eminent in chemical systems containing unpaired electrons (usually higher spin multiplicities, but also singlet states with spatially remote open shell electrons, i.e., biradicals) appears to range between 1.5 and 2 kcal/mol, and hence is nonnegligible. Thus, the g1 corrected zero order Hamiltonian should be used (CASPT2[g1] approach[18]).

In order to judge the quality of the miscellaneous isodesmic reactions proposed previously for determining the enthalpy of formation of *p*-benzyne, the C−H bond strengths of several relevant molecules were calculated, using the assortment of methods and basis sets mentioned above. These results again show that basis set extrapolation is a prerequisite for quantitatively correct results. Moreover, it turned out that in contrast to CASPT2 (or CASRS2) the CASRS3 method is plagued by a sizable *nonsystematic error*, not canceling when constructing the isodesmic reactions from the non-isodesmic hydrogen abstraction reactions. Therefore, the CASRS3 method seems to be less appropriate in the context of isodesmic reactions.

The extended and computationally demanding study demonstrates excellent agreement between theory and experiments. Furthermore, after employing the CASPT2[g1] approach, all four isodesmic reactions 11−14 behave equally well.

The present study also has, in a vivid way, illustrated the extreme demands on the level of theory required for a quantitative description of the chemistry of biradical species.

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References and Notes

(1) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.
(2) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907.
(3) Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1993**, *216*, 333.
(4) Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11958.
(5) Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1994**, *116*, 4929.
(6) Lindh, R.; Persson, B. J. *J. Am. Chem. Soc.* **1994**, *116*, 4363.
(7) Lindh, R.; Lee, T. J.; Bernhardsson, A.; Persson, B. J.; Karlström, G. *J. Am. Chem. Soc.* **1995**, *117*, 7186.
(8) Lindh, R.; Schütz, M. *Chem. Phys. Lett.* **1996**, *258*, 409.
(9) Cramer, C. J.; Nash, J. J.; Squires, R. R. *Chem. Phys. Lett.* **1997**, *277*, 311.
(10) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.
(11) Malcolm, N. O. J.; McDouall, J. J. W. *J. Phys. Chem.* **1996**, *100*, 10131.
(12) Borowski, P.; Jordan, K. D.; Nichols, J.; Nachtigall, P. *Theor. Chem. Acc.* **1998**, *99*, 135.
(13) Cramer, C. J. *J. Am. Chem. Soc.* **1998**, *120*, 6261.
(14) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765.
(15) Wenthold, P. G.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 7414.
(16) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.
(17) Andersson, K.; Roos, B. O. *Int. J. Quantum Chem.* **1993**, *45*, 591.
(18) Andersson, K. *Theor. Chim. Acta.* **1995**, *91*, 31.
(19) Schütz, M.; Lindh, R.; Werner, H.-J. *Mol. Phys.* **1998**, *96*, 719.
(20) Bernhardsson, A.; Lindh, R.; Olsen, J.; Fülscher, M. *Mol. Phys.* **1998**, *96*, 617.

(21) Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1993**, *97*, 4392.

(22) Moriarty, N. W.; Lindh, R.; Karlström, G. *Chem. Phys. Lett.* **1998**, *289*, 442.

(23) The structures, energetics and the harmonic frequencies listed for the species are available on http://www.teokem.lu.se/~roland/benzyne/harm.

(24) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

(25) Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645.

(26) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(27) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(28) Woon, D. E.; Dunning, T. H, Jr. *J. Chem. Phys.* **1994**, *100*, 2975.

(29) Kutzelnigg, W.; Morgan, J. D. *J. Chem. Phys.* **1992**, *96*, 4484.

(30) Martin, J. M. L.; Taylor, P. R. *J. Chem. Phys.* **1997**, *106*, 8620.

(31) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

(32) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS Version 4.1*; Dept. of Theor. Chem., Chem. Center, Univ. of Lund: P.O.B. 124, S-221 00 Lund, Sweden, 1996.

(33) Molpro is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, M. Schütz, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, H. Stoll, and T. Thorsteinsson.

(34) Roos, B. O. The complete active space self-consistent field method and its applications in electronic structure calculations. In: *Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry—II*; Lawley, K. P., Ed.; John Wiley & Sons Ltd.: Chichester, England, 1987; Chapter 69, p 399.

(35) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279.

(36) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(37) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

(38) Pedley, J. G.; Naylor, R. D.; Kirby, S. P. *Thermochemistry of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

(39) Gurvich, L. V.; Veyts, I. V.; Alcook, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1989; Vol. 1.

(40) Gurvich, L. V.; Veyts, I. V.; Alcook, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1991; Vol. 2, Parts 1 and 2.

(41) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Chem. Phys.* **1994**, *98*, 2744.

(42) Leopold, D. G.; Miller, A. E. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1379.