Equilibrium Geometries and Relative Energies of the Lowest Singlet and Triplet States of *o*-, *m*-, and *p*-Benzyne

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Abstract: The lowest lying singlet and triplet states of each of the three isomers of benzyne have been examined at an ab initio level, using an extended basis (4-31G) of atomic orbitals. Singlet states were treated within the single-pair GVB formalism, which allowed correlation between the symmetric and antisymmetric combinations of the radical orbitals resulting from dehydrogenation of benzene. Limited geometry optimizations were performed for singlet and triplet states of the meta and para isomers. Each of the three isomers was found to have a singlet ground state, though for the para isomer this result is not conclusive. The total energy of the isomers was found to increase in the order ortho < meta < para. The equilibrium structures of the singlet meta and para isomers reflect appreciable diradical character, in sharp contrast to the aryne nature of the ortho isomer. Single-determinant RHF theory was found inadequate for the proper description of the benzynes, resulting in artificially enhanced stabilization of bicyclic structures. Results for the para isomer at the GVB level suggest that the bicyclic structure may correspond to a local minimum, but with energy far above that of the open equilibrium structure. Calculations were also performed for each of the isomers using for the carbon framework the equilibrium structure of the phenyl cation, from which they might be formed by appropriate base-induced deprotonation. The same energy ordering (ortho < meta < para) was found here, though the ortho-meta splitting was considerably reduced.

I. Introduction

In recent years each of the three possible isomers of benzyne (bisdehydrobenzene, Figures 1-3) has been cited as a potential intermediate in organic reactions.[1] By virtue of their transient nature, experimental structural characterization of these species has proved difficult. Laing and Berry have attempted to determine the normal coordinates of the ortho isomer (Figure 1), from which they have inferred an aryne-like structure.[2] The only experimental clues to the structures of the remaining two isomers derive from their relative propensities toward nucleophilic addition and hydrogen abstraction reactions, suggesting that the most stable form of *p*-benzyne (Figure 3) has a diradical nature[1e] while *m*-benzyne (Figure 2) is perhaps more accurately described as a bicyclic compound.[1b-d] For the case of the para isomer, it appears possible at low temperatures to generate a higher energy bicyclic structure.[1f]

In light of the experimental difficulties in direct characterizations for the three isomers, it is not surprising that the field has generated active interest among theoretical investigators. A few years ago Wilhite and Whitten carried out ab initio restricted Hartree-Fock (RHF) and extensive π-electron configuration interaction calculations for the lowest singlet and triplet states of each of the three isomers and concluded that both *o*- and *m*-benzyne have singlet ground states while the para isomer is a triplet.[3] Their calculations also indicated a relative energy ordering of ortho < meta < para. The significance of these conclusions is limited by the fact that all of the computations were done with the skeletal framework frozen at the benzene equilibrium geometry. A priori it is not totally clear how the results would be modified if geometrical relaxation were allowed. Dewar and Li[4a] avoided this problem in their later semiempirical study, performing unconstrained geometrical optimizations for the singlet and triplet states of each isomer using MINDO/3. The singlet calculations were done both at a single-determinant and a two-determinant CI level. At the CI level their results indicate that all three isomers have singlet ground states. In addition, the relative stabilities of the three isomers are altered with respect to Wilhite and Whitten's work, *m*-benzyne now being predicted to be lower in energy than *o*-benzyne. It is difficult to assess the reliability of these MINDO/3 CI calculations. Without inclusion of configuration interaction, MINDO/3 is not expected to treat properly the diradical character expected of these species (particularly the meta and para isomers).[4] Straightforward inclusion of CI, however, is not likely to be completely satisfactory, since the method was parametrized at the single-determinant level to include part of the correlation energy.[4a,5] While the regular MINDO/3 method has enjoyed considerable success in accounting for thermochemistry, it suffers from a variety of systematic errors (e.g., in comparisons involving differing amounts of strain energy and different numbers of single, double, and triple C-C bonds).[5-8] Hence an independent prediction of the relative stabilities of the energy-optimized benzyne isomers would be highly desirable.

At the ab initio level, there have been several published reports in which at least partial geometry optimizations have been performed. Newton and Fraenkel[9] have examined the geometry of *o*-benzyne at both minimal (STO-3G)[10] and extended basis (4-31G)[11] levels. The salient feature of this study was the finding of a C_1-C_2 bond length (see Figure 1) only 0.03 Å longer than that of acetylene. Washburn, employing the minimal basis STO-3G set, performed a limited optimization of *m*-benzyne.[1b] His finding of a bicyclic structure with a C_1-C_3 separation of 1.5 Å is in contrast to Dewar and Li's equilibrium distance of 1.95 Å.[4] Furthermore, these results, in conjunction with those of ref 9, imply that the meta isomer is 11.0 kcal/mol[12] *less* stable than the ortho isomer, qualitatively consistent with the earlier ab initio CI results based on the benzene framework geometry, and differing from the MINDO/3 prediction. This energy splitting must be accepted with caution, however, as the deficiencies of the STO-3G basis in treating strained hydrocarbons are well documented.[7,9b]

