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p-Benzyne Derivatives That Have Exceptionally Small Singlet−Triplet Gaps and Even a Triplet Ground State

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In an effort to find a *p*-benzyne (1,4-didehydrobenzene) derivative with a triplet ground state, we have investigated tetrasubstitution by $-F$, $-NH_2$, $-CH_3$, and $-NO_2$ groups. These were predicted to reduce the singlet−triplet gap, but none led to a triplet ground state because of unexpected destabilization of one of the radical orbitals. This effect is likely the result of rehybridization of the substituted C atom, which has been observed for substituted benzene and perturbs the side σ and σ* orbital energies of the phenyl ring. The role of substituent rotation on the energy difference between the two nominally singly occupied orbitals (S and A) was then investigated. The energy of the A radical orbital was found to be much more sensitive to perturbations within the σ C−C framework than the S MO. Consequently, we believe that rehybridization of the ring carbons destabilizes the A radical orbital and can lead to large singlet−triplet splittings. To test this hypothesis, calculations on a *p*-benzyne with 2,6 substitution by oxygen were performed. Interestingly, a triplet ground state was predicted. Yet, examination of the geometry and wave function showed that 2,6-quinone *p*-benzyne is a very twisted molecule with a C3−C4−C5 allene linkage and a C1 triplet carbene center.

Introduction

p-Benzyne (formally called 1,4-didehydrobenzene) and its derivatives have attracted considerable attention in the last 30 years because (1) the σ,σ nature of the diradical poses a unique hazard to many computational methods and, hence, is a challenge to theoretical chemists[1−18] and (2) they are the key reactive intermediates in the Bergman cyclization of the enediyne class of antitumor antibiotics that results in DNA scission.[19] Unlike doublet radicals, *p*-benzyne exhibits selectivity in the type of X−H bond that is cleaved during H atom abstraction. Several explanations have been posited in the literature. One argument is based on the assumption that the triplet state is a noninteracting diradical and is consequently nonselective. Therefore, the selectivity of the singlet ground state is attributed to an additional energy component of the H abstraction activation barrier due to spin uncoupling of the singlet electrons.[20,21] Alternatively, it has been posited that the radical centers

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in the triplet state do interact and that the diradical selectivity of the singlet state instead derives from the weakly avoided crossing of the dominant valence bond configurations of the ground-state singlet and first singlet excited state along the H abstraction reaction coordinate.[22,23] In either case, the reactivity of triplet *p*-benzyne has not been experimentally investigated because *p*-benzyne has not yet been generated in the triplet state and a ground-state triplet benzyne derivative has not been synthesized. From an experimental viewpoint, the thermally induced enediyne cycloaromatization reaction (a singlet pathway) could only produce a triplet benzyne if intersystem crossing occurred between the singlet benzyne that was generated by the cyclization and its triplet counterpart, regardless of whether the $S = 1$ benzyne state is higher or lower in energy than the $S = 0$ state.

This paper illustrates potential *p*-benzyne analogues that theoretically have triplet ground states, or possess such a small energy difference between the $S = 0$ and $S = 1$ states that thermal population of the $S = 1$ state may be possible. There are several contributing factors to the preference of $S = 0$ coupling in *p*-benzyne that must be overcome in order to observe a triplet ground-state species. The seminal paper of Hoffman, Imamura, and Hehre[1] (HIH) first addressed the issue of stabilizing indirect "through-bond" versus direct "through-space" interactions between the radical centers. The through-bond interactions between the radical centers are facilitated by the symmetries of the two nominally singly occupied MOs. These orbitals are formed primarily from the symmetric (S) and antisymmetric (A) combinations of what used to be the sp^2 atomic orbitals in benzene at the radical sites C1 and C4. The S MO interacts strongly with the σ bonding orbitals of the side C$-$C bonds of the benzyne ring. This is a destabilizing interaction because of overlap repulsion between the partially filled S and lower energy filled σ bonding orbitals. In contrast, the A MO interacts with the σ^* orbital of the side C$-$C bond which is stabilizing. Thus, the A orbital is lower in energy than the S orbital, resulting in a dominant configuration in the wave function that has the A orbital doubly occupied. The wave function is best described using delocalized symmetry orbitals as $b_2^2 - a_2^2$ or $A^2 - S^2$ which are analogous to the valence bond Heitler London spin coupling of the centers.

Two related strategies exist for generating a ground-state triplet benzyne. Mostly, substitution has been randomly applied by computational and experimental chemists to alter the energetic stabilization of the singlet state relative to the triplet state, ΔE_{ST}. Indeed, virtually every style of *ab initio* MO, semiempirical MO, and DFT calculation has been used to investigate the geometries, electronic structure, energy, and reactivity of *p*-benzyne and its derivatives. Mono- and disubstitution of *p*-benzyne with NH_2,[17] OH,[15] CN,[17] SiH_3,[17] CH_3,[24] F,[24] Cl,[24] BH_2,[24] SH,[24] NO_2,[24] NH_3^+,[24] and BH_3^-[24] as well as incorporation of the benzyne into fused ring systems[24] have been examined. Matrix isolation techniques have recently generated the first tetrasubstituted benzyne derivatives. First speculated in 1971,[2] tetrafluoro *p*-benzyne has recently been experimentally observed and has a calculated ΔE_{ST} of only ~1.5 kcal/mol.[25] Such decreases in ΔE_{ST} have been generally rationalized by differences in the donating ability of the substituent to the π electron density as well as hyperconjugation into the σ and σ^* orbitals of the substituents. An alternative to studying changes in ΔE_{ST} is monitoring how substitution affects the energies of the S and A radical orbitals since energetic degeneracy between these orbitals will lead to a triplet ground state.

In light of these studies, it appears that the chemistry community does not yet understand the electronic perturbations induced by substitution so that a triplet ground-state *p*-benzyne analogue can be predicted a priori. We have therefore examined the molecular properties of a select series of tetrasubstituted *p*-benzynes as a function of substitution. In particular, the energy difference between the S and A orbitals, the fractional AO contributions that make up the σ and π orbitals, ΔE_{ST}, and the local spin quantities $\langle \boldsymbol{S}_A^2 \rangle$ and $\langle \boldsymbol{S}_A \cdot \boldsymbol{S}_B \rangle$ have been examined. These studies indicate that perturbation of the π space decreases the energy difference between the S and A MOs, while perturbation of the σ space can increase the energy separation. 2,6-Quinone *p*-benzyne seemed an ideal candidate to examine the role of delocalization effects on the S and A orbital energies because of its distorted π diradical electronic structure and significant hybridization differences at the substituted C atoms. This ground-state triplet species exhibits unique and unexpected electronic properties that are distinct from either the σ,σ benzyne diradical or the π,π diradical *m*-quinone moieties.

