

Tetradehydrobenzenes: Singlet–Triplet Energy Separations and Vibrational Frequencies

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Abstract: The energies and structures of the three tetradehydrobenzene (C₆H₂) isomers (“ortho”, “meta”, and “para”) were studied employing density functional theory (BLYP and B3LYP), complete active space SCF (CASSCF), and the coupled-cluster method with single, double (CCSD), and perturbative triple excitations [CCSD(T)] in conjunction with basis sets of up to triple- ζ plus double polarization quality. The meta isomer, 1,2,3,5-tetradehydrobenzene, is the most favorable cyclic isomer, but is 38 kcal mol⁻¹ less stable than the hexatriyne C₆H₂ global minimum. All of the cyclic isomers have singlet ground states, but these are less stable for the ortho and para isomers; hence, the singlet–triplet energy splittings for 1,2,4,5- and 1,2,3,4-tetradehydrobenzene are smaller than for *ortho*-benzynes. Harmonic vibrational frequency analyses [up to CCSD(T)/TZ2P] suggest that the $\nu_{\text{as}}(\text{C}\equiv\text{C})$ vibration should be observable in the IR spectra of 1,2,4,5-tetradehydrobenzene at ca. 1675 cm⁻¹ but that this vibration might be too weak to be seen for 1,4-bis-(trifluoromethyl)-2,3,5,6-tetradehydrobenzene.

Introduction

In contrast to the didehydrobenzenes^{1–26} (benzynes, **1a–c**) and their isomers,^{26–30} the even more highly unsaturated C₆H₂ tetradehydrobenzenes (benzdiynes, **2a–c**, Scheme 1) have only received limited attention experimentally^{31,32} and theoretically.^{15,33,34} Fields and Meyerson pyrolyzed mellophanic (1,2,3,4-) and pyromellitic (1,2,4,5-) dianhydrides in 1966 and inferred the formation of 1,2,3,4- (**2b**) and 1,2,4,5-tetradehydrobenzenes (**2a**) as reactive intermediates from product analyses.^{31,35,36} It took,

however, more than 30 years until a benzdiyne derivative **3** (Scheme 1) was observed spectroscopically by Moriyama et al.³⁷ While no direct UV or IR spectroscopic evidence for the existence of **2a** could be deduced from the photolysis of pyromellitic dianhydride (the products were butadiyne and 1,3,5-hexatriyne, **4**),³² irradiation of 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride in an argon matrix at 248 nm was reported to give 1,4-bis(trifluoromethyl)-2,3,5,6-tetradehydrobenzene (**3**).³⁷ The peak at 1466 cm⁻¹ in the IR spectrum was assigned to the aromatic ring stretching vibration,³⁷ since the corresponding vibration of *ortho*-benzynes (**1a**) is at 1451 cm⁻¹.³⁸ Also, HF/6-31G* vibrational frequencies for **3** at 1431

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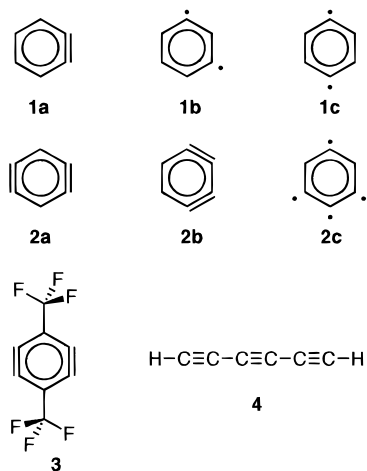
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Scheme 1. Di- and Tetradehydrobenzenes **1**, **2**, and **3** and Hexatriyne **4**

cm^{-1} (as well as at 1616 cm^{-1}) support this assignment. Although Moriyama et al. suggested a benzdiyne structure with two triple bonds for **3**, no IR peak corresponding to the $\text{C}\equiv\text{C}$ stretching vibration was observed.³⁷ The authors did not consider this to be “negative proof for assignment of benzdiyne”, as their HF/6-31G* vibrational frequency computation for **3** was said not to give a “definite peak for the $\text{C}\equiv\text{C}$ stretching.”³⁷ These results are inconsistent with two earlier studies, as (a) the $\text{C}\equiv\text{C}$ stretching band for **1a** could be observed at 1846 cm^{-1} with an intensity of $2.0 \pm 0.4 \text{ km mol}^{-1}$,³⁸ and (b) Zahradnik et al. computed a 1867 cm^{-1} band for the asymmetric $\text{C}\equiv\text{C}$ stretching of **2a** with an intensity of 3.7 km mol^{-1} at the MP2/6-31G* level.³⁴

There was much controversy about the triple bond stretching vibration of **1a** after Chapman³⁹ first reported its infrared spectrum in 1973. From IR matrix spectroscopy a band around 2085 cm^{-1} was deduced for the $\text{C}\equiv\text{C}$ stretching vibration.^{40–45} However, Leopold et al.⁴⁶ assigned the $\nu(\text{C}\equiv\text{C})$ vibration to a band at 1860 cm^{-1} in their 1986 gas-phase photodetachment study, which was confirmed later by Radziszewski et al.³⁸ All theoretical studies of the *ortho*-benzyne vibrational frequencies agree with these experiments^{11,12,14,15,25,38} but overestimate the $\text{C}\equiv\text{C}$ stretching vibration in *ortho*-benzyne somewhat.