In continuing work at the single-determinant level McKelvey, Komornicki, and Washburn have optimized the structures of the singlet states of *o*- and *m*-benzyne and the singlet and triplet states of *p*-benzyne, using the STO-3G and 4-31G basis sets.[13] Their results are similar to the single-determinant results found in the present study, and one of the goals in the remainder of this paper will be to assess the utility of a single-determinant model for structural predictions in cases like the benzynes where a fair degree of diradical character is expected. Problems with the energetics at the one-determinant level have already been noted.[3]

Our interest in the benzyne problem arose both from the conflicting status of previously published results and from the ongoing work of Hehre and his group, in which attempts are being made to determine experimentally via ion cyclotron

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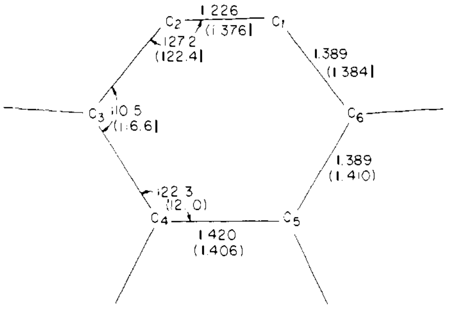


Figure 1. Structure of singlet and triplet (parameters in parentheses) *o*-benzyne. The singlet structure is the 4-31G, single-determinant, equilibrium structure.[9] The triplet structure is the equilibrium MINDO/3 result.[4a]

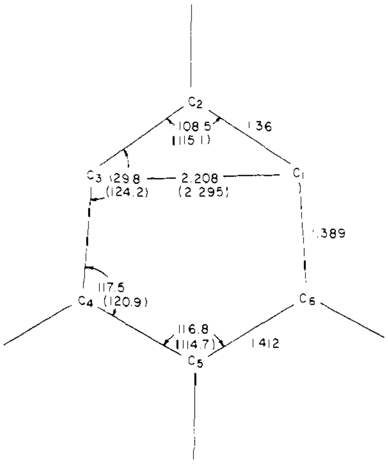


Figure 2. Equilibrium singlet (4-13G, GVB) and triplet (parameters in parentheses, 4-31G, RHF) structures of *m*-benzyne.

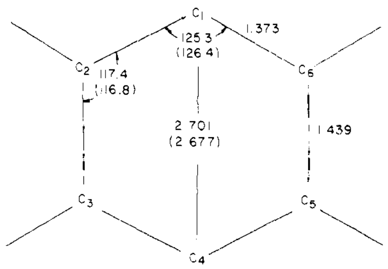


Figure 3. Equilibrium singlet (4-31G, GVB) and triplet (parameters in parentheses, 4-31G, RHF) structures of *p*-benzyne.

resonance (ICR) the relative stabilities of the three isomers.[14] The primary objective of the work reported here is to make predictions regarding these stabilities and the corresponding structures, employing ab initio quantum chemical techniques. The level of theory at which we chose to address the problem was the single-pair GVB method,[15] utilizing the double ζ valence, 4-31G basis.[11] The utility of the 4-31G basis for studying the energetics of organic systems has been extensively tested and documented. It should be noted, however, that this basis is known to systematically overestimate the strain energy of small rings and cyclic alkenes,[7,9b] and this point will be considered below.

The GVB method was employed in view of the likelihood of appreciable diradical character in these molecules, and we felt it essential to correlate that pair of orbitals which in a localized orbital picture may be viewed as the symmetric (ϕ_s) and antisymmetric (ϕ_a) combination of the pair of carbon valence orbitals made available by the dehydrogenation of benzene. This marks the first effort on benzynes in which the two configurations associated respectively with double occupancy of ϕ_s or ϕ_a have been generated and allowed to mix in an iterative, fully self-consistent manner, though, as already noted, previous investigations have included two-determinant CI calculations.[3,4,9]

In addition to calculations at the isomer equilibrium geometries, we have investigated the relative stabilities of the three isomers using for the carbon framework the 4-31G equilibrium geometry of the phenyl cation.[16] These computations were done in anticipation of Hehre's experimental results, as the phenyl cation is the immediate precursor of the benzynes in those ICR experiments.[14] The goal was to determine the significance of internal energy effects which might result if the initial geometry of the nascent benzynes reflected not their equilibrium configurations but rather that of the parent cation.

Energies and structures of triplet states were also calculated,

II. Calculational Details

It has been noted by several workers[3,17] that single-determinant calculations for any of the three isomeric benzynes yield a pair of orbitals, ϕ_s and ϕ_a, which even at the canonical MO level are moderately well localized on the dehydro centers and easily distinguishable as the symmetric and antisymmetric pairings of the radical orbitals discussed above. These two orbitals, in each case, constitute the highest occupied and lowest vacant orbitals of σ symmetry and are those which were GVB paired in each of the two-configuration singlet calculations.[18] This pairing is expected to be especially important in making reliable predictions regarding the meta and para isomers, which have unusual 1-3 and 1-4 interactions, respectively (see Figures 2 and 3). In addition it affords a better reference level for energy comparisons with the computed triplet states. As both singlet and triplet calculations yield fully optimized two-configuration wave functions (for $m_s = 0$), one expects that short of much more complete CI this scheme should provide the most consistent treatment of the two states.

