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# The Fulvenediyls and Related Biradicals: Molecular and Electronic Structure

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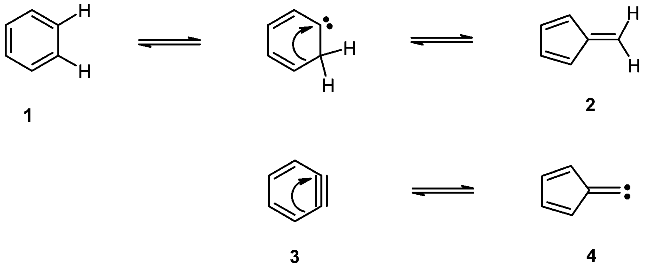
The structures, stabilities, and electronic properties of the nine fulvenediyls have been investigated and compared to the isomeric benzynes using density functional theory (DFT) and ab initio multireference configuration interaction methods (MRCI). Given the significant biradical character of several singlet fulvenediyls, the BLYP method reproduces the relative energies of these systems rather accurately. In contrast, some triplet states ($^3$A′-**12**, $^3$A′-**13**, and $^3$B$_2$-**14**) suffer from artifactual symmetry breaking towards a nonplanar geometry at the DFT level. The structures and properties of the title biradicals are readily rationalized within the framework of *through-space* and *through-bond* molecular orbital interactions. The degree of coupling between the formally unpaired electrons strongly depends on the number and arrangement of intervening $\sigma$-bonds, and often parallels the trends observed for annellated arynes of similar topology. In some cases, novel structural patterns can be identified that are characteristic of five-membered-ring systems. These similarities and differences between five- and six-membered-ring arynes are discussed on the basis of molecular orbital arguments.

## 1. Introduction

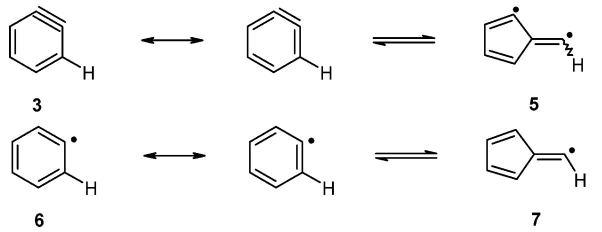
The ring contraction of benzene derivatives to five-membered-ring systems is a common rearrangement in the high-temperature chemistry of aromatic compounds.[1,2] The degenerate isomerization of naphthalene has been demonstrated by Scott et al. in 1977,[1a] and an unimolecular mechanism involving benzofulvene as an intermediate has been suggested to account for the observed isotopic scrambling. The analogous topomerization[3] of benzene (**1**) at 1100 °C has been reported 10 years later.[1b,c] According to recent calculations,[4] this process is rather complex from a mechanistic point of view. Apart from fulvene (**2**) formation (Scheme 1), additional pathways (e.g., via benzvalene) may be relevant simultaneously under these conditions. A related rearrangement of *o*-benzyne (**3**) to fulvene-1,1-diyl (**4**) has been proposed by Brown and co-workers.[2] Despite some controversy regarding the mechanistic interpretation of the observed isotopic distributions (see, ref 2c for a detailed discussion of this point), the acetylene−vinylidene rearrangement is nowadays generally accepted as a key reaction mode of arynes[5] at elevated temperatures.

**SCHEME 1**



Fulvene-1,3-diyls (**5**) have been considered as alternative intermediates during rearrangements of *o*-benzyne derivatives, but their formation has not yet been established definitively (Scheme 2).[2b] Related reactions of (substituted) aryl radicals, on the other hand, were explained by the assumption of intermediate fulvene-1-yl radicals (**7**).[2b,c] More recently, we considered the involvement of **5** in the course of the thermal ring opening of *m*-benzyne (**8**) to (*Z*)-hex-3-ene-1,5-diyne (**9**).[6] On the basis of high-level calculations, it has been shown, however, that a more favorable pathway from **8** to **9** exists, which combines ring rupture and hydrogen shift in a single step (Scheme 3).[6,7] Nonetheless, fulvene-1,3-diyls might be acces-

**SCHEME 2**



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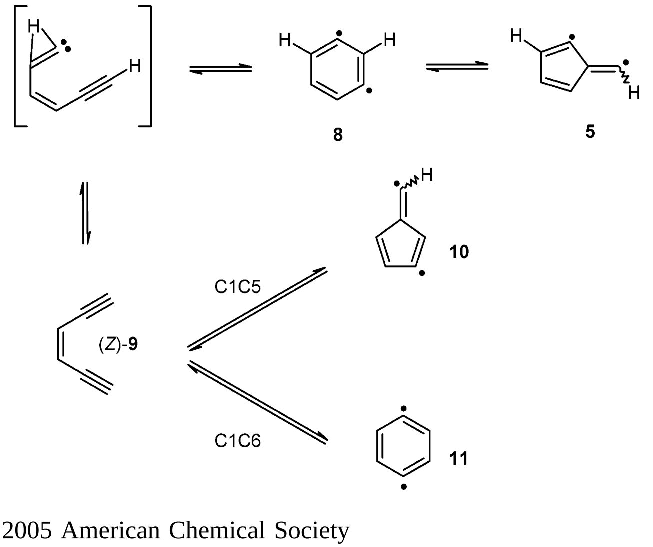

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sible from *m*-benzynes in suitably annellated or substituted systems. Formation of fulvene-1,4-diyls (**10**) has been suggested as an alternative to the well-known Bergman cyclization of (*Z*)-**9** (C1C6-cyclization) by Schreiner et al.,[8] and although the C1C5-cyclization is less favorable for the parent enediyne, some closely related reactions could be observed experimentally.[8,9]