Previous theoretical investigations of tetradehydrobenzenes found that the para isomer **2a** is higher in energy than the ortho compound **2b** by $1.2 \text{ kcal mol}^{-1}$ (CASSCF/3-21G)¹⁵ and $11.5 \text{ kcal mol}^{-1}$ (MP2/6-31G*³⁴). However, the third possible cyclic C_6H_2 isomer, meta **2c**, has not been the subject of any investigation. It is well-established for the didehydrobenzenes that *ortho*-benzyne is significantly lower in energy than the *meta*- ($15.3 \text{ kcal mol}^{-1}$) and *para*-benzynes ($31.4 \text{ kcal mol}^{-1}$).^{47–49}

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Since the two triple bonds in **2a** and **2b** can be expected to induce large ring strain, the biradical **2c** might be energetically competitive in the tetradehydrobenzene series. We investigated the geometries, relative energies, and singlet–triplet energy splittings for all three tetradehydrobenzene isomers as well as the vibrational frequencies for **2a** and **3** at high levels of theory.

Computational Methods

The geometry optimizations of **2** employed density functional theory, second-order perturbation theory, and complete active space (CAS) SCF, as well as the coupled-cluster method with single and double excitations (CCSD) and a perturbative treatment of triple excitations [CCSD(T)]. Becke's⁵⁰ exchange–correlation functional and Becke's⁵¹ three-parameter hybrid functional together with the correlation functional of Lee, Yang, and Parr⁵² (BLYP and B3LYP, respectively) were utilized as implemented⁵³ in Gaussian 94.⁵⁴ The 10-electron/10-orbital active space in the CASSCF computations consisted of the six benzene π orbitals and the four σ orbitals displayed in Figure 2. Harmonic vibrational frequencies were evaluated analytically (BLYP and B3LYP) or via finite differences of analytic gradients [CCSD and CCSD(T)]. The basis sets were 6-31G*⁵⁵; DZP, constructed from Dunning's⁵⁶ double- ζ contraction and augmented with one set of d (for C) and p (for H) polarization functions with orbital exponents of $\alpha_d(\text{C}) = 0.75$ and $\alpha_p(\text{H}) = 0.75$; and TZ2P constructed from Dunning's⁵⁶ triple- ζ (10s6p/5s3p) contraction augmented with two sets of d (for C) and p (for H) polarization functions with orbital exponents of $\alpha_d(\text{C}) = 1.500/0.375$ and $\alpha_p(\text{H}) = 1.500/0.375$. The TZ2P basis set was obtained by augmenting the TZ2P basis with one set of f polarization functions for carbon with orbital exponents of $\alpha_f(\text{C}) = 0.8$. The coupled cluster geometry optimizations were performed with Cartesian d functions; spherical harmonic functions were used otherwise.

Single-point energy computations on the CCSD/DZP geometries with the CCSD(T)/TZ2P method accounted for electron correlation more extensively. The reaction enthalpies at 0 K of isodesmic eqs 1 to 8 involving **2a–c**, the 1,2,3- (**5**), 1,2,4- (**6**), and 1,3,5-tridehydrobenzene (**7**) as well as the phenyl radical (**8**) and benzene (**9**) were evaluated at CCSD(T)/TZ2P//CCSD/DZP with BLYP/6-31G* zero-point vibrational energy (ZPVE) corrections. The core orbitals were frozen in the single point computations. The coupled-cluster computations were performed with ACES2;⁵⁷ all other data were obtained with Gaussian 94.⁵⁴

Results and Discussion

Geometries and Energies. Structures with two CC bonds shorter than ca. 1.28 \AA are obtained for the D_{2h} **2a** and C_{2v} **2b** C_6H_2 singlet isomers at all levels of theory employed (Figure 1). Note that increasing the level of theory in the geometry optimization of **2a** from CCSD/DZP to CCSD(T)/TZ2P does not change the structure significantly (Figure 1). The CC “triple” bonds of **2a** and **2b** should be analogous to the $1.24 \pm 0.02 \text{ \AA}$ *ortho*-benzyne (**1a**) dehydro-CC bond lengths determined