In view of our interest in making reliable predictions regarding both the qualitative ordering of the various isomers and the nature of their equilibrium structures, we have performed a series of limited geometry optimizations. The extent of these optimizations, as outlined below, varied from one isomer to another depending on the present uncertainty of its equilibrium configuration. Owing to the remaining ambiguities in structure as well as limitations in the split valence 4-31G basis set, we do not attribute much significance to total energy differences of less than 5 kcal/mol.[7,9b] This should be borne in mind during the discussions of relative energetics.

The ortho isomer has been the most intensively studied and well characterized of the three structures. Its equilibrium single-determinant structure has been determined at the 4-31G level[9b] and is very similar to the MINDO/3 results.[4] In addition, two-configuration CI at both the ab initio (STO-3G)[9] and MINDO/3[4a] levels was found to have little effect on the equilibrium structure; in particular the length of the C_1-C_2 bond (see Figure 1) was not appreciably altered. In light of these results, further geometry optimization at the GVB level was not felt necessary. Calculations reported were done at the single-determinant equilibrium geometry as depicted in Figure 1. The triplet state, on the basis of previous studies,[3,4] was expected to lie significantly above the singlet. Accordingly, we did not invest effort in its optimization either and employed the MINDO/3 geometry in these calculations.

The structures of the singlet and triplet states of *m*-benzyne have not been nearly so well delineated as have those for the ortho isomer, with previously published structures being in discord concerning qualitative features. Specifically, it is not clear where the equilibrium structure lies between the extremes

Table I. Energy of Equilibrium Benzyne Configurations

	energy, au	rel energy, kcal/mol
ortho		
singlet	−229.107 97	0.00
triplet[a]	−229.063 26	28.06
meta		
singlet	−229.084 87	14.49
triplet	−229.065 37	26.73
para		
singlet	−229.070 83	23.30
triplet	−229.068 61	24.70

[a] Ortho triplet structure not optimized; calculation done at MINDO/3 equilibrium triplet structure.[4]

Table II. Overlap Populations for Equilibrium Benzynes[a]

	σ	π
	A. Benzyne	
ortho (C_{2v})		
C_1–C_2	1.1725	0.3838
C_2–C_3	0.7364	0.2290
C_3C_4	0.7593	0.3329
C_4–C_5	0.7625	0.2472
meta (C_{2v})		
C_1–C_2	0.6934	0.2875
C_3–C_4	0.7656	0.2938
C_4–C_5	0.7215	0.2817
C_1–C_3[b]	−0.0964	−0.0167
para (D_{2h})		
C_1–C_2	0.7576	0.2960
C_2–C_3	0.7206	0.2669
C_1–C_4[b]	−0.0584	−0.0227
	B. Kekule Benzene	
C_1–C_2[c]	0.7464	0.2906
C_1–C_3[d]	−0.1224	−0.0145
C_1–C_4[e]	−0.0154	−0.0244

[a] Values given for all unique bonded pairs of carbon atoms and in the case of meta and para isomers for the nonbonded pair of dehydro carbon atoms. The values for the nonbonded carbon atom interactions in Kekule benzene are also given for comparison. [b] Nonbonded pair of dehydro carbon atoms. [c] Bonded pair. [d] Meta pair. [e] Para pair.

of a bicyclic structure on the one hand and an open diradical structure on the other. It was, therefore, felt necessary to perform a geometry optimization at the GVB level, concentrating efforts on the length of the C_1–C_3 separation. We carried out such an optimization with the following constraints. All C–H bonds were held invariant at 1.08 Å, which is close to the equilibrium value in benzene,[19] and were assumed to bisect their respective CCC angles. In addition each C–C bond length in the six-membered ring was held fixed at the corresponding SCF MINDO/3 equilibrium value.[4a,20] This assumption was predicated on the qualitative structural agreement between MINDO/3 and 4-31G for *o*-benzyne and should not be an overly severe limitation. Washburn's[1b] STO-3G structure, though qualitatively different in character from the MINDO/3 solution, nonetheless differs from it by an average of only 0.009 Å in the ring C–C bond lengths. By employing these constraints and restricting the molecule to C_{2v} symmetry, optimization of *m*-benzyne becomes a two-parameter problem. We arbitrarily defined these as the C_1–C_3 separation and the distance from the midpoint of the C_1–C_3 linkage to C_5. The latter choice was based on the empirical observation that this distance varied little in previously published structures.[21] The optimized structures obtained for the $^1A_1$ and $^3B_2$ states are depicted in Figure 2. It should be noted that the triplet state was optimized with the same ring bond distances as the singlet, and hence its energy is probably somewhat artificially raised with respect to the singlet.

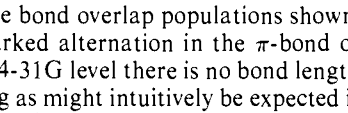
To date, the only reported optimizations of either the singlet or triplet states of *p*-benzyne are those of Dewar.[4] In view of this we felt it worthwhile to perform limited optimizations at the GVB (RHF for the triplet) level, A set of constraints analogous to those employed in the optimizations of *m*-benzyne was employed here, with the C–C ring bond lengths fixed at MINDO/3 two-determinant CI values.[22] With the additional limitation of D_{2h} symmetry the optimizations reduce to single-parameter problems, the C_1–C_4 separation being the simplest choice. The equilibrium structures are shown in Figure 3.