For many of the high-temperature processes mentioned above, it is difficult to distinguish between different possible reaction mechanisms that could lead to similar product distributions on the basis of the experimental data alone. Even carefully designed isotopic labeling experiments are often inconclusive with regard to the intermediates involved. Quantum chemical computations turned out to be very helpful to rationalize the outcome of these thermolysis experiments and to clarify remaining ambiguities. Many of the intermediates considered in aryne rearrangements are biradicals, however, and near-degeneracy of their low-energy electronic states poses special challenges to theory. In particular, the reliability of density functional theory (DFT) that is frequently applied in this context cannot be taken for granted for such systems.[10]

The benzynes (**3**, **8**, and **11**) have been the subject of numerous theoretical studies.[5c,11] On the basis of extended Hückel calculations, Hoffmann, Imamura, and Hehre first rationalized their electronic properties by distinguishing between *through-space* and *through-bond* molecular orbital interactions.[12] The qualitative predictions have been firmly established by later experimental and (numerically accurate) computational investigations.[11,13] Several recent studies have been devoted to the influence of annellation,[14] substitution,[15] or introduction of heteroatoms[6,16] on the structure, stability, and electronic properties (e.g., the singlet−triplet energy splittings, $\Delta E_{ST}$, related to the biradical character) of arynes. For the hydrocarbon systems investigated (benzynes,[11−13] naphthalynes,[14a] didehydroindenes,[14b] didehydropyrenes[14c]), the degree of interaction between the radical centers has been shown to depend strongly on their distances, relative orientations, and the shape of the molecular framework that joins them. In contrast to arynes derived from benzene, their five-membered cousins have not yet been investigated nearly as thoroughly in this respect, and only a few recent studies have focused on rearrangements of (mostly heterocyclic) five-membered-ring systems.[17]

In this contribution we present a computational study of all nine fulvenediyls (didehydrofulvenes) and a comparison with the three isomeric benzynes employing DFT and ab initio multireference configuration interaction (MRCI) methods.[18] The latter approach belongs to the most accurate quantum chemical methods for computations on biradicals available today.[10a,18] The performance of DFT for this class of arynes is validated, which should be relevant for future work on benzyne rearrangements. Qualitatively, we analyze the coupling of the formally unpaired electrons and its consequences for structure, stability, $\Delta E_{ST}$, and biradical character, and draw some general conclusions regarding the similarities and differences of five-membered- and six-membered-ring arynes.

## 2. Computational Procedures

Geometries of all species were fully optimized at the BLYP[19] and multiconfiguration self-consistent field (MCSCF) level of theory using Dunning's correlation-consistent polarized valence-triple-$\xi$ (cc-pVTZ)[20] basis set. Tight convergence criteria for gradients (with maximum residual forces on nuclei below 0.000015 au) have been used throughout. A full (99, 590) integration grid, having 99 radial shells per atom and 590 angular points per shell, has been employed in all DFT calculations. A spin-unrestricted formalism was used generally, where for calculations on singlet biradicals the initial guess frontier orbitals have been mixed to destroy (spin-)symmetry; whenever a spin-restricted solution was obtained, it was further tested for instabilities by calculating the eigenvalues of the Hermitian stability matrices **A** and **B**.[21] MCSCF computations were of the complete active space type (CASSCF).[22] For benzene and fulvene ($C_6H_6$) the 6-electron/6-orbital active space covers the six valence $\pi$ orbitals. For the $C_6H_5$ and $C_6H_4$ systems this space was extended by the formally nonbonding $\sigma$ orbitals at the dehydrocarbons, resulting in CASSCF(7,7) and CASSCF(8,8) wave functions, respectively. Vibrational frequencies of all molecules have been calculated for the DFT and CASSCF structures by using analytic second derivatives as implemented in the Gaussian 98 program package.[23] Single-point energy calculations at the MRCI level were carried out for both sets of geometries with the Molpro 2001 program suite.[24] Based on a CASSCF reference function, dynamic electron correlation is covered in this approach by internally contracted configuration interaction including single and double excitations (CAS-CISD) within the frozen core approximation.[18] If not mentioned otherwise, MRCI energies refer to Davidson-corrected values (CAS-CISD+Q).[25]

## 3. Results and Discussion

Energies of the lowest singlet and triplet states of all benzynes and fulvenediyls are given relative to *o*-benzyne (**3**) in Table 1. Before the structures and electronic properties of these biradicals are discussed, some technical remarks seem to be in order.

With regard to geometries, we note that the MRCI energies are in most cases slightly lower for the CASSCF than for the DFT structures. With few exceptions, the energy difference is less than 0.5 kcal mol$^{-1}$, and if not mentioned otherwise, all energetic considerations in this work refer to the MCSCF structures. According to the CASSCF computations, all fulvenediyls discussed here are planar. For the triplet states of 3,4- (**12**), 3,5- (**13**), and 3,6-didehydrofulvene (**14**), however, DFT predicts slight distortions from planarity, whereas $^3$A′-**12**, $^3$A′-**13**, and $^3$B$_2$-**14** are transition states (NIMAG = 1) on the triplet potential energy surface. Similar symmetry breaking by DFT has been reported previously for certain fluorinated triplet arynes.[26] Clear evidence for the artifactual nature of these distortions stems from the observation that the imaginary frequencies calculated for the planar structures are quite large (1262*i*, 259*i*, and 389*i* cm$^{-1}$ for $^3$A′-**12**, $^3$A′-**13**, and $^3$B$_2$-**14**, respectively), whereas the structural changes upon relaxation to a nonplanar geometry are small (cf., Supporting Information), and the corresponding energy lowering is only 0.9, 0.3, and 1.1 kcal mol$^{-1}$ for **12**, **13**, and **14**, respectively. Furthermore, $^3$B-**14** is 1.6 kcal mol$^{-1}$ higher in energy than $^3$B$_2$-**14** at the MRCI//UBLYP level, casting additional doubt on the relevance of the low-symmetry structures. The reasons for this unphysical symmetry breaking for the triplet states of some biradicals (that, in contrast to the singlet states, are qualitatively well described by single reference methods) within the framework of DFT are not yet fully understood, however.[27] Our best estimates ($E_{\mathrm{MRCI/CASSCF}}$ + ZPVE$_{\mathrm{CASSCF}}$) for the relative energies of the benzynes and fulvenediyls are depicted graphically in Figure 1.