Computational Methods

The geometries of benzene and its tetrasubstituted derivatives (F, CH_3, NH_2, and NO_2) were optimized under no symmetry constraints with the complete active space self-consistent field method (CASSCF) using a six-electron, six-orbital active space that was composed of the π and π^* orbitals and electrons of the benzene ring. Subsequent *n* electron, *n* orbital calculations will be abbreviated (*n*,*m*). The 1,4-didehydro analogues (benzynes) were optimized with a (8,8)-CASSCF wave function. The active space was expanded from the (6,6) to include the symmetric and anti-symmetric singly occupied σ molecular orbitals. The 6-31G* (6d) basis was used for all optimization. The lowest energy structures that we were able to locate of the tetraamino and tetramethyl derivatives had a single imaginary vibration (~100*i* cm^{-1}) that corresponded to rotation of a single substituent moiety. The remaining derivatives optimized to structures with no imaginary vibrations, indicating a true minimum was located. Subsequent single-point calculations were also performed with the similar cc-pVDZ (6d) basis set so that direct comparison of our data with previous literature reports of tetrafluorobenzyne could be made. Dynamic electron correlation was accounted for by performing second-order Møller$-$Plesset perturbation theory (MP2) on the CASSCF reference wave function (CASMP2) at the optimized CASSCF geometry with the cc-pVDZ basis. Three different forms of the zeroth-order Hamiltonian were investigated in the CASMP2 calculations and are labeled IOPT1-IOPT3.[26]

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The geometries of *m*-quinone and 2,6-quinone *p*-benzyne were optimized with (8,8) and (10,10) CASSCF, respectively, and using the 6−31G* (6d) basis. The (8,8) active space was composed of the 4π and π^* orbitals and electrons of the ring and the 4π and π^* orbitals and electrons of the C=O units. The (10,10) active space was obtained by expanding the (8,8) space to include the 2σ radical orbitals and electrons. The 6-31G* (6d) basis was used for several single point calculations of the singlet, triplet, and quintet excited states at the optimized ground-state geometry. Single point cc-pVDZ and subsequent CASMP2 calculations were not performed for this system. Geometry optimizations and single-point energy calculations were performed with HONDO 99.[27]

The local spin operators $\langle \boldsymbol{S}_A{}^2\rangle$ and $\langle \boldsymbol{S}_A\cdot\boldsymbol{S}_B\rangle$ were used to analyze the CASSCF wave functions using the MELD suite of programs.[28] The derivation of local spin operators has been shown previously,[29] and only the final equations are presented here. Essentially, position space operators, P_A, are used to partition the molecule into fragments. These P_A are then applied to the total spin operator for the electrons in the molecule. Thus, a spin operator, $\boldsymbol{S}_A$, is associated with a center or molecular fragment. The projection operators used here are based on atomic volumes and utilize the function $w_A(\boldsymbol{r})$, which is defined to be one for $\boldsymbol{r}$ in the volume associated with the atom A and zero otherwise.

In the context of the Wiberg−Mayer definition of bond order (B_{AB}),[30,31] the average of S_{zA} for each center (m_A), and the intrinsic delocalization of the unpaired electron density (U_{AB}),[29] for A ≠ B, the average quantities $\langle \boldsymbol{S}_A\cdot\boldsymbol{S}_B\rangle$ and $\langle \boldsymbol{S}_A{}^2\rangle$ may be written for a single Slater determinant wave function as:

$$\langle \boldsymbol{S}_A\cdot\boldsymbol{S}_B\rangle = -{}^3/{}_8B_{AB} + m_Am_B + {}^1/{}_2U_{AB} \tag{1}$$

and

$$\langle \boldsymbol{S}_A{}^2\rangle = {}^3/{}_8\sum_{B\neq A}B_{AB} + m_A{}^2 + {}^1/{}_2F_A \tag{2}$$

where F_A is Mayer's definition of free valence.[31] More generally, the scalar product $\boldsymbol{S}_A\cdot\boldsymbol{S}_B$ is

$$\boldsymbol{S}_A\cdot\boldsymbol{S}_B = {}^3/{}_8\delta_{AB}\sum_{i=1}^{N}P_A(i) + \sum_{i>j}\boldsymbol{S}(i)\cdot\boldsymbol{S}(j)[P_A(i)P_B(j) + P_B(i)P_A(j)] \tag{3}$$

and standard rules for forming matrix elements of the symmetric sum of two-body operators can be used to compute the average value with a multi-determinant wave function. This methodology, like any partitioning of a molecule into fragments, is somewhat arbitrary, and local spin operators experience some of the difficulties associated with any fragment population analysis. We have shown previously[29] that the partitioning scheme has a significant effect on the calculated charge about each center, while $\langle \boldsymbol{S}_A{}^2\rangle$ and $\langle \boldsymbol{S}_A\cdot\boldsymbol{S}_B\rangle$ exhibit much less dependence.

The atomic volumes used in the projection operators of the local spin method were defined by partitioning space so that a point $\boldsymbol{r}$ is assigned to volume *A* if the distance of the point from A divided by the atomic radius of A is less than this ratio for any other atom. We have modified the atomic radii of Clementi et al.[32] for neutral atoms (C, 0.67 Å; H, 0.44 Å; N, 0.66 Å; F, 0.80 Å; O, 0.85 Å). The actual integrals are computed numerically using the same grid and weights as defined in Gaussian 98.[33] The atomic volumes defined in this way resemble the Bader atomic volumes[34] and result in similar charges to Bader's Atoms in Molecules as implemented in Gaussian 98, but are easier to determine.

Results and Discussion

Tetrasubstitution in Benzene. The geometries of benzene derivatives have been the subject of countless reports[35] because the phenyl ring shape is easily perturbed as a function of substitution. If the substituent contains π electrons (e.g., N_2, $CHCH_2$, or fused ring systems), the perturbation can be manifested in a bond length alternation that is the result of an imbalance in the weights of the two possible Kekule structures of the benzene ring. If such an imbalance is not observed, then the ring perturbation is likely the result of two independent distortions that may be interpreted as due to σ and π electronic perturbations of the substituent.[36] In monosubstituted species, the π effect has been shown to increase the bond length $r_{C1,C2}/r_{C2,C3}$ ratio in the ring (this distortion decreases as the substituent group electronegativity increases). The local σ effect is generally understood in terms of a hybridization model on the substituted carbon and is associated with a shortening of $r_{C1,C2}$ and an increase in $\alpha_{C3,C4,C5}$. During the rehybridization process at the substituted carbon atom, the *p* character of the substituent increases. The perturbation has been observed to increase with substituent electronegativity. In particular, the study by Campos et al.[36] examined the effect of monosubstitution of benzene by F, NO_2, and NH_2 using MO SCF and semiempirical methods. There, the NH_2 π effect was larger than that for F or NO_2 because of extensive delocalization of the NH_2 with the π orbitals of the benzene ring. The rehybridization effect at the substituted C atoms was shown to be the largest for F and NO_2, followed by NH_2 derivatization.