III. Results and Discussion

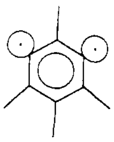
A. Equilibrium Structures. The results of primary interest are the relative energetics. These are summarized in Table I. For each isomer we find the ground state to be the singlet, though the separation in *p*-benzyne is sufficiently small that this conclusion is certainly not definitive. Indeed, there is evidence to suggest that more careful geometry optimizations including relaxation of the ring bond lengths may reverse the singlet-triplet ordering of this isomer.[13] At any rate, it is safe to say that the lowest singlet and triplet states are within a few kilocalories per mole of one another. Of particular interest is the fact that our calculations indicate a relative energy ordering for the three isomers of ortho < meta < para. The splittings are sufficiently large (14.49 and 8.81 kcal/mol) that one might reasonably expect that this stability ordering of the isomers is not an artifact of the level of the computations. We shall return to this question in a later section in which the expected reliability of the results is discussed.

Since the isomers of benzyne, particularly the singlet states, have opportunities for rather unusual bonding interactions, it seems worthwhile to discuss the implications of our calculations regarding the characterization of the bonding in these molecules, including the degree of diradical character in the coupling of the dehydro carbon atoms. Before turning to a detailed discussion of each isomer, we note that for all three singlet isomers, the GVB calculations yield ϕ_s,ϕ_a orbital pairs which roughly speaking can be described as linear combinations of two carbon hybrid atom orbitals directed *outward* from the benzyne rings. This directionality allows for a bonding type of in-plane π overlap in the case of *o*-benzyne, but suggests that the absence of appreciable 1-3 and 1-4 bonding in the case of the meta and para isomers, respectively.

***o*-Benzyne.** The nature of the bonding in *o*-benzene has previously been discussed in considerable detail.[9] The most prominent feature of *o*-benzyne is its short acetylenic C_1–C_2 bond, which results in a preference for the first of the two following resonance structures. Such an interpretation is consistent with the bond overlap populations shown in Table II. There is a marked alternation in the π-bond overlaps even though at the 4-31G level there is no bond length alternation around the ring as might intuitively be expected in light of the above discussion.[23] This latter feature, along with the concomitant lack of alternation in the σ-bond overlap populations, has been explained in terms of the s–p hybridization necessitated by the acetylenic C–C bond.[9]



***m*-Benzyne.** At the GVB level, *m*-benzyne has a singlet structure which is only moderately distorted from benzene, with the C_1–C_3 contact being reduced by only 0.19 Å, and attaining a value of 2.21 Å while the C1-C2-C3 angle is contracted to 108.6°. This structure is, of course, not compatible with significant bond formation between the radical centers. Indeed, it is not clear that the geometrical deformations observed are properly ascribed to an incipient bond. Similar effects might be expected merely from the presence of the two radical centers. For example, the optimal C-C-H angle in the vinyl radical is 136.6°.[24] An analogous trend in the C2-C3-C4 and C2-C1-C6 angles might well lead to a closing of the C1-C2-C3 angle and shortening of the C_1-C_3 separation without necessarily implicating bond formation. This view is concordant with the overlap populations of Table II. It is notable that both the σ and π overlap populations between the C_1 and C_3 centers are negative. Indeed, the σ overlap population is only slightly less negative than that in benzene. The evidence clearly suggests an interpretation of the structure based on the σ-diradical resonance form shown below. Thus



it is not surprising that single-determinant calculations do not yield a structure in qualitative accord with that found at the GVB level. Forcing the two electrons to occupy a single orbital (i.e., RHF) yields a bicyclic equilibrium structure with a C_1-C_3 separation of 1.50 Å,[25] 17.0 kcal/mol more stable than the GVB equilibrium structure. On the other hand, at the GVB level the open equilibrium structure lies 32.0 kcal/mol below the bicyclic structure. No attempt was made to ascertain if the GVB level would yield a local minimum for a bicyclic geometry. The MINDO/3 study[4a] suggested that no such minimum exists. Clearly the diradical nature of the singlet ground state requires the GVB formulation (or some alternative means of incorporating the necessary correlation) for a qualitatively correct interpretation of the molecular structure.

The equilibrium structure of the triplet isomer as depicted in Figure 2 is even less distorted from that of benzene than is the singlet state. As expected from the above discussion, qualitatively similar distortions from benzene are observed here, i.e., shortening of the C_1-C_3 separation and closing of the C_1-C_2-C_3 angle. These effects are quite modest, however, with the C_1-C_3 separation being only 0.1 Å less than the corresponding distance in benzene. The smaller ring distortion in the case of the triplet might be taken as indicative of a small amount of bonding between the radical centers in the singlet structure, except for the unfavorable orientation of the atomic orbitals associated with the diradical sites, as noted above. By contrast, when the GVB wave function is forced to accommodate the strained bicyclic structure defined above, these hybrid orbitals are indeed directed inward to facilitate the formation of the C_1-C_3 bond.