Following earlier studies on arynes, we also calculated biradical stabilization energies (BSE) for the singlet and triplet states of all systems separately (Table 2).[11,28] The BSE is defined here as the reaction energy of isodesmic eq 1 at 0 K, where *m* and *n* indicate specific radical positions in fulvene or benzene.

**TABLE 1: Energies of $C_6H_4$ Isomers (in kcal mol$^{-1}$) Relative to *o*-Benzyne, Zero Point Vibrational Energies (ZPVE) and $\langle S^2 \rangle$ Expectation Values (DFT) Are Given for Comparison**

| isomer | compd | state | $E_{DFT}$ | $\langle S^2 \rangle_{DFT}$ | $ZPVE_{DFT}$ | $E_{CASSCF}$ | $ZPVE_{CASSCF}$ | $E_{MRCI/DFT}$ | $E_{MRCI/CASSCF}$ |
|---|---|---|---|---|---|---|---|---|---|
| benzynes | | | | | | | | | |
| 1,2 | **3** | $^1A_1$ | 0.0[a] | 0.000 | 45.7 | 0.0[b] | 49.3 | 0.1 | 0.0[c] |
| | | $^3B_2$ | 36.1 | 2.006 | 45.1 | 35.5 | 48.9 | 37.2 | 37.0 |
| 1,3 | **8** | $^1A_1$ | 12.3 | 0.000 | 44.9 | 17.2 | 48.6 | 14.1 | 14.2 |
| | | $^3B_2$ | 32.0 | 2.012 | 45.0 | 33.0 | 48.8 | 33.9 | 33.7 |
| 1,4 | **11** | $^1A_g$ | 26.2 | 0.768 | 44.5 | 29.3 | 48.6 | 29.2 | 29.1 |
| | | $^3B_{1u}$ | 30.7 | 2.005 | 45.1 | 32.0 | 48.8 | 32.9 | 32.7 |
| fulvenediyls | | | | | | | | | |
| 1,1 | **4** | $^1A_1$ | 33.8 | 0.000 | 44.1 | 29.9 | 47.8 | 32.4 | 32.2 |
| | | $^3B_2$ | 80.6 | 2.030 | 45.0 | 67.1 | 47.9 | 75.3 | 75.1 |
| (*Z*)-1,3 | (*Z*)-**5** | $^1A'$ | 68.1 | 0.954 | 43.2 | 64.2 | 47.1 | 68.3 | 68.1 |
| | | $^3A'$ | 68.7 | 2.019 | 43.3 | 63.9 | 47.1 | 68.3 | 68.2 |
| (*E*)-1,3 | (*E*)-**5** | $^1A'$ | 68.6 | 0.982 | 43.0 | 65.1 | 46.9 | 69.5 | 69.4 |
| | | $^3A'$ | 68.1 | 2.020 | 43.3 | 63.4 | 47.1 | 67.7 | 67.5 |
| (*Z*)-1,4 | (*Z*)-**10** | $^1A'$ | 64.6 | 0.807 | 42.5 | 61.7 | 46.9 | 65.3 | 65.1 |
| | | $^3A'$ | 67.5 | 2.011 | 43.4 | 63.5 | 47.1 | 67.4 | 67.2 |
| (*E*)-1,4 | (*E*)-**10** | $^1A'$ | | | | 58.1 | 47.0 | 60.8[e] | 59.8 |
| | | $^3A'$ | 68.8 | 2.010 | 43.3 | 64.0 | 47.1 | 68.3 | 68.2 |
| 3,4 | **12** | $^1A'$ | 57.5 | 0.000 | 44.0 | 46.9 | 47.9 | 52.9 | 52.3 |
| | | $^3A$ | 76.3 | 2.006 | 44.0 | | | | |
| | | $^3A'$ | 77.3[d] | 2.005[d] | 43.3[d] | 70.3 | 47.7 | 75.5 | 75.3 |
| 3,5 | **13** | $^1A'$ | 57.9 | 0.000 | 43.6 | 55.3 | 47.3 | 57.4 | 56.9 |
| | | $^3A$ | 72.8 | 2.014 | 43.6 | | | | |
| | | $^3A'$ | 73.1[d] | 2.025[d] | 43.2[d] | 68.3 | 47.5 | 72.9 | 72.6 |
| 3,6 | **14** | $^1A_1$ | 67.1 | 0.626 | 43.7 | 58.8 | 47.6 | 63.2 | 63.1 |
| | | $^3B$ | 73.1 | 2.007 | 43.6 | | | 75.4 | |
| | | $^3B_2$ | 74.1[d] | 2.009[d] | 43.4[d] | 69.1 | 47.5 | 73.8 | 73.5 |
| 4,5 | **15** | $^1A_1$ | 63.0 | 0.250 | 43.3 | 60.4 | 47.3 | 62.0 | 61.8 |
| | | $^3B_2$ | 72.8 | 2.015 | 43.5 | 67.0 | 47.5 | 71.7 | 71.5 |

[a] Absolute energy: $E_{DFT} = -230.905\,574$. [b] $E_{CASSCF} = -229.597\,795$. [c] $E_{MRCI/CASSCF} = -230.431\,463$; all MRCI energies are given relative to this value. [d] Transition state, NIMAG = 1. [e] UBLYP/cc-pVDZ geometry.