Our tetrasubstituted examples agree fairly well with the previously examined monosubstituted species. We

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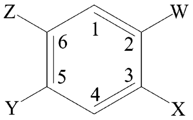
TABLE 1. Structural Features[a] of the Optimized Geometries of Tetrasubstituted Benzenes and *p*-Benzynes Obtained from (6,6) and (8,8) CASSCF/6-31G*, Respectively. 2,6-Quinone *p*-Benzyne Utilized (10,10)CASSCF/6-31G*, and *m*-Quinone Used (8,8)CASSCF/6-31G*



	state	sym	$r_{1,2}$	$r_{2,3}$	$r_{1,4}$	$r_{2,W}$	$\alpha_{1,2,3}$	$\alpha_{3,4,5}$	$\alpha_{1,2,W}$
benzene	1^1A_2	D_{2h}	1.40	1.40	1.40	1.08	120.0	120.0	120.0
p-benzyne	1^1A_2	D_{2h}	1.38	1.41	2.71	1.07	118.0	124.0	121.8
tetramethylbenzene	1^1A	C_1	1.39	1.42	2.74	1.51	118.5	123.0	119.4
tetramethylbenzyne	1^1A	C_1	1.38	1.42	2.65	1.51	116.3	127.3	121.0
tetrafluorobenzene	1^1A_g	D_{2h}	1.39	1.39	2.80	1.32	120.7	118.6	119.9
tetrafluorobenzyne	1^1A_g	D_{2h}	1.38	1.39	2.69	1.32	118.0	124.0	121.1
tetranitrobenzene	1^1AN	C_s	1.39	1.39	2.80	1.46	120.5	120.6	117.1
tetranitrobenzyne	1^1AN	C_s	1.38	1.39	2.69	1.46	118.0	124.0	118.7
tetraaminobenzene	1^1A	C_1	1.40	1.40	2.75	1.42	119.0	121.9	120.0
tetraaminobenzyne	1^1A	C_1	1.39	1.41	2.65	1.41	116.7	126.6	121.5
m-quinone	1^3B_2	C_{2v}	1.45	1.46	2.85	1.24	117.7	121.7	121.0
2,6-quinonebenzyne	1^3B	C_2	1.48	1.50	2.67	1.21	111.0	131.5	123.1

[a] Averages of bond lengths and bond angles.

observe deviations in the ring bond angles by up to 3° and deviations in bond lengths between 0.01−0.02 Å relative to benzene. CH_3 and NH_2 cause expansion of $\alpha_{C3,C4,C5}$ and compression of $\alpha_{C1,C2,C3}$, while NO_2 and F compress $\alpha_{C3,C4,C5}$ relative to benzene (Table 1). In general, the charge neutral substituents CH_3 and NH_2 induce slight lengthening of the C2−C3 and C5−C6 side bonds and shortening of the apical C1−C2, C3−C4, C4−C5, and C1−C6 bonds by 0.01−0.02 Å. According to the monosubstitution results, the apical bond lengths should be shortened along with expansion of $\alpha_{C3,C4,C5}$ for less electronegative substituents. In contrast, both the F and NO_2 substituents decrease the side and apical bond lengths by 0.01 Å relative to benzene. This result is exactly what is expected based upon the rehybridization model at the substituted C centers. The geometries of tetrasubstituted benzene are also not very dependent on substituent rotation. In the case of tetramethylbenzene, one set of *cis*-methyl units optimized to a staggered position relative to one another, while the second set of *cis*-methyl units optimized to an eclipsed conformation. Although the conformation was not a minima on the CH_3 rotational PES, only a 0.01 Å difference between the side C2−C3 and C5−C6 bond lengths was observed. A similar effect of substituent rotation was calculated for tetraamino benzene, while tetranitrobenzene optimized to a structure that had the plane of the NO_2 units intersecting the plane of the phenyl ring at an angle of ~41° under C_s symmetry.

Tetrasubstitution of *p*-Benzyne. Relative to the (6,6)CASSCF/6-31G* structure of benzene, the (8,8)-CASSCF/6-31G* geometry of *p*-benzyne exhibits shortened apical C−C bonds to the dehydro carbon centers (~0.01 Å) and longer side C−C bonds (~0.01 Å) (Table 1). The source of the shortening is typically attributed to enhanced *s* character in the contribution of the dehydro carbon in the apical C−C σ bonding orbital.[1] This corresponds to a net decrease in the fractional (Löwdin population) s atomic orbital contributions from sp^2 (~33%) in the C−H bonding orbital of benzene to 12.3% and 9.6% in the singly occupied S and A natural radical orbitals of benzyne, respectively. The apical bonding carbons C2, C3, C5, and C6 also contribute significantly to these radical orbitals. The sum of all contributions from C2, C3, C5, and C6 to the A MO is 15.9%, while the sum of contributions to the S MO is 18.0%. The lengthening effect is thus attributed to conjugation between the A radical orbital and the σ^* antibonding orbital of the side C−C bonds. Concomitant to these bond length changes is compression of $\alpha_{C1,C2,C3}$ and expansion of $\alpha_{C3,C4,C5}$.

In light of the presence of unpaired electrons within this system, the local spin properties of benzyne may prove to be a useful analysis tool. To understand these quantities, the local spin properties of benzene must first be examined in terms of the contributions to eqs 1−2. The Hückel description of benzene predicts a nearest neighbor π bond order of $^2/_3$, while the C1−C3 Hückel bond order (HBO) is 0 and the C1−C4 HBO is $-^1/_3$. The CNDO2[37] description, which takes into account the σ bonding in benzene, predicts that each carbon participates in two C−C σ bonds, one C−H σ bond, two nearest neighbor π bonds, and one C1−C4 π interaction. The C1−C3 σ and π interactions are zero. In the single determinant MO description of benzene, the value of $\langle \boldsymbol{S}_A{}^2 \rangle$ is $^3/_8$ of the total number of bonds to A and $\langle \boldsymbol{S}_A \cdot \boldsymbol{S}_B \rangle$ is $-^3/_8$ of the bond order between A and π (eqs 1 and 2). These definitions utilize the Wiberg−Mayer bond order[30,31] (WMBO) which is given by the sum of the diagonal elements of $\Pi_{AB}\Pi_{BA}$, where Π_{AB} is the charge density matrix (Π) between centers A and B. Since the WMBO is analogous to the square of the Hückel BO (HBO) it may be unnaturally small if the HBO is less than 1. Also, the WMBO does not discern between bonding and antibonding interactions since the sign of the coefficients in Π is lost in taking $\Pi_{AB}\Pi_{BA}$. Using the CNDO2 bond orders in eqs 1 and 2 we obtain $\langle \boldsymbol{S}_H{}^2 \rangle = 0.37$, $\langle \boldsymbol{S}_C{}^2 \rangle = 1.31$, $\langle \boldsymbol{S}_C \cdot \boldsymbol{S}_H \rangle = -0.29$, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C2} \rangle = -0.39$, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C3} \rangle = 0.00$, and $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle = -0.04$. The use of a (6,6)CAS wave function yields spin quantities that are slightly larger because the π electrons have more VB character than in a single determinant wave function such as in the Hückel de-

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(37) Pople, J. A.; Beveridge, D. L *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

scription: $\langle \boldsymbol{S}_{C}^{2} \rangle = 1.63$, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C2} \rangle = -0.59$, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C3} \rangle = 0.01$, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle = -0.08$.[23]

The local spin quantities of *p*-benzyne reveal that the spin expectation value for each radical center [$\langle \boldsymbol{S}_{C1}^{2} \rangle = \langle \boldsymbol{S}_{C4}^{2} \rangle = 2.01$] is nearly that found in the phenyl radical and what is expected from eq 2. Moreover, the spin coupling between these centers is also close to what is expected for two noninteracting but spin-coupled radicals that are well described by the Heitler–London VB model [$\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle = -0.75$]. However, it is important to note that -0.08 of $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle$ is due to the C1–C4 antiferromagnetic π coupling that is present in benzene. Thus, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle$ is slightly less than the ideal value of $-^{3}/_{4}$.