***p*-Benzyne.** In view of our diradical interpretation of the meta isomer, it is not surprising that a similar picture is obtained for *p*-benzyne, in which the dehydro centers are still further separated. The equilibrium singlet structure is only very modestly distorted from that of benzene, the C_1-C_4 separation of 2.70 Å being only 0.08 Å less than the analogous separation in benzene. As in the meta isomer, this contraction may be ascribed to the influence of the radical centers: opening of the C_2-C_1-C_6 (C_3-C_4-C_5) angle with corresponding shortening of the C_1-C_4 separation. For this isomer, the distance between the radical centers is somewhat less for the triplet structure than for the singlet (see Figure 3). As expected from the structure, the C_1-C_4 overlap population is small and consistent with a diradical interpretation of the molecule. Both the σ and π overlap populations between C_1 and C_4 are small and negative. The remaining overlap populations reflect the radical-induced bond-length alternations about the ring.

As in the case of *m*-benzyne, single-determinant RHF theory is inappropriate for a proper description of this isomer. A cursory, single-determinant examination at the 4-31G level indicated the intersection of the two surfaces which correspond, respectively, to double occupany of ϕ_s and ϕ_a (see sections I and II). The latter surface has a minimum at an open, benzene-like structure (C_1-C_4 = 2.71 Å). The former has a minimum at a bicyclic structure (C_1-C_4 = 1.54 Å), the energy being only 4.7 kcal/mol above the more stable open structure. This description is in sharp contrast to the GVB potential energy surface, in which a bicyclic structure[26] was found to lie 77.2 kcal/mol above the lowest energy diradical structure. The GVB orbitals (ϕ_s, ϕ_a) of the bicyclic structure are characterized by inward directed hybrid orbitals, as opposed to the case for the open diradical structure. This situation is completely analogous to that found for the meta isomer.

Although a complete search for a local bicyclic minimum was not carried out, a variation of the C_1-C_4 distance (keeping the nearest-neighbor carbon atom distances frozen[26]) yielded an inflection point at 1.67 Å (close to the optimal value in Dewar's bicyclic structure[4a]), thus suggesting that a complete optimization would lead to a second local minimum. The calculated energies indicate that the second minimum would be far above the lowest energy structure (similar to the MINDO/3 results[4a]), even though the value of 77.2 kcal/mol might be too large by as much as a factor of 2, as inferred from a comparison of the 4-31G energetics of the analogous pair—Kekule and Dewar benzene.[9b]

Analysis of the GVB Wave Functions. In much of the discussion thus far we have attempted to infer the extent of the diradical character in the singlet equilibrium configurations. The GVB formalism affords an opportunity to at least partially quantify such a discussion. The GVB wave function for each of the singlet configurations may be written as the following antisymmetrized ($\mathcal{a}$) product:[15d]

$$\psi = \frac{1}{\sqrt{2(1 + S_{AB}^2)}} \mathcal{a} \{\text{core } \phi_A(1)\phi_B(2)(\alpha\beta - \beta\alpha)\} \quad (1)$$

where ϕ_A and ϕ_B are linear combinations of the natural orbitals ϕ_s, ϕ_a defined earlier and are in general nonorthogonal, their overlap being S_{AB}. The space and spin wave functions for the remainder of the electrons, all singlet paired in doubly occupied space orbitals, are here designated as "core". In the present discussion the labels A and B refer to the dehydro centers (C_A, C_B) in the benzyne isomers.

In the generalized valence bond framework,[15] the ϕ_A and ϕ_B are not confined to single atomic centers, in contrast to the traditional Heitler-London type of wave function, and accordingly ψ will have ionic as well as diradical or covalent components associated with centers A and B, plus additional terms arising from delocalization onto other atomic centers. The ϕ_A and ϕ_B obtained for the benzynes are reasonably well localized (for a given ϕ_A, basis functions on centers other than A always have coefficients < 0.1). In terms of the CI coefficients in the natural orbital expansion of the wave function

$$\psi = \mathcal{a} \{\text{core } (C_s\phi_s^2 - C_a\phi_a^2)(\alpha\beta - \beta\alpha)\} \quad (2)$$

we have[15d,27]

$$S_{AB} = (C_s - C_a)/(C_s + C_a) \quad (3)$$

where C_s and C_a have the same sign and a magnitude ≤ 1.

In cases where the interaction between centers A and B is primarily a direct one, as for the ortho and meta isomers (in contrast to the dominant through-bond coupling for the para isomer[17]), one finds $S_{AB} > 0$ since ϕ_s^2 is the more important configuration ($C_s > C_a$ in eq 3). The location of $|S_{AB}|$ between zero and unity provides a rough estimate of the relative importance of diradical (or covalent) and ionic character in ψ. At one limit of possible GVB solutions is the RHF wave function, where ionic character attains its maximum impor-

Table III. Overlap of GVB Orbitals[a] Associated with Dehydro Centers

	S_{AB}	
isomer	from equilibrium structure	from reference structure
ortho	0.508	0.695[b]
meta	0.248	0.781[c]
para	−0.115	0.691[c]

[a] Overlap, S_{AB}, between GVB orbitals ϕ_A and ϕ_B associated with the C_1–C_2, C_1–C_3, and C_1–C_4 interactions in the ortho, meta, and para isomers, respectively (see eq 1–3). [b] The acetylene π bond (based on the 4-31G RHF geometries[11a]). [c] Bicyclic structures defined in section III.