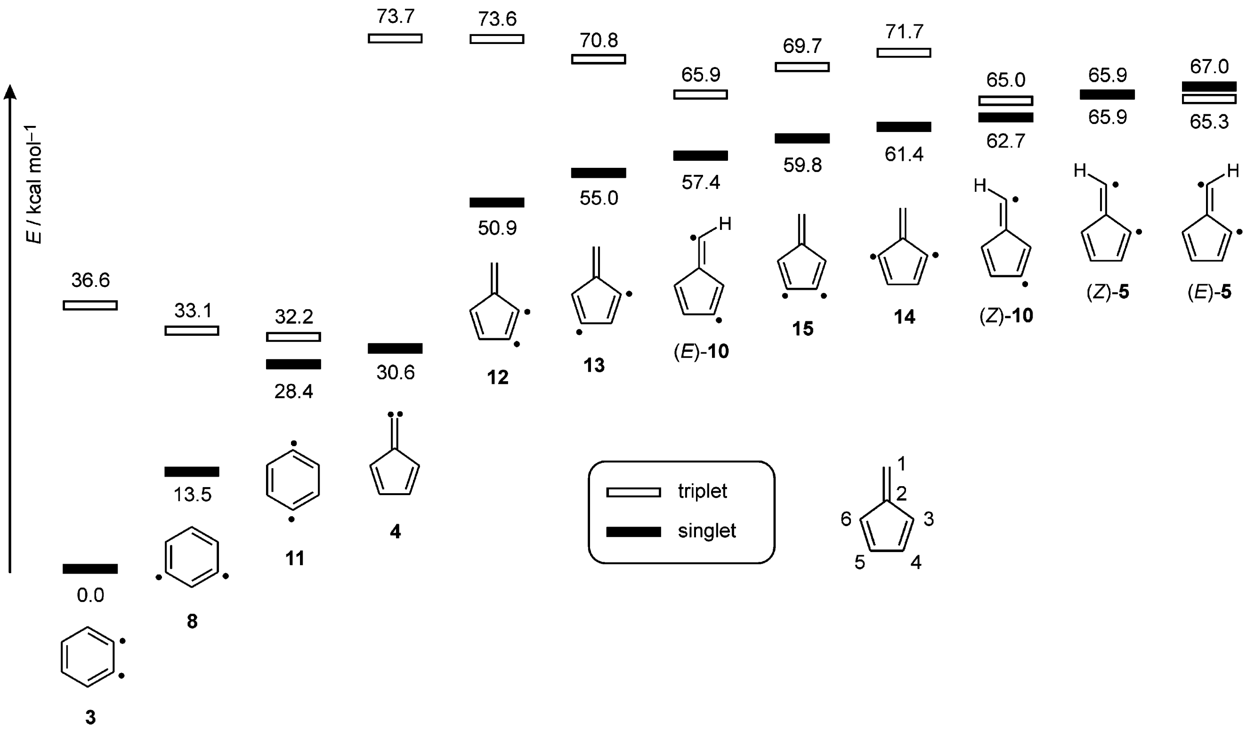


**Figure 1.** Energies of $C_6H_4$ isomers relative to *o*-benzyne (**3**) calculated at the CAS(8,8)-CISD+Q/cc-pVTZ//CASSCF(8,8)/cc-pVTZ+ZPVE(CASSCF) level.

The BSE provides a measure for the stabilization (BSE positive) or destabilization (BSE negative) involved when the two radical centers interact within the same molecule.

$$m,n\text{-}C_6H_4 + C_6H_6 \rightarrow m\text{-}C_6H_5 + n\text{-}C_6H_5 \quad \Delta_R E_0 \equiv \text{BSE} \quad (1)$$

In the following the structures and properties of individual species will be discussed in more detail. According to the number of intervening $\sigma$-bonds, the different $C_6H_4$ structures are designated and grouped as ortho, meta, and para isomers for 1, 2, or 3 bonds between the radical sites, respectively.

**TABLE 2: Biradical Stabilization Energies (BSEs) and Singlet−Triplet Energy Splittings [$\Delta E_{ST} \equiv E_0$(triplet) − $E_0$(singlet)] of $C_6H_4$ Isomers; Experimental Singlet−Triplet Splittings[11e] Are Included for the Benzynes**

| isomer | compd | state | $BSE_{DFT}$ | $BSE_{CASSCF}$ | $BSE_{MRCI/CASSCF}$ | $\Delta E_{ST,DFT}$ | $\Delta E_{ST,CASSCF}$ | $\Delta E_{ST,MRCI/CASSCF}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | benzynes | | | |
| 1,2 | **3** | $^1A_1$ | 28.1 | 30.9 | 31.3 | 35.5 | 35.1 | 36.6 |
| | | $^3B_2$ | −7.3 | −4.2 | −5.3 | | exp: 37.5 ± 0.3 | |
| 1,3 | **8** | $^1A_1$ | 16.7 | 14.4 | 17.9 | 19.9 | 15.9 | 19.7 |
| | | $^3B_2$ | −3.1 | −1.6 | −1.8 | | exp: 21.0 ± 0.3 | |
| 1,4 | **11** | $^1A_g$ | 3.1 | 2.3 | 2.9 | 5.1 | 2.9 | 3.8 |
| | | $^3B_{1u}$ | −1.9 | −0.6 | −0.9 | | exp: 3.8 ± 0.5 | |
| | | | | | fulvenediyls | | | |
| 1,1 | **4** | $^1A_1$ | 27.7 | 28.7 | 30.0 | 47.7 | 37.4 | 43.1 |
| | | $^3B_2$ | −20.1 | −8.8 | −13.1 | | | |
| (*Z*)-1,3 | (*Z*)-**5** | $^1A'$ | −0.1 | −0.4 | −0.1 | 0.8 | −0.3 | 0.1 |
| | | $^3A'$ | −0.8 | −0.1 | −0.2 | | | |
| (*E*)-1,3 | (*E*)-**5** | $^1A'$ | −0.4 | −1.2 | −1.2 | −0.1 | −1.5 | −1.6 |
| | | $^3A'$ | −0.3 | 0.3 | 0.4 | | | |
| (*Z*)-1,4 | (*Z*)-**10** | $^1A'$ | 2.8 | 1.5 | 1.9 | 3.8 | 1.9 | 2.3 |
| | | $^3A'$ | −1.0 | −0.4 | −0.4 | | | |
| (*E*)-1,4 | (*E*)-**10** | $^1A'$ | | 5.0 | 7.1 | | 6.0 | 8.5 |
| | | $^3A'$ | −2.3 | −1.0 | −1.4 | | | |
| 3,4 | **12** | $^1A'$ | 13.9 | 19.9 | 18.8 | 18.7 (19.0)[a] | 23.1 | 22.8 |
| | | $^3A'$ | −4.8 (−5.1)[a] | −3.3 | −4.0 | | | |
| 3,5 | **13** | $^1A'$ | 14.0 | 12.1 | 14.7 | 14.9 (14.8)[a] | 13.1 | 15.8 |
| | | $^3A'$ | −0.9 (−0.8)[a] | −1.0 | −1.1 | | | |
| 3,6 | **14** | $^1A'$ | 6.1 | 9.0 | 9.4 | 6.0 (6.8)[a] | 10.1 | 10.3 |
| | | $^3B_2$ | 0.1 (−0.7)[a] | −1.0 | −0.9 | | | |
| 4,5 | **15** | $^1A_1$ | 7.9 | 6.1 | 8.7 | 10.0 | 6.8 | 10.0 |
| | | $^3B_2$ | −2.2 | −0.6 | −1.2 | | | |