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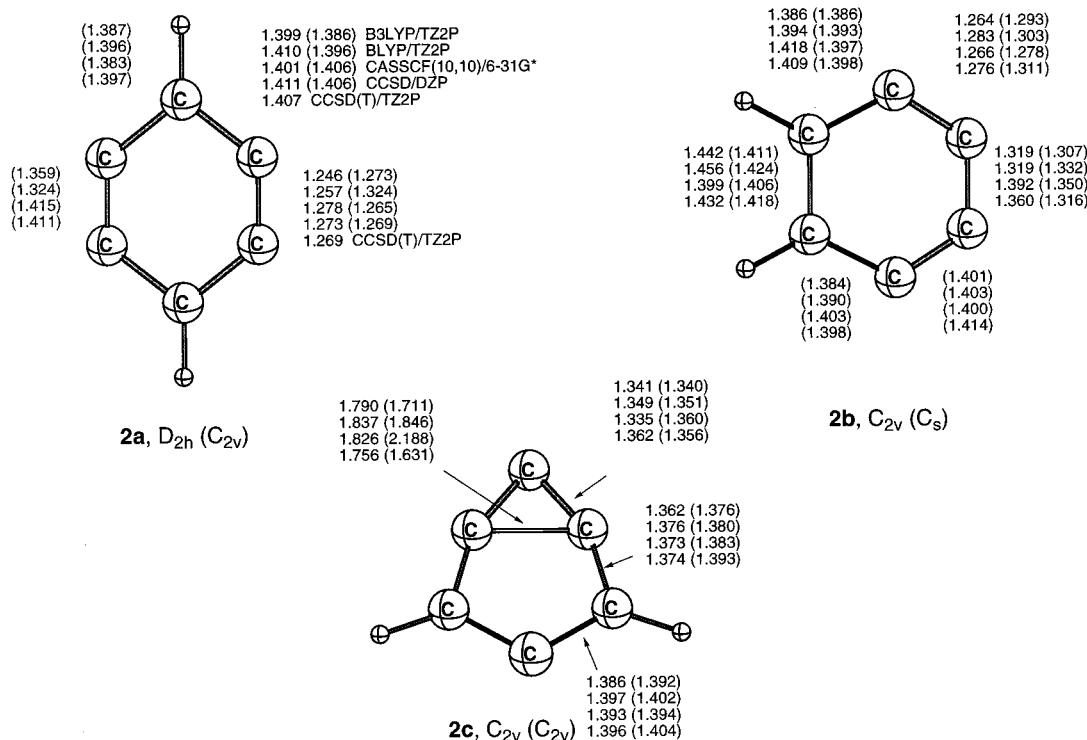


Figure 1. Geometries of tetradehydrobenzene singlets and triplets (bond lengths and point group in parentheses) at various levels of theory (see **2a** for labeling). All bond lengths are in Å.

experimentally.⁵⁸ Our recent analyses of the geometry, Wiberg bond indices (WBI), and magnetic properties concluded that the structure of **1a** is more acetylene- than cumulene-like.²⁴ The B3LYP/6-311+G** geometry [$r(\text{C}_1\text{C}_2) = 1.245$ Å] should be close to the actual structure of **1a** since the computed ¹H and ¹³C chemical shifts are in very good agreement with experiment.^{24,58,59} Larger deviations are found when the CASSCF(8,8)/DZP or CCSD(T)/6-31G** geometries^{4,21} are employed for the chemical shift computations.²⁴

The triple bonds in **2a** are slightly shorter than in **2b** (Figure 1). The four electrons in the benzene ring plane of **2b** are delocalized over the four σ orbitals, as in the π system of butadiene (Figure 2).¹⁵ This results in an elongation of the terminal C1–C2 and C3–C4 bonds and a shortening of the intervening C2–C3 bond in **2b** compared to **2a**, where the presence of the two CH units precludes such σ conjugation. As a consequence of the σ (in-plane) conjugation, isomer **2b** is 6 kcal mol⁻¹ lower in energy than **2a** (Table 1).

The reaction energies of the isodesmic eqs 1 to 6 (Scheme 2) were computed to delineate the energetic effect of combining two CC triple bonds in one six-membered ring. This is unfavorable for the singlet states of **2a** and **2b**, as indicated by the large exothermicities, 11.5 kcal mol⁻¹ and 5.7 kcal mol⁻¹, of eqs 1 and 2, respectively. The ring strain due to the didehydrogenation is smaller for the triplet **2a–T**, because one of the dehydro-CC bonds is significantly longer than in **2a–S** (Figure 1). Hence, the isodesmic eq 3 is endothermic (5.9 kcal mol⁻¹) for **2a–T**. Mainly as a consequence of the singlet state destabilization, the singlet–triplet splitting (ΔE_{ST}) of **2a** is decreased to 18 kcal mol⁻¹ with respect to **1a** (35.8 kcal mol⁻¹) (Table 2). Note that our CCSD(T)/TZ2P//CCSD/DZP ΔE_{ST} for **1a** is in good agreement with the experimental result of 37.5 ± 0.3 kcal mol⁻¹.⁶⁰

The geometry of **2b–T** (Figure 1) suggests the presence of a σ -allyl type radical moiety with an adjacent radical center. The repulsive interaction between the two electrons of same spin is only 1 kcal mol⁻¹ from eq 5. According to isodesmic eq 4, the tetradehydro arrangement of **2b–T** is more stable than separated **1a–S** and **1a–T** by 3.9 kcal mol⁻¹, due to the σ allyl radical moiety in **2b–T**. In the radical **5–D**, the delocalization of the three electrons over three σ type orbitals is a 3.9 kcal mol⁻¹ attractive interaction, as obtained from eq 6. The singlet destabilization (5.7 kcal mol⁻¹) and the triplet stabilization (3.9 kcal mol⁻¹) of **2b** result in a singlet–triplet gap ($\Delta E_{\text{ST}} = 26.3$ kcal mol⁻¹) which is roughly 10 kcal mol⁻¹ smaller than in **1a**.