On the basis of the effects of substitution in benzene, it is not surprising that the (8,8)CASSCF geometries of tetrasubstituted benzynes are somewhat distorted from *p*-benzyne. Table 1 presents key structural parameters of each benzyne derivative. In general, the π effect of NH_2 observed in benzene serves to compress $\alpha_{C1,C2,C3}$ and expand $\alpha_{C3,C4,C5}$ by an additional 2°–3° relative to *p*-benzyne. The lengthening of the side C–C bonds $r_{C3,C4}$ and $r_{C5,C6}$ is much more pronounced in tetramethyl- and tetraaminobenzyne than in tetranitro- and tetrafluorobenzyne, and tetrafluorobenzyne actually has shorter side bonds than *p*-benzyne (similar to the rehybridization distortion in tetrafluorobenzene).

At this point, it is beneficial to examine the differing electronic structures within the derivatives. Here, several questions need to be addressed. First, what is the effect of tetrasubstitution on ΔE_{ST}? Second, is there a direct correspondence between ΔE_{ST} and the changes in geometry and electronic structure that are induced by the π and σ effects of electronegative substituents? Third, do these perturbations have the same or competing net effects on ΔE_{ST}? Last, what will maximize the desired effects in order to obtain a triplet ground state *p*-benzyne derivative? To answer these questions, we have compared the following quantities as a function of substitution, substituent rotation, and the presence/absence of H atoms at the C1 and C4 positions: (1) ΔE_{ST}; (2) the coefficients of the dominant configurations in the CAS wave functions; (3) the energy of and fractional AO contributions to the σ radical and π orbitals; (4) the local spin quantities $\langle \boldsymbol{S}_{A}^{2} \rangle$ and $\langle \boldsymbol{S}_{A} \cdot \boldsymbol{S}_{B} \rangle$.

Within the series studied, CASSCF predicts that each tetrasubstituted benzyne is a ground-state singlet with a smaller singlet–triplet gap than *p*-benzyne. Experimentally, the singlet–triplet gap is typically reported as a 0 K, adiabatic 0–0 transition. In Table 2, we present the vertical singlet–triplet splittings, $\Delta E_{V\text{-}ST}$, at the optimized ground-state geometry because true minima on the rotational PES for systems with amine and methyl substituents were not found. However, the calculated geometric similarities between the singlet and triplet states should make the difference between the vertical and adiabatic 0–0 transitions minor. For purposes of comparison with literature data we report these values for both the 6-31G* and cc-pVDZ basis sets. The smallest $\Delta E_{V\text{-}ST}$ was found for tetraaminobenzyne (0.97 kcal/mol), followed by tetranitro- (1.14 kcal/mol), tetramethyl- (1.32 kcal/mol), and tetrafluorobenzynes (1.62 kcal/mol), and the largest $\Delta E_{V\text{-}ST}$ was calculated for unsubstituted *p*-benzyne (2.93 kcal/mol), as observed in Table 2 (6-31G* values). Such small energy separations (~1 kcal/mol) for the tetrasubstituted benzynes are not clearly within the realm of accuracy of the CASSCF calculation. Consequently, second-order perturbation theory was used to retain some of the correlation energy contribution to the total energy. It is likely that the correlation contribution is larger in the singlet state than the triplet state, and thus the CASMP2 $\Delta E_{V\text{-}ST}$ values should be larger than those obtained by CASSCF alone. The CASPT2 method has been previously used to study benzynes in the literature, however, the CASMP2 method has also been shown to be highly useful for calculating $\Delta E_{V\text{-}ST}$ of radicals and diradicals in general.[38] Here, the CASMP2 method was utilized with three different effective Hamiltonians, IOPT1-IOPT3. The first form, IOPT1, is the most similar to what is utilized in the CASPT2 method and should yield results similar to CASPT2 with the [g1] Hamiltonian.

TABLE 2. (8,8)CASSCF Vertical Energy Difference, $\Delta E_{V\text{-}ST}$ (kcal/mol) between the Lowest Energy Singlet and Triplet States of (A) *p*-Benzyne, (B) Tetramethyl-*p*-benzyne, (C) Tetraamino-*p*-benzyne, (D) Tetrafluoro-*p*-benzyne, and (E) Tetranitro-*p*-benzyne at the Optimized Ground-State Geometry[a]

ΔE_{ST}	A	B	C	D	E
expt[39]	3.8, 2.1[b]				
CAS/6-31G* $\Delta E_{V\text{-}ST}$	2.93	1.32	0.97	1.62	1.14
CAS/cc-pVDZ $\Delta E_{V\text{-}ST}$	3.06	1.31	0.93	1.57	
CASPT2/cc-pVDZ $\Delta E_{V\text{-}ST}$	4.9,[c] 2.9[d]			1.5[40]	
CASMP2(IOPT1)/6-31G* $\Delta E_{V\text{-}ST}$	2.93	−3.65	−0.39	−1.93	
CASMP2(IOPT2)/6-31G* $\Delta E_{V\text{-}ST}$	10.58	3.69	4.78	5.62	
CASMP2(IOPT3)/6-31G* $\Delta E_{V\text{-}ST}$	4.71	−6.17	−9.90	−6.35	

[a] Positive number indicates singlet ground state; negative number indicates triplet ground state. [b] The 0–0 transition, differing from 3.8 kcal/mol by a quanta of vibrational energy. [c] [g0] Hamiltonian: unpublished result provided by W. T. Borden. [d] [g1] Hamiltonian.[12]

In the case of *p*-benzyne, the value of $\Delta E_{V\text{-}ST}$ was found to be highly sensitive to the effective Hamiltonian; however, similar values were obtained for CASPT2[g1] and CASMP2(IOPT1). It is important to appreciate that the large distribution of $\Delta E_{V\text{-}ST}$ values with the IOPT2 and IOPT3 Hamiltonians is the result of only a small correlation energy difference in the singlet state relative to the triplet. The differences in the amount of dynamic correlation energy recovered between the singlet and triplet states for each of the Hamiltonians were the following: IOPT1 = 8.7×10^{-6} au, IOPT2 = 0.01 au, and IOPT3 = 2.8×10^{-3} au. Such differences are less than 1.0% of the total dynamic correlation energy, and thus, a very high accuracy is required by the perturbation theory in order to obtain reasonable $\Delta E_{V\text{-}ST}$ values. The results obtained with *p*-benzyne do, however, indicate that CASMP2(IOPT1)/cc-pVDZ should yield results similar to those from previous CASPT2[g1]/cc-pVDZ calculations performed on tetrafluorobenzyne with an (8,8) active space.[40] However, CASMP2(IOPT1) results in a ground-state triplet tetrafluorobenzyne, while CASPT2[g1] predicts that tetrafluoro is a singlet ground

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(38) See, for example: Vila, F.; Borowski, P.; Jordan, K. D. *J. Phys. Chem. A* **2000**, *104*, 9009. Castano, O.; Frutos, L.; Palmeiro, R.; Notario, R.; Andres, J.; Gomperts, R.; Blancafort, L.; Robb, M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2095. Bray, J. A.; Bernstein, E. R. *J. Phys. Chem. A* **1999**, *103*, 2208. Hoffner, J.; Schottelius, M. J.; Feichtinger, D.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 376. Gonzalez, L.; Mo, O.; Yanez, M. *Chem. Phys. Lett.* **1996**, *263*, 407.

state (Table 2). The IOPT2 Hamiltonian predicts a singlet ground state for this derivative. Similar results were obtained for the tetramethyl and tetraamino analogues. Severe convergence problems were encountered for tetranitrobenzyne. Since the CASPT2 method has only been previously applied to benzynes with calculated $\Delta E_{\text{V-ST}}$ larger than 2.00 kcal/mol, it is unclear how it would perform for tetraamino-, tetramethyl-, and tetranitrobenzynes because accuracy within 0.1% of the total dynamic correlation energy is required to obtain reasonable results.