[a] Values in parentheses refer to the planar transition state structures for the triplet states of **12**, **13**, and **14** at the (U)BLYP level. See text for details.

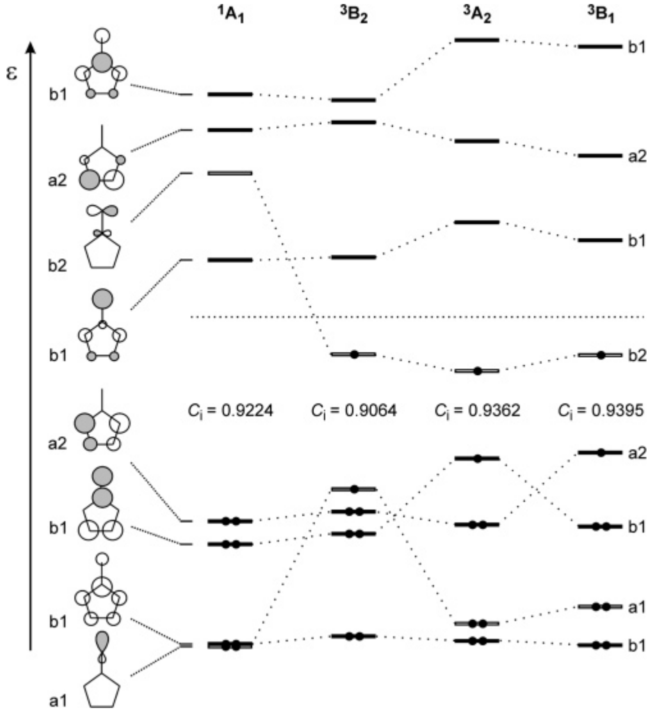


**Figure 2.** Orbital energy diagram for the leading configurations of vinylidene **4** in the ground ($^1A_1$) and low-lying triplet states. The CI coefficient of the respective configuration in the CASSCF wave function ($C_i$) is given for comparison.

**Fulvene-1,1-diyl.** Fulvene-1,1-diyl (**4**) is the most stable didehydrofulvene and only 2.2 kcal mol$^{-1}$ less stable than *p*-benzyne (**11**). Electronically, **4** is a typical vinylidene[29] with a $\tilde{X}\ {}^1A_1$ singlet ground state. The vertical excitation energies to the $\tilde{a}\ {}^3B_2$ and $^3A_2$ triplet states are 43.1 and 58.1 kcal mol$^{-1}$, respectively (MRCI). The active molecular orbitals of **4** in its ground and first excited triplet states are shown schematically in Figure 2.

The $\tilde{a}\ {}^3B_2$ state derives formally from a single excitation from the HOMO−3 ($a_1$) to the LUMO+1 ($b_2$), whereas the $^3A_2$ state wave function is dominated by a HOMO−1 ($b_1$) → b2 excited configuration. The lowest triplet state of $B_1$ symmetry that derives from a HOMO ($a_2$) → LUMO+1 excitation is vertically 61.9 kcal mol$^{-1}$ above the ground state. With regard to the ground and first two triplet states, **4** resembles the parent vinylidene $H_2CC$ (**16**), where $\tilde{a}\ {}^3B_2$ and $\tilde{b}\ {}^3A_2$ are vertically 45.5 and 67.0 kcal mol$^{-1}$ above $\tilde{X}\ {}^1A_1$-**16** at the CAS(10,10)-CISD+Q/cc-pVTZ//CASSCF(10,10)/cc-pVTZ level of theory.[29,30]

**Ortho Isomers.** The structures of **2**, **12**, and **15** are compared to those of **1** and **3** in Figure 3. In contrast to benzene, the double bonds in fulvene are localized to some degree, and the C3−C4/C5−C6 bonds in **2** are approximately 5 pm shorter than the C−C distance in **1**, whereas the C4−C5 bond is ca. 8 pm longer at both levels of theory. The formal C−C triple bonds in **3** and **12** are of almost equal length.[31] This similarity is attributable to a larger $\pi$ bond order (as in the parent hydrocarbon), but a weaker $\sigma$ bond in **12** compared with that in *o*-benzyne. Overlap of the exocyclic in-plane orbitals is maximized by increasing the bond angles α at the radical carbon atoms (and, hence, the p-character of the exocyclic orbitals).[32] In the five-membered-ring systems the bond angles are inherently smaller than in their six-membered counterparts ($\alpha_5 < \alpha_6$), and the former are conformationally more rigid, giving rise to a weaker in-plane interaction. Despite the similar bond length, coupling of the electrons is, thus, less effective in **12** than in **3**, leading to a more pronounced biradical character of the fulvenediyl and a significant reduction of the singlet−triplet splitting by 13.8 kcal mol$^{-1}$. In **15** the weaker $\pi$ component favors a longer C−C bond, and a further decrease of $\Delta E_{ST}$ which is reduced to 10.0 kcal mol$^{-1}$, half the state splitting in *m*-benzyne (**8**).