The meta isomer **2c** is the lowest energy form of tetradehydrobenzene, 11 kcal mol⁻¹ below **2a**. The hexatriyne global minimum on the C₆H₂ PES, **4**, is 38.0 kcal mol⁻¹ lower in energy than **2c**. Bicyclic structures of **2c** with partial σ bonds between C1 and C3 (1.76 Å to 1.84 Å) result at all levels of theory. In contrast, the “bicyclic” density functional geometries for *meta*-benzyne (**1b**) with a CC partial bridging bond (1.6 to 1.8 Å using B3LYP and Becke’s⁵⁰ exchange functional together with the correlation functional of Perdew and Wang,⁶¹ BPW91) are considered to be artifacts.⁶ For *meta*-benzyne considerably longer distances between the radical centers are obtained with CCSD(T)/6-31G**^{2,21} (2.106 Å) and CASSCF(8,8) using an averaged atomic natural orbital basis set (aANO, 2.178 Å).^{4,5} The zwitterionic contribution to the electronic structure of the *meta*-benzyne biradical is overestimated, due to the single-configuration character of DFT, resulting in a C1–C3 distance which is 0.3 Å shorter (1.874 Å at BPW91/cc-pVDZ) than at CASSCF/cc-pVDZ.⁶ Interestingly, it has been reported that hybrid functionals including Hartree–Fock exchange, e.g., B3LYP, perform worse than “pure” density functional methods such as BPW91 and BLYP for energies and structures of diradicaloid molecules such as *meta*- and *para*-benzyne.^{6,29,30}

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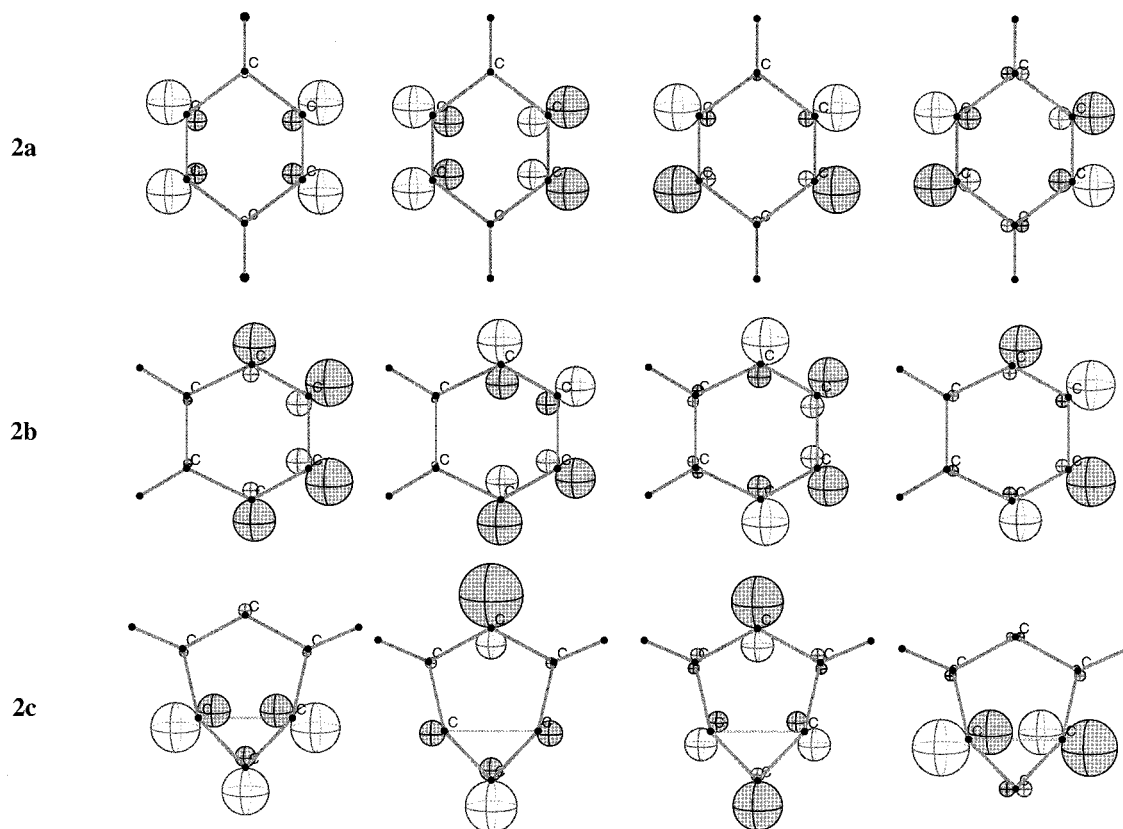


Figure 2. The two doubly occupied and the two unoccupied (from left to right) in-plane molecular orbitals of singlet tetrahydrobenzenes **2a–c**.