Table IV. Energy of Benzynes Based on Phenyl Cation Framework

	energy, au	rel energy, kcal/mol
ortho		
singlet	−229.067 18	0.00
triplet	−229.006 56	38.04
meta		
singlet	−229.060 14	4.41
triplet	−229.031 87	22.16
para		
singlet	−229.024 33	26.89
triplet	−229.024 59	26.73

tance: ϕ_A and ϕ_B are equivalent and hence their overlap is unity ($C_a = 0$). The implication of such a solution would be that the energy stabilization due to bond formation was sufficient to compensate for the repulsion attendant on having both electrons occupy the same space. At the other limit, S_{AB} goes to zero ($C_s = C_a$), and one might speak of a purely diradical state. As noted by Salem and Rowland,[28] a true diradical would also require the exchange interaction between ϕ_A and ϕ_B to be small (hence a small singlet–triplet separation).

Clearly, if S_{AB} is to be a meaningful index of orbital interaction in the sense defined above, it must be based on variationally determined values of C_s and C_a (eq 3). Otherwise one could, for example, trivially constrain S_{AB} to be unity in all cases, by remaining within the closed-shell RHF framework. Values of S_{AB} for the equilibrium benzyne isomers are listed in Table III, along with appropriate reference values.

The acetylenic C_1–C_2 π interaction in *o*-benzyne is seen to be far from the diradical limit. The somewhat reduced magnitude of S_{AB} relative to that for π bond in acetylene itself may be interpreted as evidence for the strained nature of the acetylenic moiety in the benzyne due to its forced nonlinearity in the ring.

The diradical nature of the equilibrium meta isomer is underscored by a comparison with the S_{AB} value for the corresponding bicyclic structure (Table III).

The negative value[27] of S_{AB} for *p*-benzyne arises from the fact that $C_a > C_s$ (eq 3), and thus indicates that a simple two-center analysis of the C_1–C_4 interaction is inadequate,[17] as noted above. S_{AB} has several small negative contributions, including the ionic terms from C_1 and C_4. However, in spite of these complications, the small magnitude of the negative terms as well as of S_{AB} itself, coupled with the small singlet–triplet splitting[28] (Table I), makes it reasonable to describe *p*-benzyne as essentially a pure diradical.

Since both *m*- and *p*-benzyne are found to have appreciable diradical character and thus correspondingly weak transannular coupling, the differing chemistry of the two isomers apparently reflects subtler differences in molecular and electronic structure than were originally envisioned.[1b–e]

B. Phenyl Cation Structures. As noted above, our interest in the benzynes arose from planned ICR experiments which will attempt to assess the relative stabilities of the three isomers. The immediate precursor of the benzynes in such experiments is the phenyl cation, $C_6H_5^+$. We have, therefore, performed GVB calculations for each of the isomers, freezing the carbon skeleton at the parent cation structure. The intent here was to determine what differences in stability one might observe if the ICR thresholds should correspond to this structure rather than to the equilibrium benzyne structures.

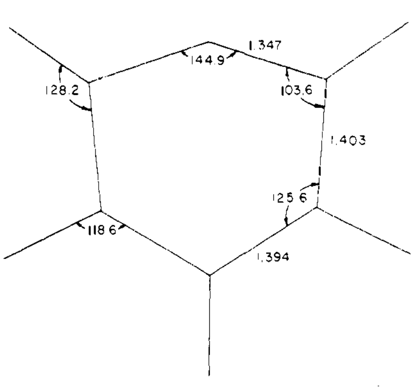


Figure 4. Equilibrium structure (4-31G, RHF) of the phenyl cation (ref 16).

Dill et al. have determined the equilibrium singlet configuration at the 4-31G level.[16] This structure is depicted in Figure 4. The energies of the singlet and triplet states for each isomer using this framework geometry are collected in Table IV. We obtain the same relative energy ordering here as at the respective equilibrium geometries, though the splitting between the ortho and meta states is now much smaller. In fact, this splitting (4.4 kcal/mol) is of the order of the expected accuracy of our calculated relative energies (see below). Thus the calculations suggest qualitatively that if the benzyne framework geometries were close to the cation framework structure, the ortho and meta isomers would be quite close in energy, while the para isomer would remain separated from the other two isomers by ~1 eV. Experimentally, the nonequilibrium geometries might be pertinent to threshold behavior if the time for removal of the light hydrogen atom was sufficiently shorter than that required for relaxation of framework modes dominated by the heavier carbon atoms.