The same arguments can be applied to rationalize the (more subtle) stability differences of the triplet states. Assuming a

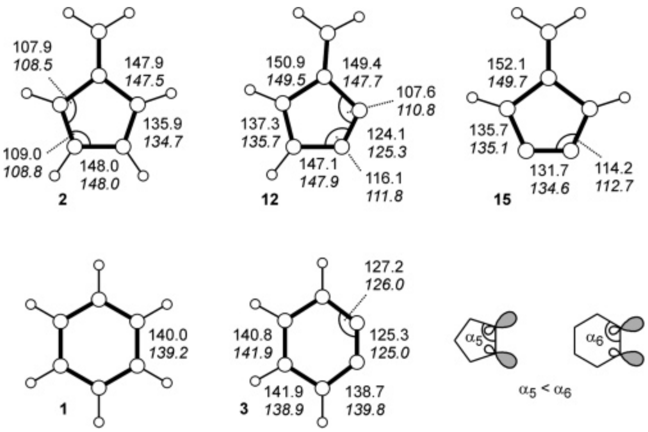


**Figure 3.** Selected structural parameters of **3**, **12**, and **15** (bond lengths in pm, angles in deg) calculated at the BLYP/cc-pVTZ (normal print) and CASSCF(8,8)/cc-pVTZ level of theory (in italics).

destabilization with increasing overlap of the exocyclic orbitals,[33] it is immediately obvious that $^3B_2$-**15** is less destabilized (BSE = −1.2 kcal mol$^{-1}$) than $^3A'$-**12** (BSE = −4.0 kcal mol$^{-1}$), because the distance of the radical centers is larger in the former ($R_{45}$ = 147.7 pm) than in the latter ($R_{34}$ = 135.1 pm at the CASSCF level). In *o*-benzyne ($^3B_2$-**3**) the distance takes an intermediate value (139.6 pm), but the destabilization (BSE = −5.3 kcal mol$^{-1}$) is even more pronounced than in the case of **12** due to the stronger overlap (higher p-character) of the exocyclic orbitals.

**Meta and Para Isomers.** The structure of *m*-benzyne has been investigated in detail previously.[6,7,11,34] The best estimate for the interradical distance in **8** is 205 ± 5 pm, but the energy required to bring the radical centers into closer proximity is very low. With the BLYP functional $R_{13}$ is somewhat smaller (199.7 pm), whereas the separation is overestimated (217.4 pm) at the CASSCF level. We will first discuss the structures of **13** and **14**, where both radical centers are located at ring carbon atoms. These biradicals can be compared with either *m*- or *p*-arynes. The distance of the dehydrocarbons is slightly shorter in **13** than in **8**, whereas it is larger in **14** (Figure 4).

Compared with *m*-benzyne, the singlet−triplet splittings of **13** and **14** are reduced by 3.9 and 9.4 kcal mol$^{-1}$, respectively. In **8** the formally nonbonding orbitals at the radical centers interact primarily *through-space* (with some contributions of a σ-allyl interaction via the intermediate σ*(C2−H) orbital).[14a,34a] These mechanisms stabilize the bonding combination of the radical lobes (denoted *S*) below the out-of-phase combination (denoted *A*). The same mode of interaction is operative in **13** and **14** as shown schematically on the right-hand side of Figure 5.

At the same time, the radical centers in **13** and **14** are connected by three intervening σ-bonds, analogous to *p*-benzyne. In **11** the well-known *through-bond* coupling drops the *A* orbital below the *S* combination as shown on the left-hand side of Figure 5.[11−13,35] The orbital energy splittings of **13** and **14** at the CASSCF level (Table 3) take an intermediate value between **8** and **11** (just as $\Delta E_{ST}$) and indicate the presence of both interactions. Whereas direct overlap of the radical lobes is very weak in *p*-benzyne, *through-space* coupling outweights the *through-bond* interaction in the five-membered-ring systems and leads to an overall *S* below *A* situation, but a reduction of $\Delta\epsilon_{SA}$ and $\Delta E_{ST}$ compared with *m*-benzyne.