Table 1. Relative Energies (in kcal mol⁻¹) for the Three Isomers of Singlet and Triplet Tetrahydrobenzene at Various Levels of Theory

	CASSCF/ 6-31G* ^a	BLYP/ TZ2P ^a	B3LYP/ TZ2P ^a	CCSD(T)/ TZ2P ^{a,b}
2a-S	0	0	0	0
2b-S	-3.1	-12.2	-9.9	-5.8
2c-S	+11.4	-19.4	-16.9	-11.0
2a-T	0	0	0	0
2b-T	+1.2	+0.7	-3.1	+2.2
2c-T	+16.4	+9.4	+4.1	+8.2

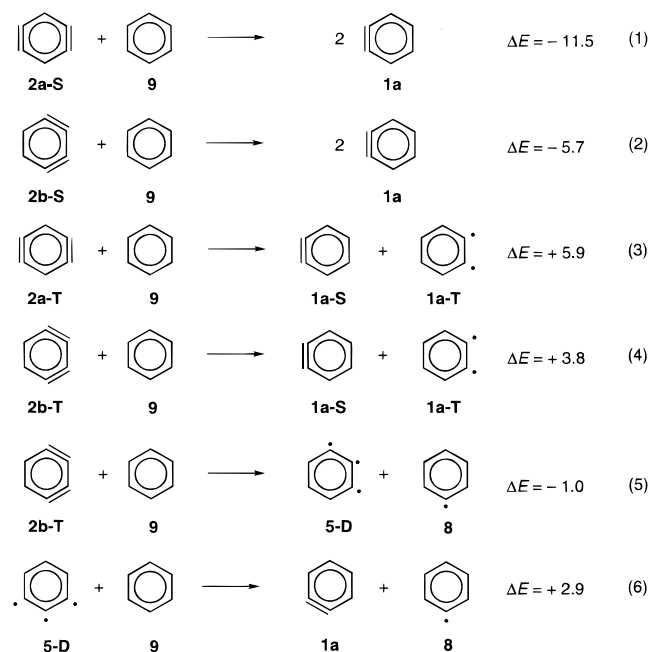
^a ZPVE at BLYP/6-31G*. ^b CCSD/DZP geometries.

The better agreement among theoretical methods for **2c** as compared to **1b** is readily understood when the molecular orbitals are considered (Figure 2). The HOMO and LUMO of **2c** are essentially the antibonding and bonding combinations of the σ radical orbitals centered at C2 and C5. The bonding and antibonding combinations of the C1 and C3 σ radical orbitals, the HOMO and LUMO of **1b**, are lower and higher lying orbitals for **2c**. Thus, insufficient inclusion of HOMO–LUMO excitations, a possibility with DFT, does not effect the C1–C3 distance as much as in **1b**.

The bicyclic structure of **2c** results from the bonding interaction between the meta dehydro atoms and σ delocalization over C1, C2, and C3, similar to a π allyl system. The isodesmic eqs 7 to 9 (Scheme 3) define the biradical stabilization energies (BSE),⁶ which describe the energetic effect of combing two radical sites in one six-membered ring. The large BSE [30.5 kcal mol⁻¹, eq 7] for **2c-S** indicates a large attractive interaction between the radical center at C5 and the σ allyl system.

The differences in BSEs from eqs 7 to 9 reflect the relative stabilities of the trihydrobenzenes. The 1,2,4-tridehydrobenzene radical (**6-D**) and the 1,3,5-tridehydro isomer (**7-D**) are 4.0 kcal mol⁻¹ and 11.8 kcal mol⁻¹ higher in energy, respec-

Scheme 2. Reaction Enthalpies at 0 K for Isodesmic Equations 1 to 6 at the CCSD(T)/TZ2P//CCSD/DZP + ZPVE (at BLYP/6-31G*) Level of Theory



tively, than the 1,2,3-tridehydro isomer **5-D** (Figure 3) with the σ allyl system. In contrast to the D_{3h} “doubly aromatic” 3,5-didehydrophenyl cation,⁶² the global $C_{6H_3^+}$ minimum,^{62,63} the corresponding radical **7-D** has C_{2v} symmetry due to the Jahn–