If the (8,8)CASSCF $\Delta E_{\text{V-ST}}$ is taken as being the most reliable value, then several comments may be made as to the viability of experimentally observing the triplet state of these tetrasubstituted benzynes. First, it is quite possible that the tetrasubstituted benzynes are indeed ground-state triplets because the calculated $\Delta E_{\text{V-ST}}$ is within what is typically considered the error of CASSCF calculations (±5 kcal/mol).[41] Previous studies of dialkyl-substituted benzynes have tested the change in rate of product formation from the benzyne intermediate as a function of an applied magnetic field.[42] No dependence was observed, which indicates that the intersystem crossing (ISC) between the singlet and triplet states did not occur. Since the lifetime of the benzyne intermediates has been measured to be on the order of the time scale of ISC ($\sim 10^{-10}$ s or longer), it is possible that the $\Delta E_{\text{V-ST}}$ of those compounds was not small enough to facilitate state crossing. The current study presents several tetrasubstituted benzynes that have a much smaller $\Delta E_{\text{V-ST}}$ than even *p*-benzyne and that should certainly be able to allow transition between the singlet and triplet states.

The most apparent query is to ask whether the calculated changes in $\Delta E_{\text{V-ST}}$ are due to perturbations in the "through-space" or "through-bond" interactions between the diradical centers. The internuclear separation between the radical centers, $r_{\text{C1,C4}}$, is the most probably structural feature to have a direct influence on the electronic interaction between radical centers. The "through-space" interaction between the radical centers in *p*-benzyne is considered to be minimal; however, a significant decrease in $r_{\text{C1,C4}}$ has the possibility of stabilizing the S MO to produce nearly degenerate radical orbitals and thus a small $\Delta E_{\text{V-ST}}$. Although $r_{\text{C1,C4}}$ steadily decreases from 2.71 Å in *p*-benzyne to 2.69 Å in tetrafluoro- and tetranitrobenzyne, to 2.65 Å in tetraaminobenzyne to 2.64 Å in tetramethylbenzyne, there is no discernible trend in the relative order of $\Delta E_{\text{V-ST}}$ or the S and A orbital energies. It is then evident that the steric interactions that distort the geometry of substituted benzynes relative to *p*-benzyne are not *directly* related to differences in $\Delta E_{\text{V-ST}}$.

The effect of tetrasubstitution on the "through-bond" pathways that allow the radical electrons to interact should then be investigated. The σ space of the diradical electrons can first be examined through the ratio of C_S^2 to C_A^2, the squares of the natural orbital CAS coefficients obtained for the dominant electron configurations involving double occupation of either the S or A radical orbitals, respectively (Table 2). A "pure" diradical may be defined as having the two configurations equally populated, and hence $C_S^2/C_A^2 = 1.00$, while systems with significant covalent interaction between the formally unpaired electrons have ratios that are substantially greater than 1.00 (for S lower in energy than A) or less than 1.00 (for A lower in energy than S). In unsubstituted *p*-benzyne, the A MO is stabilized relative to the S MO which leads to a C_S^2/C_A^2 ratio of 0.63. Interestingly, tetramethyl benzyne has $C_S^2/C_A^2 < 1$ similar to *p*-benzyne, while tetraamino benzyne has $C_S^2/C_A^2 \sim 1$, and tetranitro- and tetrafluorobenzynes have $C_S^2/C_A^2 > 1$ (Table 3).

TABLE 3. Orbital Energies (kcal/mol) for the Symmetric (S) and Antisymmetric (A) Singly Occupied Radical Orbitals and the Ratio of the Squares of the (8,8)CASSCF/6-31G* Configuration Coefficients, C_S^2/C_A^2, for the Singlet States of (A) *p*-Benzyne, (B) Tetramethyl-*p*-benzyne, (C) Tetraamino-*p*-benzyne, (D) Tetranitro-*p*-benzyne, and (E) Tetrafluoro-*p*-benzyne at the Optimized Ground-State Geometry

	A	B	C	D	E
CAS/6-31G* C_S^2/C_A^2	0.63	0.79	1.00	1.09	1.24
CAS/cc-pVDZ C_S^2/C_A^2	0.61	0.78	1.01	–	1.25
CAS/6-31G* S orbital energy	−64.07	−67.02	−86.91	−178.21	−146.90
CAS/6-31G* A orbital energy	−111.82	−91.68	−86.78	−168.92	−124.12

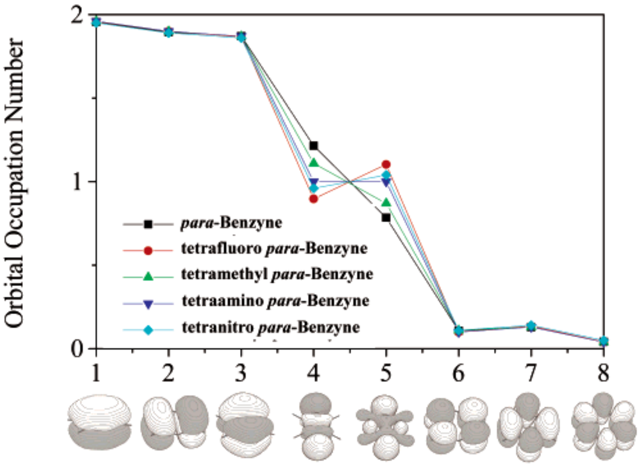

FIGURE 1. Occupation number of the active space orbitals of *p*-benzyne and its tetrasubstituted derivatives obtained by (8,8)CASSCF/6-31G*.

Alternatively, the occupation numbers of the S and A radical orbitals can be studied (Figure 1). Here, the change in C_S^2/C_A^2 as a function of substitution is manifested in the following manner: (1) a higher occupation number is observed for the A orbital relative to the S in *p*-benzyne and tetramethylbenzyne; (2) equal occupation for both S and A orbitals is observed in tetraaminobenzyne; (3) a higher occupation number is observed for the S orbital relative to the A orbital in tetranitro- and tetrafluorobenzynes.

The trend in CAS configuration coefficients and orbital occupation numbers agrees with the observation that every tetrasubstituted analogue with the exception of the tetramethylbenzyne has the S MO lower in energy than

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

(40) Henk, H. H.; Balster, A.; Sander, W.; Hrovat, D. A.; Borden W. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2295.

(41) Staroverov, V. N.; Davidson, E. R. *THEOCHEM* **2001**, *573*, 81.

(42) Lott, W. B.; Evans, T. J.; Grissom C. B. *J. Chem. Soc., Perkin Trans. 2* **1994**, *12*, 2583.