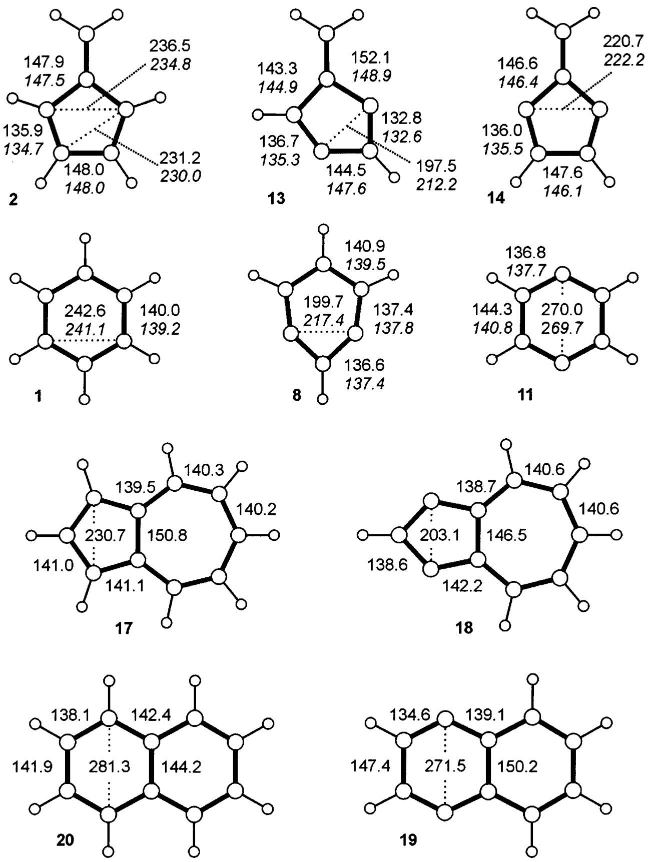


**Figure 4.** Selected structural parameters of *m*- and/or *p*-arynes (bond lengths in pm, angles in deg) calculated at the (U)BLYP/cc-pVTZ (normal print) and CASSCF(8,8)/cc-pVTZ level of theory (in italics).

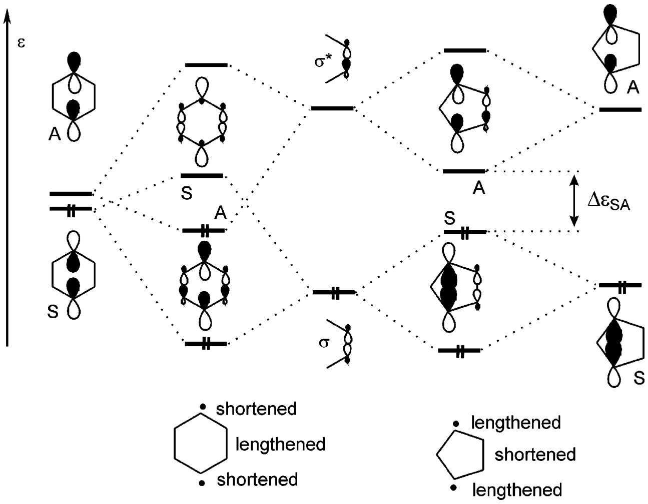


**Figure 5.** *Through-bond* interaction in five- and six-membered-ring arynes leads to characteristic and opposite changes of bond lengths within the 1,4-diyl moiety.

With regard to geometries, the larger occupation of *A* in *p*-benzyne and related 1,4-biradicals has characteristic consequences for the structures of the six-membered-ring arynes that have been discussed in detail previously.[11−13,35] Because *A* is antibonding between C$_{ortho}$ and C$_{meta}$, but bonding between C$_{ipso}$ and C$_{ortho}$, the vicinal C2−C3/C5−C6 bonds in **11** are lengthened, whereas the other bonds are shortened compared with those in the parent benzene (Figures 4 and 5). The stronger overlap of the exocyclic orbitals in **13** and **14**, on the other hand, leads to higher occupation of the in-phase combination, so that the vicinal bonds (C2−C6 in **13**, C4−C5 in **14**) are shortened, whereas the geminal bonds (C2−C3 and C5−C6 in **13**, C3−C4 and C5−C6 in **14**) are lengthened in comparison with fulvene. The same pattern is observed for other five-membered-ring arynes: Removing two hydrogens from azulene (**17**) results in

**TABLE 3: Orbital Energies ($\epsilon$) of the Bonding and Antibonding Molecular Orbitals Corresponding to the In-Phase ($S$) and Out-of-Phase Combinations ($A$) of the Radical Lobes (in atomic units), and Natural Orbital Occupation Numbers (NOON) for 8, 11, 13, and 14 at the CASSCF(8,8)/cc-pVTZ Level[a]**

| | 8 | 11 | 13 | 14 |
|---|---|---|---|---|
| $\epsilon(S)$ | −0.264 | −0.105 | −0.274 | −0.254 |
| $\epsilon(A)$ | 0.023 | −0.185 | −0.008 | −0.045 |
| $\Delta\epsilon_{SA}$[a] | 0.287 | −0.080 | 0.266 | 0.209 |
| NOON($S$) | 1.669 | 0.772 | 1.615 | 1.504 |
| NOON($A$) | 0.331 | 1.228 | 0.385 | 0.496 |

[a] A negative value indicates $A$ below $S$.

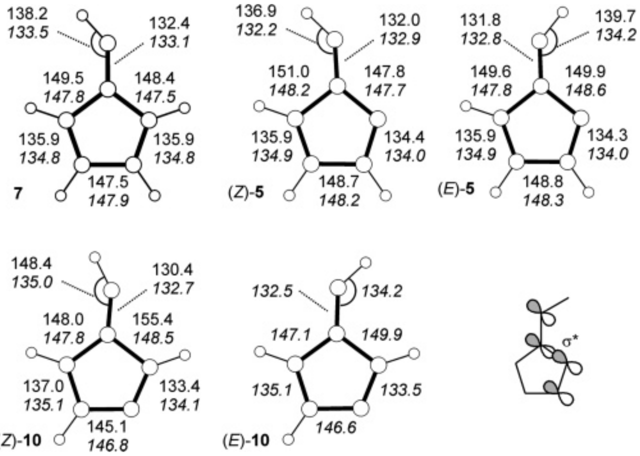
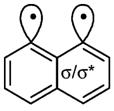


**Figure 6.** Selected structural parameters of 1,3- and 1,4-didehydrofulvenes (bond lengths in pm, angles in deg) calculated at the UBLYP/cc-pVTZ (normal print) and CASSCF(8,8)/cc-pVTZ level of theory (in italics).

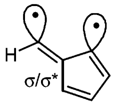
a shortening of the central C−C bond in 1,3-azulyne (**18**), whereas the central bond in 1,4-naphthalyne (**19**) is longer than that in naphthalene (**20**).