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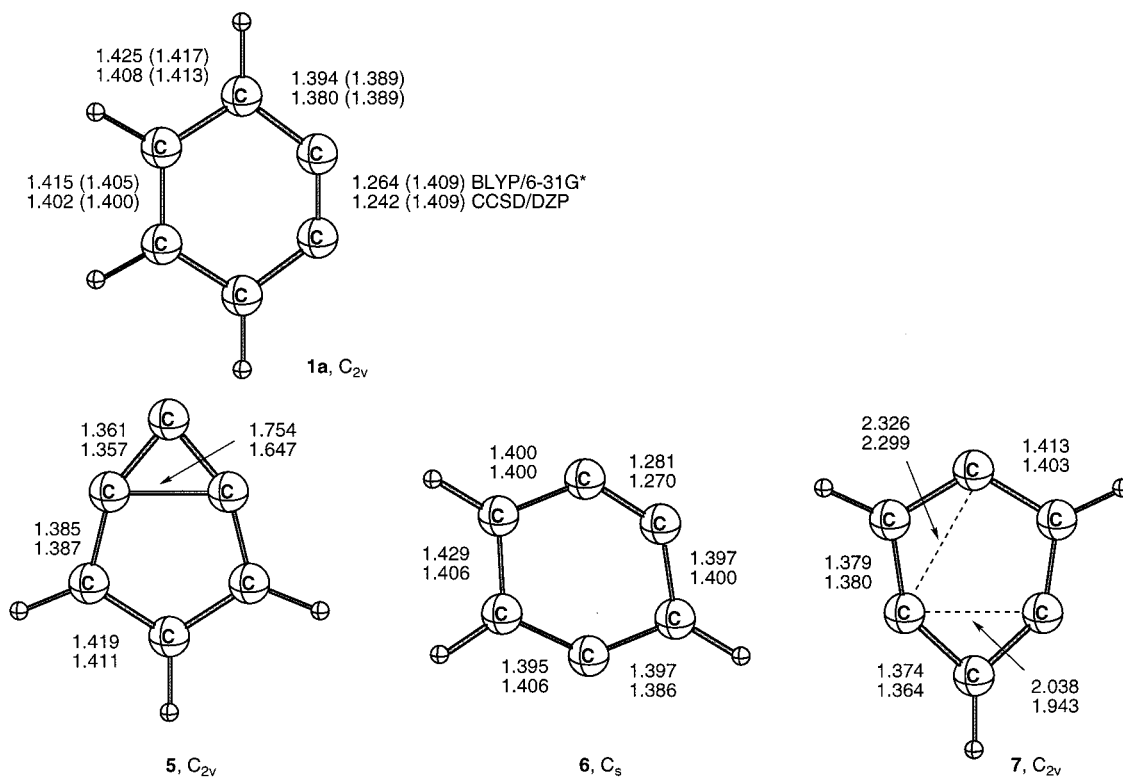


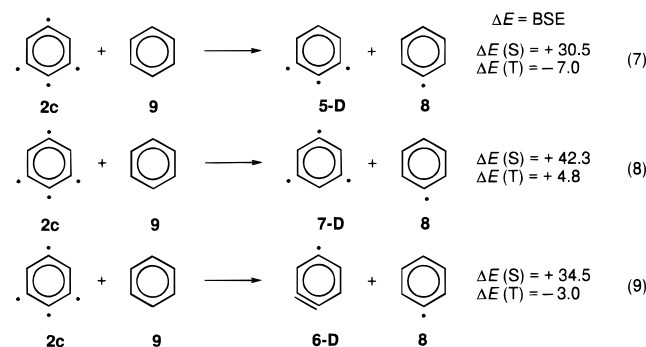
Figure 3. Geometries of singlet and triplet (in parentheses) *ortho*-benzyne (**1a**) and the tridehydrobenzene radicals **5**, **6**, and **7** at various levels of theory (bond lengths are in Å).

Table 2. Singlet–Triplet Energy Separations (in kcal mol⁻¹) for *ortho*-Benzyne (**1a**) and the Three Isomers of Tetradehydrobenzene at Various Levels of Theory. A Positive Energy in This Table Means that the Singlet State Lies Lower

	CASSCF/ 6-31G* ^a	BLYP/ TZ2P ^a	B3LYP/ TZ2P ^a	CCSD(T)/ TZ2P ^{a,b}
1a		35.5	31.3	35.8
2a	20.5	6.4	7.2	18.3
2b	24.7	19.2	14.0	26.3
2c	25.5	35.2	28.2	37.5

^a ZPVE at BLYP/6-31G*. ^b CCSD/DZP geometries.

Scheme 3. Biradical Stabilization Energies for **2c** at the CCSD(T)/TZ2P//CCSD/DZP + ZPVE (at BLYP/6-31G*) Level of Theory



Teller distortion. The distance between the C1 and C5 dehydro atoms are closer than the C1–C3 and C3–C5 distances, 1.94 Å vs. 2.30 Å at CCSD/DZP, respectively. Whereas the structure of **6-D** resembles that of triplet **2b-T**, **7-D** is bicyclic and very similar to **2c**.

Considering that the ΔE_{ST} values of the diradicaloid *meta*- and *para*-benzyne are significantly smaller than for *ortho*-benzyne (21.1 ± 0.3 ,⁶⁰ 3.8 ± 0.4 ,⁶⁰ and 37.5 ± 0.3 ,⁶⁰ respectively), the large singlet–triplet separation of 38 kcal

mol⁻¹ obtained for the biradical **2c** is surprising (Table 2). The negative BSE [–7.0 kcal mol⁻¹, eq 7] for **2c-T** reveals that the interaction of the two triplet-coupled electrons is unfavorable, in contrast to the singlet state. The LUMO of **2c-S** involves bonding between C1 and C3 but also a strong antibonding interaction with an in-plane sp²-type orbital centered at C5 (Figure 2). Hence, a large HOMO–LUMO gap (0.30 eV) results for **2c-S**. The singlet LUMO is occupied in the triplet state, which consequently is energetically unfavorable.