TABLE 4. Local Spin Quantities Obtained from (8,8)CASSCF/6-31G* Wave Functions of *p*-Benzyne and Tetrasubstituted Derivatives[a]

	C1	C2	C3	C4	C5	C6	W	X	Y	Z
p-benzyne										
C4	−0.76	0.03	−0.63	2.01						
C5	0.03	−0.08	0.01	−0.63	1.62					
C6	−0.63	0.01	−0.08	0.03	−0.58	1.62				
W	−0.01	−0.35	−0.01	0.00	0.00	−0.63	0.39			
tetramethyl-*p*-benzyne										
C1	2.03									
C2	−0.60	1.65								
C3	0.02	−0.56	1.65							
C4	−0.76	0.03	−0.60	2.03						
C5	0.03	−0.07	0.01	−0.63	1.65					
C6	−0.62	0.01	−0.07	0.03	−0.54	1.65				
W	−0.03	−0.38	−0.02	−0.01	0.00	0.00	1.53			
X	−0.01	−0.02	−0.38	−0.03	0.00	0.00	−0.01	1.52		
Y	−0.01	0.00	0.01	−0.03	−0.38	−0.02	0.00	0.00	1.52	
Z	−0.03	0.00	0.00	−0.01	−0.02	−0.38	0.00	0.00	−0.01	1.52
tetrafluoro-*p*-benzyne										
C4	−0.77	0.02	−0.57	2.00						
C5	0.02	−0.06	0.00	−0.57	1.52					
C6	−0.57	0.00	−0.06	0.02	−0.52	1.52				
W	−0.06	−0.35	−0.04	−0.01	−0.01	0.00	0.48			
tetranitro-*p*-benzyne										
C1	2.00									
C4	−0.75	0.03	−0.59	2.00						
C5	0.03	−0.06	0.01	−0.59	1.62					
C6	−0.59	0.01	−0.06	0.03	−0.54	1.62				
W	−0.01	−0.31	−0.01	0.00	0.00	0.00	1.49			
X	0.00	−0.01	−0.31	−0.01	0.00	0.00	0.00	1.49		
tetraamino-*p*-benzyne										
C1	2.03									
C2	−0.58	1.66								
C3	0.02	−0.56	1.66							
C4	−0.78	0.02	−0.58	2.03						
C5	0.02	−0.06	0.01	0.62	1.66					
C6	−0.62	0.01	−0.06	0.02	−0.52	1.66				
W	−0.03	−0.42	−0.03	0.00	−0.01	0.00	1.23			
X	0.00	−0.03	−0.42	−0.03	0.00	−0.01	−0.01	1.23		
Y	0.00	−0.01	0.00	−0.04	−0.42	−0.03	0.00	0.00	1.24	
Z	−0.04	0.00	−0.01	0.00	−0.03	−0.42	0.00	0.00	−0.01	1.24

[a] $\langle \mathbf{S}_A{}^2 \rangle$ on diagonal elements, $\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle$ on off-diagonal elements. Symmetry equivalent data has been omitted for clarity.

the A MO (Table 3). These orbital energies are the eigenvalues of the Fock operator constructed by inserting the CASSCF density matrix into the equation for the Hartree−Fock operator. The source of the switch in energy order of the S and A orbitals is not readily apparent from the net charges (Mulliken or Bader) on the C1 or C4 atoms or any perturbation within the A and S orbitals themselves. The fractional AO contributions to these orbitals do *not* change in a manner that is consistent with the deviations in orbital energy as a function of substitution. For example, the S AO contribution to both the S and A orbitals of each benzyne follows the order: tetramethyl (11.32% and 8.54%, respectively) < tetraamino (11.93% and 8.68%, respectively) < *p*-benzyne (12.33% and 9.57%, respectively) < tetrafluoro (13.61% and 9.63%, respectively) < tetranitro (14.00% and 10.04%, respectively). Similarly, the role of the substituent AOs in the two radical orbitals does not follow any immediately recognizable trend. The substituent AO contributions to the S MO of each derivative is the following: *p*-benzyne (3.04%) < tetrafluoro (3.17%) < tetraamino (4.44%) < tetranitro (4.89%) < tetramethyl (5.10%). Examination of the participation of the C2, C3, C5, and C6 in either of the radical orbitals also does not yield fruitful information that correlates to the S and A orbital energies. One can say, however, that systems that have the S orbital lower in energy than the A orbitals have a much higher contribution (~14%) of the substituent AOs to the ($C2p_y + C3p_y - C5p_y - C6p_y$) π orbital than systems that have the A orbital lower in energy than the S (~7% or less). These observations indicate that perhaps the σ and π effects that were observed in tetrasubstituted benzene may be the source of the energy redistribution of the S and A orbitals. The σ effects were primarily localized on the substituted atoms and may not be manifested in the radical MOs.

The local spin properties of the tetrasubstituted benzynes exhibit the same general trends as observed in the tetrasubstituted benzenes. First, each tetrasubstituted benzyne exhibits smaller spin couplings within the apical carbon bonds, $\langle \mathbf{S}_{C1} \cdot \mathbf{S}_{C2} \rangle$, as well as the side carbon bonds, $\langle \mathbf{S}_{C1} \cdot \mathbf{S}_{C2} \rangle$, than *p*-benzyne (Table 4). This may be indicative of the rehybridization at the substituted C centers, or merely a reminder of the increase in substituent contributions to the π MOs. Also, tetramethylbenzyne exhibits local spin quantities that are the most similar to *p*-benzyne, in contrast to tetraamino-, tetranitro-, and tetrafluorobenzynes.

At first glance, the most significant differences between CH_3 (A lower in energy than S, small substituent contribution to π MOs) and NH_3, NO_2, or F (S lower in energy than A, large substituent contribution to π MOs)

TABLE 5. Changes in Orbital Energies, Configuration Coefficient Ratios, and the Vertical Energy Difference between the Lowest Energy Singlet and Triplet States at the Ground-State Singlet Geometry of Tetranitrobenzyne as a Function of NO_2 Rotation in C_s Symmetry Using the (8,8)CASSCF/6-31G* Wave Function[a]

rotation conformation	S MO energy	A MO Energy	C_S^2/C_A^2	$\Delta E_{V\text{-}ST}$
$\omega = 0°$	−177.08	−155.31	1.23	1.55
$\omega = 41°$ (opt)	−178.09	−168.93	1.09	1.14
$\omega = 90°$	−175.45	−177.84	0.98	1.14

[a] Energy in kcal/mol. ω is the angle between the plane of the NO_2 unit and the plane of the benzyne ring.

is the absence of LP orbitals and a small amount of electronegativity. Since these two properties are known to effect the C−C bonding framework in benzene through rehybridization of the substituent C atoms, it is possible they could enhance or disrupt the interaction between the radical centers. If the property of electronegativity is kept constant, the role of LP conjugation with the σ space can be examined as a function of substituent rotation. This will also allow us to distinguish which of the radical orbitals is the most sensitive to changes in the σ C−C framework. Table 5 illustrates the dependence of $\Delta E_{V\text{-}ST}$, the S and A MO energies and the C_S^2/C_A^2 ratio upon rotation of the NO_2 units in tetranitrobenzyne.