In the remaining fulvenediyls (**5** and **10**) one radical center is located at the exocyclic carbon atom (C1) of fulvene, and two different isomers ($E$ and $Z$) have to be considered in both instances. The structures of these molecules are given in Figure 6. Among the four species, ($E$)-**10** is thermodynamically the most stable (BSE = 7.1 kcal mol$^{-1}$). However, no stationary point associated with this isomer can be located on the PES at the UBLYP/cc-pVTZ level, and only with the less flexible cc-pVDZ basis set could a minimum energy structure with a very long C2−C3 bond ($R_{23}$ = 159.1 pm) be found. At the CASSCF level this bond is still longer ($R_{23}$ = 149.9 pm) than that in **2**, but the deviation between the two levels of theory is rather large in this case. At the MRCI level, the CASSCF structure is only 1.0 kcal mol$^{-1}$ lower in energy than the UBLYP/cc-pVDZ geometry, indicative of a very flat potential along the ring opening reaction coordinate of ($E$)-**10** to ($Z$)-**9**, as discussed previously by Schreiner and co-workers.[8] The stabilizing interaction between the formally unpaired electrons as well as the long C2−C3 bond in ($E$)-**10** (and hence the low kinetic stability toward ring opening) reflect strong *through-bond* coupling as shown schematically in Figure 6. For the ($Z$)-**10** isomer, the orientation of the radical lobe at C1 is less favorable for efficient overlap with the $\sigma$*(C2−C3) orbital, so that the coupling of the electron spins is somewhat weaker (the C2−C3 bond is still rather long, particularly at the DFT level), and $\Delta E_{ST}$ is 6.2 kcal mol$^{-1}$ smaller for ($Z$)-**10** than for ($E$)-**10**.

The fulvene-1,3-diyls (**5**) are the least stable $C_6H_4$ isomers considered in this study, and the only didehydrofulvenes with slightly negative BSEs for the singlet states. In ($Z$)-**5** the lowest singlet and triplet states are degenerate, whereas ($E$)-**5** even has a triplet ground state ($\Delta E_{ST}$ = −1.6 kcal mol$^{-1}$). An almost vanishing $\Delta E_{ST}$ has been found by Cramer et al. for 1,8-naphthalyne (**21**), where the arrangement of the radical lobes closely resembles the orientation in ($Z$)-**5**.[14a]



**21**



($Z$)-**5**

In their seminal contribution, Hoffmann, Imamura, and Hehre already noted that stabilizing two-electron interactions with intervening $\sigma$*(C−C) orbitals in **21** might be compensated by destabilizing four-electron interactions with intervening filled $\sigma$ orbitals.[12,14a] In **5** the situation is even more complex than in **21**, because interaction of the out-of-phase combination with $\sigma/\sigma$* is no longer prohibited strictly by symmetry. Anyway, the preference for a triplet ground state (which should at least be thermally populated in ($Z$)-**5**) might facilitate experimental detection of fulvene-1,3-diyls by EPR spectroscopy (e.g., in cryogenic matrices). Despite their low stability, these biradicals could be accessible from $m$-benzyne derivatives, when vinylidene formation is blocked by appropriate substitution or annellation (cf., Scheme 3 and ref 6).

## 4. Conclusions

The nine didehydrofulvenes have been investigated at the MRCI//DFT and MRCI//CASSCF level of theory, and compared to the isomeric benzynes. Apart from vinylidene **4** all fulvenediyls are considerably less stable than the six-membered-ring arynes. The ortho isomers **12** and **15** have smaller singlet−triplet gaps than $o$-benzyne (**3**), because overlap of the exocyclic orbitals is reduced with increasing twist of the formal C−C triple bond. The $\pi$ bond order is larger in **12** than in **3**, whereas it is smaller in **15**, so that the overall bond lengths are comparable in **12** and **3** (124−125 pm), whereas the distance of the dehydrocarbons is larger in **15**, and the latter is 9 kcal mol$^{-1}$ less stable than **12**. In the meta/para isomers **13** and **14** the radical sites are simultaneously connected by two and three intervening $\sigma$-bonds. With regard to the singlet−triplet energy splitting and biradical character they take an intermediate position between $m$- and $p$-benzyne. Although direct interaction outweigths *through-bond* coupling in **13** and **14**, the latter reduces $\Delta\epsilon_{SA}$ and $\Delta E_{ST}$ compared with the values for $m$-benzyne. The geometries of **13** and **14** differ from their six-membered 1,4-aryne counterparts in a well-defined manner. Abstraction of the para hydrogens in benzene results in a shortening of the geminal C−C bonds, whereas the vicinal bonds are lengthened, which reflects stronger occupation of $A$ than of $S$. In **13** and **14** the higher occupation of $S$ with its inverse nodal characteristics leads to the opposite pattern, lengthening of the geminal but shortening of the vicinal C−C bonds of the 1,4-diyl moiety. Opposing structural consequences of *through-bond* interaction are also found for other five- and six-membered-ring aryne pairs (e.g., 1,4-naphthalyne/naphthalene vs 1,3-azulyne/azulene). Among the fulvene-1,3- and 1,4-diyls, ($E$)-**10** is thermodynamically the most stable isomer. The efficient *through-bond* coupling, however, weakens the C2−C3 bond, and this biradical is highly labile towards ring opening to enediyne **9**. The singlet−triplet splitting of ($Z$)-**10** is 6.2 kcal mol$^{-1}$ lower than that of ($E$)-**10**, because the orientation of the radical lobe at C1 is less advantageous for overlap with the $\sigma$*(C2−C3) orbital. The 1,3-

didehydrofulvenes (*Z*)-**5** and (*E*)-**5** are the least stable isomers. The lowest singlet and triplet states of the former are essentially degenerate, whereas a triplet ground state is found for the latter. Despite their low stability, derivatives of **5** might be accessible from *m*-benzynes, when concurrent vinylidene formation is prevented by appropriate substitution and/or annellation. The preference for a triplet ground state should facilitate detection of these species by EPR spectroscopy.

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

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