IV. Comparison with Previous Results

A. MINDO/3 Results. Structurally, the MINDO/3 results are in qualitative accord with those found here, both studies yielding equilibrium geometries for singlet meta and para isomers which indicate a large degree of diradical character, while the ortho isomer suggests the covalent character expected of a somewhat distorted acetylenic moiety. In terms of energetics, however, the two sets of results are in rather sharp contrast. While two-determinant MINDO/3 CI results give an energy ordering of meta(0.0) < ortho(7.1) < para(9.7) (relative energy (kcal/mol) given in parentheses), our work yields the ordering ortho(0.0) < meta(14.5) < para(23.3). It is difficult to estimate the reliability of the MINDO/3 predictions for these systems, since the method displays conflicting trends. For example, if one corrects for the MINDO/3 error in the heat of formation for methane[29] then the bond separation reaction of benzene

$$C_6H_6 + 6CH_4 \rightarrow 3C_2H_4 + 3C_2H_6 \quad (4)$$

is predicted to have an endothermicity of 76.8 kcal/mol as compared with an experimental value of 64,2 kcal/mol.[6] This overestimate of the aromatic stabilization of benzene suggests that the meta and para isomers, whose aromaticity is least altered (as inferred from equilibrium geometries and overlap

Table V. Distortion of Benzyne Structures from Benzene Framework[a]

	$(\lvert\sum(\Delta\alpha)^2\rvert/6)^{1/2\,b}$	$(\lvert\sum(\Delta R)^2\rvert/6)^{1/2\,c}$
ortho		
singlet	7.01 (14.19)	0.0681 (0.0563)
triplet	2.47 (5.82)	0.0152 (0.0225)
meta		
singlet	7.61 (10.03)	0.0215 (0.0210)
triplet	3.85 (12.63)	0.0215 (0.0210)
para		
singlet	3.72 (12.70)	0.0315 (0.0208)
triplet	4.53 (12.51)	0.0315 (0.0208)

[a] Values in parentheses refer to deviation of equilibrium structure from phenyl cation structure. [b] $\Delta\alpha$ denotes deviation of each internal C–C–C angle from 120°. [c] ΔR denotes deviation of each C–C bond length from 1.39 Å.

populations), are artificially lowered in energy with respect to *o*-benzyne, On the other hand, MINDO/3 consistently underestimates heats of formation for strained cyclic alkenes,[30] Since our previous analysis of bonding indicates that the ortho isomer would be subject to the greatest angle strain, one might infer an energy error opposite to that based on consideration of aromaticity—i.e., an error which would favor the ortho isomer. A similar bias would probably also arise from the fact that the MINDO/3 heats of formation for alkynes are typically underestimated by a few kilocalories per mol.[5] The reliability of MINDO/3 for these systems is further clouded by the uncertain effects of appending configuration interaction to a wave function already parametrized to include correlation, as already noted. In view of these difficulties the MINDO/3 prediction that the meta isomer is the most stable ion might be subject to question, especially since the ab initio results reported here yield a substantial energetic preference for the ortho isomer. Before considering possible errors associated with use of the 4-31G basis in section V, we relate the present results to the earlier work of Wilhite and Whitten.

B. Ab Initio Results. As noted previously, Wilhite and Whitten performed rather extensive configuration interaction calculations for each of the benzyne isomers under the constraint that their carbon skeletons retain a benzene configuration.[3] Despite this rather severe geometrical limitation some comparisons can be made between their work and that reported here by considering in a qualitative fashion how one would expect their results to be modified upon relaxation of the geometry constraint, Table V presents the root mean square deviations of the equilibrium benzyne geometrical parameters from their benzene analogues. One would hope that these quantities would provide an estimate of the relative degree to which each isomer would be stabilized by geometrical relaxation. Comparing the singlet states, one finds nothing which indicates that the meta isomer should be preferentially stabilized upon relaxation in comparison with *o*-benzyne. Indeed, since their angular deviations are of the same order of magnitude, it is reasonable that inclusion of bond length relaxation (principally the C_1-C_2 bond of *o*-benzyne) should result in preferential stabilization of the ortho isomer. The para isomer with its benzene-like equilibrium structure evidently has the least to gain from geometrical relaxation. On the basis of these comparisons, it is not surprising that the present relaxed-geometry calculations reproduce the energy ordering of the previous constrained-framework results (ortho(0.0) < meta(12.8) < para(15.5)[3]), but with increased splittings between the isomers.

The fact that we find the ground state of the meta isomer to be a singlet in contrast to Wilhite and Whitten's prediction of a triplet is resolvable in terms of the greater stabilization expected in the singlet state upon geometry relaxation (see Table V). In this regard our finding of a singlet ground state for the para isomer might seem surprising since the triplet state, already the more stable spin state at a frozen benzene geometry, appears to have more to gain from relaxation of geometrical constraints, As alluded to earlier, our result (which involves a very small splitting, at any rate) could be an artifact of assuming identical ring bond lengths for the singlet and triplet calculations.

We note in passing that an analysis similar to that just made for distortions relative to the benzene framework can also be made using the structure of the phenyl cation (a potential precursor[14]) as the reference geometry: the calculations at the phenyl cation structure can be rationalized in terms of the degree of geometrical relaxation required to attain the equilibrium structures, The salient point, as is evident in Table V, is that the ortho isomer is altered the most upon relaxation from its parent phenyl cation structure to its equilibrium configuration. This implies the above-noted result that the meta-ortho splitting should be less at the phenyl cation structures than at the respective equilibrium geometries.