The first geometry places the four substituents in the plane of the benzyne ring, which maximizes the σ interaction of the NO_2 units with the radical centers because of the close proximity of the O atoms to C1 and C4. The resulting $\Delta E_{V\text{-}ST}$ (1.55 kcal/mol) is larger than that calculated at the optimized structure as a result of the A MO being significantly higher in energy than the S MO ($\Delta E = 25.10$ kcal/mol). Examination of the doubly occupied HF orbitals outside the active space reveals that the oxygen LP orbitals are low in energy because they mix with the apical and side C−C σ orbitals, which is stabilizing for the lone pair orbitals but destabilizing for the σ orbitals of the C−C framework. As a result of the S and A orbitals significantly mixing with the apical and side σ and σ* orbitals of the C−C framework, the O induced perturbation of the σ bonding framework also allows for significant fractional contributions of the NO_2 AO's to the S and A radical orbitals (14.6% and 10.04%, respectively). Additionally, there is significant delocalization between the benzyne σ orbitals into the partial N−O in-plane π bond of each NO_2 substituent. Within the π space, we observe a very large contribution of the substituent AOs to the $(C2p_y + C3p_y - C5p_y - C6p_y)$ π MO of the benzyne ring (14.53%). Such strong interactions with the substituents are manifested in the local spin properties. First, each O atom has significant $\langle \boldsymbol{S}_A \cdot \boldsymbol{S}_B \rangle$ coupling to the C atoms two, three, and even four bonds away. For example, C−O coupling between two bonds is −0.05, while coupling between three or four bonds is −0.02. Second, the $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle$, −0.73, is larger than that found in any of the other benzyne derivatives (−0.75 to −0.79). Thus, the interaction between the radical centers has changed from being completely described by VB or Heitler London ($\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle = -^3/_4$ for two noninteracting radical centers) to having some MO type character ($\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle = -^3/_8$ for a C−C single bond. Enhanced MO character increases $\Delta E_{V\text{-}ST}$.

At the CAS-optimized geometry, the four NO_2 units rotate so that they form a ~41° angle with the plane of the benzyne ring. This conformation decreases the σ interaction of the oxygen LP with the C−C framework relative to the planar geometry. In general the oxygen LP are higher in energy and the σ orbitals of the C−C framework are lower in energy relative to the planar geometry. Although the A MO is still higher in energy than the S MO, the energy difference is only 6.23 kcal/mol. Consequently, the vertical singlet−triplet gap decreases to 1.14 kcal/mol. Additionally, the substituent fractional AO contributions to the S and A radical orbitals decrease significantly. Interestingly, the largest energetic perturbation relative to the planar geometry appears to be a significant stabilization of the A orbital (13.62 kcal/mol), rather than destabilization of the S MO (1.01 kcal/mol). Thus, the fractional contribution of the oxygen AOs to the A MO has a larger energetic effect than the same contribution to the S MO. The decreased MO mixing within the σ space is also reflected in an increase in the magnitude of $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle$ to −0.75. However, it is important to note that −0.08 of $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle$ is due to the C1−C4 π antiferromagnetic coupling that is present in benzene. Thus, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle$ is slightly less than the ideal value of $-^3/_4$. Interestingly, the C−O coupling through two and three bonds is the same as in the planer geometry, while the four bond C−O coupling decreases.

Continuing the rotation of the NO_2 units until they bisect the plane of the benzyne ring ($T = 90°$), we observe that the oxygen LP have no interaction with the σ system of the benzyne ring. This is verified not only by the fractional contribution to the S and A radical orbitals, but also by enhanced spin coupling between the radical centers [$\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C4} \rangle = -0.78$]. At this geometry, the A orbital is slightly lower in energy than the S orbital, as in unsubstituted *p*-benzyne, and $\Delta E_{V\text{-}ST}$ is unchanged relative to the optimized conformation. Concomitant with the decrease in interaction of the NO_2 with the σ orbitals, is an increase in the fractional contribution from the C2, C3, C5, and C6 AOs to the S and A radical orbitals. As a result, the A MO is stabilized by 8.91 kcal/mol and the S MO is destabilized by 2.64 kcal/mol relative to the orbital energies at the tilted conformation (Table 5). Importantly, the local spin properties reveal significant (−0.05 to −0.02) coupling between the O of the NO_2 and the ring C's that make up the $(C2p_y + C3p_y - C5p_y - C6p_y)$ π MO. Moreover, the fractional substituent AO contributions to the π orbital decreases only slightly (~2.00%) upon rotation from $T = 0°$ to $T = 90°$. This indicates that approximately the same amount of π influence on the benzyne ring is retained throughout the entire rotation.

The molecular properties of the tetrasubstituted benzynes, as well as the perturbations that occur as a function of substituent rotation, indicate that perturbation of the C−C bonding framework influences the energy distribution of the S and A radical orbitals. As in benzene itself, we believe that electronegative substituents induce rehybridization of the substituted C atoms which destabilizes the A radical orbital. If the rehybridization is minimal, the singlet−triplet gap decreases. However, if a large amount of rehybridization occurs, then the S MO becomes much lower in energy than the A MO and a large singlet−triplet gap occurs. Mixing of the substituent orbitals with the nominally singly occupied A MO is also significantly destabilizing to the A MO. This leads to larger singlet−triplet splittings than would occur if the rehybridization of the substituted C atoms was the only electronic effect.

We became intrigued with the concept of rehybridization of the substituted C atoms and its role on the S and A orbital energies. Thus, the model compound 2,6-quinone *p*-benzyne was examined. The model has a π diradical electronic structure that is quite disparate from benzene. The participation of the C═O bonds in the π space of the ring may prove useful in understanding the mechanism that facilitates the energy redistribution of the S and A orbitals.

The Unique Properties of *m*-Quinone and 2,6-Quinone *p*-Benzyne. *m*-Quinone is a ground-state triplet π diradical that has a C−C framework that is structurally much more similar to benzene than any of the benzyne diradicals (Table 1). The (8,8)CASSCF C_{2v} ground state exhibits shortened C3−C4 and C4−C5 bonds (1.39 Å) and similar C1−C2 and C2−C3 bond lengths (1.45 and 1.46 Å, respectively) relative to benzene. With respect to bond angles, the largest computed structural perturbations occurs in $\alpha_{C3,C4,C5}$ and $\alpha_{C6,C1,C2}$, which are expanded to 121.7°, and 121.2°, respectively, and in $\alpha_{C1,C2,C3}$, which is compressed to 117.7°. Each C═O bond is 1.24 Å. This geometry is quite similar to that predicted by UHF, RHF, and GVB methods.[43] The two singly occupied π orbitals are of b_2 and a_2 symmetry. The b_2 orbital is localized on the two oxygen centers and on C1, while the a_2 orbital is localized on the O atoms, C3, and C5. A unique bonding picture is then observed that has delocalized π diradicals on the benzyne ring and partial C−O π bonds. The energy difference between the triplet ground state and the first vertical singlet state is 12.58 kcal/mol.[44]

The delocalized nature of the diradical character is manifested in the local spin properties. In particular, $\langle \boldsymbol{S}_{C1}^2 \rangle$, $\langle \boldsymbol{S}_{C3}^2 \rangle$, and $\langle \boldsymbol{S}_{C5}^2 \rangle$ exhibit larger values, and thus more radical character, than $\langle \boldsymbol{S}_{C2}^2 \rangle$, $\langle \boldsymbol{S}_{C4}^2 \rangle$, or $\langle \boldsymbol{S}_{C6}^2 \rangle$ (Table 6). The S_{zA} indicates that the unpaired electrons are also fairly evenly distributed between C1, C3, and C5 (m_{C1} = 0.30, m_{C3} = 0.21, m_{C5} = 0.21) and that the radical delocalization does go onto the O centers (m_O = 0.18). Interestingly, spin polarization is observed since m_{C2} = m_{C6} = −0.02 and m_{C4} = −0.05.