Comparison of Theoretical Methods

CCSD(T)/TZ2P single-point computations were performed for tetradehydrobenzene isomers employing the BLYP, B3LYP, CASSCF, and CCSD structures (Figure 1). The CCSD(T) energies of the singlet states are insensitive to the geometry as the BLYP, B3LYP, CASSCF, and CCSD structures of **2a-S**, **2b-S**, and **2c-S** are all within 1.2 kcal mol⁻¹ at the CCSD(T)/TZ2P level. This is remarkable for **2c-S**, in view of the C1–C3 distance ranging from 1.756 to 1.837 Å. In contrast, the CCSD(T)/TZ2P energies of the triplet states are more sensitive to the geometry employed for the single-point runs. Especially the CASSCF geometries of **2b-T** and **2c-T** are higher in energy (1.6 and 5.7 kcal mol⁻¹, respectively) than the CCSD and BLYP structures, which are almost isoenergetic at the CCSD(T)/TZ2P level. The latter result is remarkable as the C1–C3 distance in **2c-T** differs significantly between the CCSD/DZP (1.631 Å) and the BLYP/TZ2P (1.711 Å) geometries.

The relative stabilities of the various singlet and triplet tetradehydrobenzene isomers vary enormously across the various levels of theory [using the most reliable CCSD(T)/TZ2P//CCSD/DZP method as reference]. According to the CASSCF(10,10)/6-31G* wave function, the singlet states **2a–b** have a larger multireference character (the HF configuration contributions are 0.83 and 0.84, respectively) than their corresponding triplet states (0.87 and 0.91). Whereas DFT methods underestimate the

Table 3. The Harmonic Vibrational Frequencies (in cm^{-1} and the infrared intensities (in km mol^{-1}) of 1,2,4,5-tetrahydrobenzene (**2a**) at the B3LYP/TZ2P and CCSD(T)/TZ2P (only for Infrared-Active Vibrations) Levels of Theory

sym	B3LYP/TZ2P		CCSD(T)/TZ2P	
	ω_0	I	ω_0	I
a_g	3231	0		
	2040	0		
	1097	0		
a_u	690	0		
	418	0		
b_{3g}	1342	0		
	1211	0		
	237	0		
b_{2g}	902	0		
	584	0		
b_{3u}	336	13	337	12
	846	30	826	33
b_{1u}	3227	6	3249	7
	1287	1	1259	3
	547	270	619	157
b_{2u}	1858	0.3	1675	8
	1310	0	1318	0
	977	48	956	35

stability of **2a-S**, the isomer with the least multireference character, **2c-S** is much too high in energy at CASSCF. Note that B3LYP and CASSCF predict **2b-T** to be the lowest energy triplet isomer, in contrast to BLYP and CCSD(T). The failure of the CASSCF approach to give energies in reasonable agreement with CCSD(T) might be due to the rather small basis set and to the neglect of dynamical electron correlation. Among the density functional methods, the pure BLYP functional seems to perform slightly better than the HF/DFT hybrid B3LYP, in agreement with the observations of Cramer et al. and Schreiner (vide supra).^{6,29,30}

Vibrational Frequencies of **2a** and **3**

The harmonic vibrational frequencies and the infrared intensities determined for **2a** at the B3LYP/TZ2P level agree very well with the CCSD(T)/TZ2P data (Table 3). Only for the asymmetric CC triple bond valence vibration, $\nu_{\text{as}}(\text{C}\equiv\text{C})$, the difference between B3LYP (1858 cm^{-1}) and CCSD(T) (1675 cm^{-1}) is sizable. To further ascertain the reliability of B3LYP/TZ2P for dehydrobenzene systems, the vibrational frequencies of **1a** are compared to experimental data (Table 4).³⁸ Again, very good agreement is found, only the $\text{C}\equiv\text{C}$ valence vibration deviates somewhat. Indeed, the $\nu(\text{C}\equiv\text{C})$ vibrations are found to be very much dependent on the basis set as well as on the level of electron correlation (Table 5). However, scaling the B3LYP/TZ2P data to eliminate the error for $\nu(\text{C}\equiv\text{C})$ of **1a** brings B3LYP/TZ2P in good agreement with CCSD(T)/TZ2P for **2a**. From our highest level data, CCSD(T)/TZ2P, we expect that the asymmetric $\text{C}\equiv\text{C}$ stretching vibration should be IR observable at about 1675 cm^{-1} with an intensity of 8 km mol^{-1} .

In addition, we determined the geometry and the IR spectrum (B3LYP/TZ2P) of the bis-(trifluoromethyl)-substituted isomer **3**, for which Moriyama et al.³⁷ did not observe a $\text{C}\equiv\text{C}$ stretching vibration. The trifluoromethyl groups in **3** do not change the geometry of the six-membered ring significantly with respect to **2a** (see Figures 1 and 4). However, the C_{2h} form of **3** was a first-order stationary point, with a very small imaginary frequency (5i cm^{-1}) corresponding to a rotation of the trifluoromethyl groups. The C_2 minimum is essentially isoenergetic, although the fluorine atoms are rotated 18° out of the benzene ring plane. The vibrational frequencies of C_{2h} -**3** and C_2 -**3** are