V. Expected Reliability of Present Results

At this point it is pertinent to assess the expected reliability of the present ab initio calculations by considering what biases might be introduced by the basis set and level of wave function (one-pair GVB) which we have employed. In contrast to the MINDO/3 level, the 4-31G basis reproduces the resonance energy of benzene to within 1 kcal/mol (based on eq 4) at the SCF level.[6] It is well known that this level of calculation exaggerates strain energies, typically by ~10 kcal/mol for small rings, as inferred from calculated energies for hydrogenation reactions.[9b,31] If excessive strain energy is considered to be the dominant basis set defect in the present context, we anticipate that inclusion of polarization basis functions would reduce the separation between the bicyclic configuration of the meta and para isomers and the open diradical structures. However, it seems quite unlikely that such polarization effects would be dramatic enough to overturn the present picture of diradical equilibrium structures, since the bicyclic structures are presently 32.0 and 77.8 kcal/mol above the minima for the meta and para isomers, respectively. Assuming this to be the case, one is next led to the question of which of the isomers, at their present geometries, would be stabilized to the greatest extent by improvement of the basis set. As a consequence of its strained acetylenic bond, it seems reasonable to postulate that the ortho isomer should be preferentially stabilized, while the nearly benzene-like diradical structure of *p*-benzyne should be the least enhanced. Thus one might expect that polarization functions should only further accentuate the present energy separations of the three isomers.

Actually, the exaggeration of strain energy attributable to the 4-31G basis (or other double-ζ basis sets) appears to be significantly reduced when the strained bonds are treated at the more elaborate GVB level. This can be seen, for example, by noting that the calculated hydrogenation energy of *o*-benzene (o-$C_6H_4 + H_2 \rightarrow C_6H_6$) is within experimental uncertainty (cf. ref 31) if a two-pair GVB correction is adopted for each side of the equation (the in-plane π bond and the H_2 bond on the left-hand side, and two CH bonds on the right).[32]

It is not apparent what effect more complete configuration interaction might have on the relative stabilities of the isomers. The only available evidence is that of Wilhite and Whitten,[3] whose results indicate that inclusion of π-electron correlation yields only very modest changes in the relative isomer energies beyond the two-determinant CI level.

VI. Conclusions

The results reported here strongly suggest that the lowest energy structures of the singlet states of 1,3- and 1,4-bisdehydrobenzene are not bicyclic but rather are open cyclic structures with significant diradical character, For the para isomer, the GVB calculations suggest that the bicyclic structure is associated with a secondary local minimum on the potential energy surface. The energy differences between the open and bicyclic structures are sufficiently large that it seems unlikely that improved calculations will alter this qualitative description of the isomers. The prediction of these diradicals as the equilibrium structures is strongly dependent on the inclusion of the correlation between the singlet-paired "diradical" electrons. At the single-determinant level one finds qualitatively different potential energy surfaces, with the meta isomer collapsing to a bicyclic structure as the ground state. The calculated energies separating the three equilibrium isomers are large enough to suggest that the ordering (ortho < meta < para) is probably not an artifact of the level of the calculation. This same ordering is attained for calculations employing a phenyl cation carbon framework, although in this case the ortho-meta splitting is reduced to a magnitude (4.4 kcal/mol) which is of the order of uncertainty of the calculations.

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(21) This parameter has values of 2.15 and 2.14 for MINDO/3[4] with and without CI, respectively, and 2.12 for the STO-3G optimization.[1b]

(22) As CI had a significant effect on the MINDO/3 equilibrium geometry, it was felt that the C–C bond lengths from the CI calculations would be the more reliable.

(23) Such a bond length alternation was inferred from IR data by Laing and Berry,[2] but has not been obtained theoretically.[4,9]

(24) This angle was optimized at the 4-31G level with all other parameters frozen at their MINDO/3 values [P. Bischof, *J. Am. Chem. Soc.*, **98**, 6844 (1976)]. Optimization using standard geometrical parameters [J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967)] yields essentially the same result (135°) as that quoted here.

(25) This value is very near the 4-31G RHF equilibrium value;[13] in the present calculations all peripheral C–C bond lengths were left unchanged.

(26) Geometry 1j of ref 4a was employed for the carbon atom framework.

(27) The sign will be positive for typical cases of hybrid orbital interactions if the relative phases of ϕ_A and ϕ_B are defined by letting the two orbitals be mirror images of each other. A negative S_{AB} implies antibonding only with respect to the direct (through space) interaction, with the dominant bonding effects being provided by the through-bond mechanism (i.e., dominance of ϕ_a^2).[17]

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(30) E.g., the heats of formation for cyclopropene, 1-methylcyclopropene, 1,2-dimethylcyclopropene, cyclobutene, 1-methylcyclobutene, and 1,2-dimethylcyclobutene are all underestimated, by an average of 11.0 kcal/mol; see Table I of ref 5.

(31) In ref 9a it was demonstrated that the calculated and experimental energetics of *o*-benzyne can be brought into agreement if a value of 10 kcal/mol is employed as an estimate of the exaggeration of strain energy. It should be noted, however, that the calculation was based on a single-determinant wave function.

(32) The energy lowering (relative to the SCF result) for the *o*-benzyne in-plane π bond is -0.051 au (cf. ref 9b and Table I); the lowering for H_2 is only -0.0003 au. The lowering for two CH bonds is estimated as -0.030 au, based on data quoted for ethylene in ref 15b.