Removal of two hydrogens at C1 and C4 generates a structure that is distorted from either *m*-quinone or that of any benzyne derivative reported to date. Still a ground-state triplet, the 2,6-quinone benzyne analogue is twisted significantly from planarity and is of C_2 symmetry. Indeed, the dihedral angle $T_{C2,C1,C4,C3}$ is 16.2°. Significant shortening of $r_{C3,C4}$ is observed from 1.39 to 1.35 Å as well as a shortening of the C−O bond from 1.24 to 1.21 Å. This is commensurate with decreases in $\alpha_{C1,C2,C3}$ from 117.7° to 111.0° and $\alpha_{C2,C3,C4}$ from 120.9° to 114.7° (Figure 2). If C_{2v} symmetry is enforced during geometry optimization of the 2,6-quinone benzyne a large (172*i* cm^{-1}) imaginary vibration along the distortion coordinate is observed. The electronic structure in C_{2v} symmetry is merely a combination of the triplet π diradical character of *m*-quinone with the singlet σ diradical character of *p*-benzyne.

TABLE 6. Local Spin Quantities for the Lowest Energy Triplet States of *m*-Quinone and 2,6-Quinone *p*-Benzyne Obtained from (8,8) and (10,10)CASSCF Wave Functions, Respectively, with the 6-31G* Basis Set

	C1	C2	C3	C4	C5	C6	W	Z
m-quinone								
C1	1.68							
C2	−0.42	1.49						
C3	0.05	−0.40	1.66					
C4	−0.03	−0.01	−0.61	1.63				
C5	0.05	−0.02	0.06	−0.61	1.66			
C6	−0.42	−0.01	−0.02	−0.01	−0.40	1.49		
W	0.02	−0.64	0.00	−0.04	0.05	−0.01	0.97	
Z	0.02	−0.01	0.05	−0.04	0.00	−0.63	0.04	0.97
2,6-quinone *p*-benzyne								
C1	2.28							
C2	−0.37	1.49						
C3	−0.02	−0.36	1.63					
C4	0.01	−0.02	−0.84	1.87				
C5	−0.02	−0.01	−0.01	−0.84	1.63			
C6	−0.37	−0.01	−0.01	−0.02	−0.34	1.49		
W	0.04	−0.68	−0.04	−0.05	0.00	−0.01	0.91	
Z	0.04	−0.01	0.00	−0.04	−0.04	−0.68	0.01	0.91

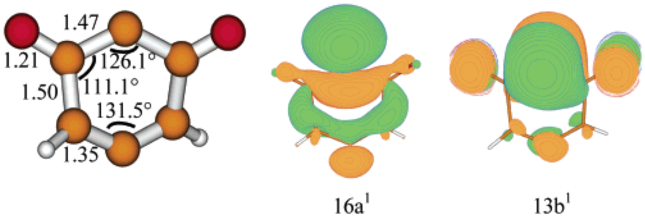

FIGURE 2. Geometry and singly occupied orbitals of the 1^3B state of 2,6-quinone *p*-benzyne in the (10,10)CASSCF/6-31G* wave function.

The global minima in C_2 symmetry, however, results in a triplet state that has the single occupation of what would be the b_2 π orbital of *m*-quinone in C_{2v} symmetry and the A σ radical orbital of *p*-benzyne. The two other nominally singly occupied orbitals in C_{2v} symmetry (the a_2 π orbital of *m*-quinone and the S MO of *p*-benzyne) mix in C_2 symmetry to yield an electronic structure that is similar to allene on C3−C4−C5 and resembles a triplet carbene on C1. It is the allene electronic structure that is the source of the geometric twisting about C3, C4, and C5. Interestingly, the lowest energy $S = 0$, $S = 1$, and $S = 2$ excited states do not exhibit the allene electronic structure or geometry and instead optimize to planar structures. The dominant configurations of these excited states correspond to the different spin pairings that are possible with four electrons in two π and two σ orbitals. Importantly, the first vertical excited state (a singlet) is 31.16 kcal/mol higher in energy than the ground state, while the adiabatic state is 9.17 kcal/mol higher than the ground state. A strong preference for the allene geometry and electronic structure over the tetraradical planar geometry in the triplet ground state is then indicated.

Local spin analysis indicates that C1 has an m_{C1} = 0.78. If used in eq 2, m_{C1} combined with two single bonds to C1 and an approximate free valence of 2.00 would yield an $\langle \boldsymbol{S}_{C1}^2 \rangle$, value of 2.35. Indeed, the (10,10)CASSCF $\langle \boldsymbol{S}_{C1}^2 \rangle$ is quite close to the approximate value at 2.28, clearly

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[43] Fort, R. C., Jr.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549.

[44] At 0 K.

indicating the presence of a carbene at C1. However, as seen in Figure 2, some unpaired electron density is put onto the O atoms, which yields an m_O value of 0.09 and slightly depresses $\langle \boldsymbol{S}_{C1}{}^2 \rangle$. Additionally, $\langle \boldsymbol{S}_{C1} \cdot \boldsymbol{S}_{C2} \rangle$, $\langle \boldsymbol{S}_{C6} \cdot \boldsymbol{S}_{C1} \rangle$, $\langle \boldsymbol{S}_{C2} \cdot \boldsymbol{S}_{C3} \rangle$, and $\langle \boldsymbol{S}_{C5} \cdot \boldsymbol{S}_{C6} \rangle$, quantities indicate the presence of a single bond because their values are quite close to $-{}^3/_8$ (eq 1).

Conclusions

This study indicates that substituents that strongly interact with the benzyne π system, do not interact with the σ space, and are only weakly electronegative should yield the smallest singlet–triplet energy differences and may possibly lead to a ground-state triplet electronic structure. In the cases studied, every tetrasubstituted *p*-benzyne had reduced singlet–triplet gaps relative to the unsubstituted analogue. The series of molecules presented exhibits unique trends in the singly occupied orbital energies. In going from tetramethyl-, to tetraamino-, to tetranitro-, to tetrafluorobenzynes, the energy difference between the S and A orbital sequentially decreases with the A orbital lower in energy than the S, then the S and A orbitals switch in energy and the energy difference sequentially increases. Analysis of the fractional contributions that make up the π and σ orbitals of the benzyne does not immediately infer the mechanism that causes the redistribution of σ radical orbital energies. However, previous studies of substitution within benzene have shown that rehybridization occurs at the substituted C atoms. This effect increases with increasing electronegativity. Structural distortions observed in the tetrasubstituted benzenes also occur in the benzynes, which indicates a similar hybridization process. If the S and A radical orbital energies are monitored as a function of substituent rotation we observe that the A orbital is significantly destabilized when (1) the radical orbital MO has a significant fractional contribution from the substituent atomic orbitals or (2) the substituent orbitals participate significantly in the C–C framework. The A MO energy then appears to be much more sensitive to rehybridization at the substituted C than the S MO energy.

To test the hypothesis, a model compound, 2,6-quinone *p*-benzyne, was studied. This molecule is a π,π diradical that has extensive delocalization of the C═O and O lone pair orbitals with the π orbitals of the benzyne ring. In fact, the parent compound, *m*-quinone, is best described as a delocalized diradical throughout the ring and only partial C═O bonds. Significant rehybridization of the substituent C atoms is observed relative to benzene. Interestingly, the 2,6-quinone *p*-benzyne is a ground-state triplet; however, the geometry and electronic structure do not resemble either the quinone or the benzyne moieties. This molecule contains a C3–C4–C5 allene linkage and is a triplet carbene at C1.

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Supporting Information Available: Cartesian coordinates of all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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