Table 4. Vibrational Frequencies (in cm^{-1}) for *ortho*-Benzyne (**1a**) from IR Experiment and at the B3LYP/TZ2P Level

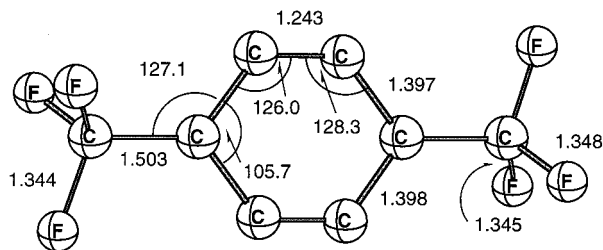
sym	experiment ^a	B3LYP/TZ2P
a_1	3094	3218
	3071	3192
	1846	2028
	1415	1503
	1271	1330
	1055	1173
	1039	1087
	982	1009
	589	622
	838	915
b_1	737	756
	388	396
b_2	3086	3214
	3049	3177
	1451	1488
	1394	1439
	1307	1286
	1094	1118
	849	844
	472	406

^a Reference 38.

Table 5. Unscaled and Scaled (in italics) Harmonic Vibrational Frequencies (in cm^{-1}) for the $\text{C}\equiv\text{C}$ Stretch in *ortho*-Benzyne (**1a**) and $\nu_{\text{as}}(\text{C}\equiv\text{C})$ in 1,2,4,5-Tetrahydrobenzenes **2a** and **3**, and their Infrared Intensities (in parentheses in km mol^{-1}) at Various Levels of Theory

level of theory	1a	2a , D_{2h}	3 , C_{2h}	3 , C_2
HF/6-31G*		1963 (0.2) ^a	1816 (361.8)	
MP2/6-31G*	1961 (3.3) ^b			
B3LYP/6-31G*	2028 (0.2)	1873 (0.5)	1876 (9.5) ^c	
B3LYP/TZ2P	2012 (0.1)	1858 (0.3)	1866 (5.3) ^a	1866 (3.8)
	(1848)	(1707)	(1714)	(1714)
B3LYP/TZ2Pf		1861 (0.4)		
CCSD(T)/DZP		1704 (6.1)		
CCSD(T)/TZ2P		1675 (8.1)		
Experiment	1848 (2.0 ± 0.4)			

^a One imaginary vibrational frequency. ^b Reference 38. ^c Two imaginary vibrational frequencies.

**Figure 4.** Geometry of C_2 symmetric 1,4-bis(trifluoromethyl)-2,3,5,6-tetrahydrobenzene (**3**) at the B3LYP/TZ2P level of theory. Bond lengths are in Å, bond angles in degrees.

very similar, but for the latter more are infrared active due to the lower point group symmetry. The B3LYP/TZ2P data is in very good agreement with the four experimentally observed vibrations of **3** (Table 6). The bands missing in the experimental IR spectrum might be obscured by the many precursor and product signals in the 1250- cm^{-1} to 1100- cm^{-1} range. In particular, the $\nu_{\text{as}}(\text{C}\equiv\text{C})$ band, which is expected to appear around 1700 cm^{-1} , has a negligibly small infrared activity compared to the very strongly absorbing asymmetric $\text{C}-\text{CF}_3$ stretch at 1172 cm^{-1} .

Conclusions

The *ortho* and *para* singlet C_6H_2 tetrahydrobenzene **2a-S** and **2b-S** isomers have CC triple bonds analogous to *ortho*-

Table 6. Comparison of the Measured and Computed IR Spectra for **3** (Vibrational Frequencies in cm^{-1} , Computed Intensities in km mol^{-1})

expt ^a	B3LYP/TZ2P, C ₂
	1866 ^b (4)
1466 (m)	1462 (119)
	1207 (107)
1183 (s)	1172 (624)
1127 (m)	1128 (357)
	1125 (71)
	1120 (366)
	1118 (180)
798 (w)	779 (21)

^a Taken from ref 37. ^b The scaled value is 1714 cm^{-1} , see Table 5.

benzyne (**1a-S**), but the singlet–triplet splittings are significantly smaller than in **1a**, mainly due to increased ring strain. The formally diradicaloid meta isomer **2c-S** is the most stable cyclic C_6H_2 form. In diradicals, two electrons occupy two (almost) degenerate orbitals. However, a large HOMO–LUMO gap is found for **2c-S**. Furthermore, the multireference character deduced from the CASSCF(10,10)/6-31G* computations is larger for **2a-S** and **2b-S** than for **2c-S** (the HF configuration contributions are 0.83, 0.84, and 0.87, respectively). Hence, the

diradical character of **2c-S** is rather small. The stability of **2c-S** arises from the strong bonding interaction between the dehydro C5 carbon atom and the σ allyl system.

The asymmetric $\text{C}\equiv\text{C}$ valence vibration should be observable in the IR spectrum of **2a-S** as a weak band close to 1675 cm^{-1} . The same vibration also is infrared active in **3** at approximately 1675 to 1700 cm^{-1} , but due to its very weak relative intensity it might not be detected experimentally.

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Supporting Information Available: One Table with absolute and zero-point vibrational energies of the three tetradehydrobenzene isomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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