FULL PAPER

Magnetic Properties and Aromaticity of *o*-, *m*-, and *p*-Benzyne

Frank De Proft,[a] Paul von Ragué Schleyer,[b, c] Joop H. van Lenthe,[d] Frank Stahl,[b, c] and Paul Geerlings*[a]

Abstract: The relative aromaticities of the three singlet benzyne isomers, 1,2-, 1,3-, and 1,4-didehydrobenzenes have been evaluated with a series of aromaticity indicators, including magnetic susceptibility anisotropies and exaltations, nucleus-independent chemical shifts (NICS), and aromatic stabilization energies (all evaluated at the DFT level), as well as valence-bond Pauling reso-
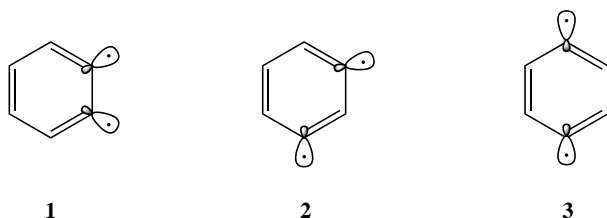
nance energies. Most of the criteria point to the *o*-benzyne < *m*-benzyne < *p*-benzyne aromaticity order, whereas the relative aromaticity of each isomer

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with respect to benzene depends on the aromaticity criterion. An additional aromaticity evaluation involved the transition state of the Bergman cyclization of (*Z*)-hexa-1,5-diyn-3-ene which yields *p*-benzyne. Dissected NICS calculations reveal an aromatic transition state with a larger total NICS but a smaller NICS(π) component and thus lower aromaticity than benzene.

Introduction

Aromatic biradicals have been the subject of many theoretical and experimental studies. The three benzyne isomers (Scheme 1), 1,2-didehydrobenzyne (*o*-benzyne; **1**), 1,3-dide

1   **2**   **3**

Scheme 1. The three benzyne isomers, 1,2-didehydrobenzyne (*o*-benzyne, **1**), 1,3-didehydrobenzyne (*m*-benzyne, **2**), and 1,4-didehydrobenzyne (*p*-benzyne, **3**).

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hydrobenzene(*m*-benzyne; **2**) and 1,4-didehydrobenzyne (*p*-benzyne; **3**) all have singlet ground states; however, the multireference and biradical character increases from *o*- to *p*-benzyne. The benzyne isomers have already been studied quite exhaustively by means of traditional ab initio techniques, both at single-reference and multireference levels, and by density functional methods.[1–38] Many other didehydro aromatic compounds, such as 1,5-didehydronaphthalene, 2,5-didehydropyridine, or 4,5-didehydropyrimidine, have also been analyzed theoretically.[1, 26, 39–43] However, the majority of these studies have focused on the thermochemistry of these compounds and less attention has been devoted to other chemical and physical properties. The increased interest in these molecules is a consequence of the involvement of *p*-benzyne-type biradical species in the Bergman cyclization reaction[44] and the highly selective antitumor activity of the reaction intermediate of this cyclization.[45] As a result, the Bergman reaction of simple and functionalized enediynes has received much attention.[3, 8–12, 14, 20–22, 28, 30, 31, 33, 46–56] In addition, other types of cyclization reactions, such as the Myers – Saito and Schmittel reactions, have been the subject of recent theoretical studies.[57–62]

Although many theoretical studies on the three didehydrobenzyne isomers have been reported, their relative aromatic character has not yet been studied in detail. The aromaticity of *o*-benzyne was assessed by Jiao et al. who employed geometric, energetic, and magnetic criteria.[18] It was concluded that this molecule is indeed aromatic, and that the in-plane π bond induces a small amount of bond localization resulting in an acetylenic-type structure. The aromaticity of the transition structure of the Bergman cyclization (**5**) of the (*Z*)-hexa-1,5-diyn-3-ene (**4**) has been studied previously

by Cossio et al.,[48] Galbraith et al.,[31] and very recently by Stahl et al.[62] Magnetic property calculations of aromatic transition states were introduced by Schleyer et al.[63, 64] The investigation by Cossio et al., conducted at the UB3LYP/6–31 + G* level, found that the transition state (TS) exhibited in-plane, that is σ-aromatic, character. The largest diamagnetic shielding was found in the center of the ring. Some π-aromaticity contribution, as a result of the evolving *p*-benzyne ring, could not be ruled out. Also Galbraith et al. concluded that the TS exhibited little delocalization of the π electrons. However, Stahl et al.[62] corrected this and suggested that the TS is dominated by cyclic electron delocalization of the perpendicular π system.

A recent analysis of basic π-aromatic (benzene) and antiaromatic (cyclobutadiene) systems conducted by Schleyer et al., which used dissected nucleus-independent chemical shifts (NICS), showed the contrasting diatropic and paratropic effects; however, it also revealed subtleties and some unexpected details.[65] The detailed analysis of different factors influencing the aromaticity of 6π-electron systems thus remains a highly important topic. The aromaticity of the *o*-, *m*-, and *p*-benzyne isomers is studied in the present work by means of both magnetic and energetic criteria. A recent review of the different aromaticity indicators and their application can be found in reference [66] and includes indicators originating from conceptual density functional theory.[67] One goal is to establish the relative aromaticity ordering of the three benzynes and to study the influence of the presence of the biradical electron pair present in these species on this property. The assignment of an extra ring bond for these species remains highly controversial. In a recent study conducted by Kraka et al., it was concluded that the corresponding bicyclic structure of the *m*-benzyne, the bicyclo-[3.1.0]hexa-1,3,5-triene does not exist.[38] Moreover, the aromaticity of the transition state of the Bergman cyclization of (*Z*)-hexa-1,5-diyne-3-ene was probed in order to yield more insight into the nature of this cyclization.

Computational Details

All geometries (Figure 1) were optimized at the UBLYP[68, 69]/6–311 + G** and UB3LYP[69, 70]/6–311 + G** levels of theory with the Gaussian 98 program.[71] For *o*- and *m*-benzene and the transition state of the Bergman cyclization, the restricted solutions were found to be externally stable, in agreement with previously published work. This obviously is also the case for the (*Z*)-hexa-1,5-diyn-3-ene (**4**). However, the restricted solution for *p*-benzyne is not externally stable and an unrestricted solution of lower energy exists (S^2 values 0.7596 and 0.9388 at the BLYP/6–311 + G** and B3LYP/6–311 + G** levels, respectively).

The resulting equilibrium structures were used to obtain nucleus-independent chemical shifts (NICS)[72] with the GIAO method[73] at the BLYP/6–311 + G** level. In addition, dissected NICS calculations,[74] including the separation of the double bonds based on σ and π components by the Pipek – Mezey orbital localization procedure,[75] were performed at the IGLO-SOS-DFPT-PW91/IGLO-III(TZ2P)[76, 77] level (Perdew – Wang 1991 exchange-correlation functional[78] in combination with the IGLO-III TZ2P basis set[79]) that used the deMon-Master module.[76, 77] Magnetic susceptibilities and susceptibility exaltations and anisotropies were obtained at the BLYP and B3LYP levels of theory with the CSGT (continuous set of gauge transformations) method.[80] The interaction of the unpaired electron in open-shell species with the applied magnetic field in NMR experiments results in an alternation of the electronic structure of the
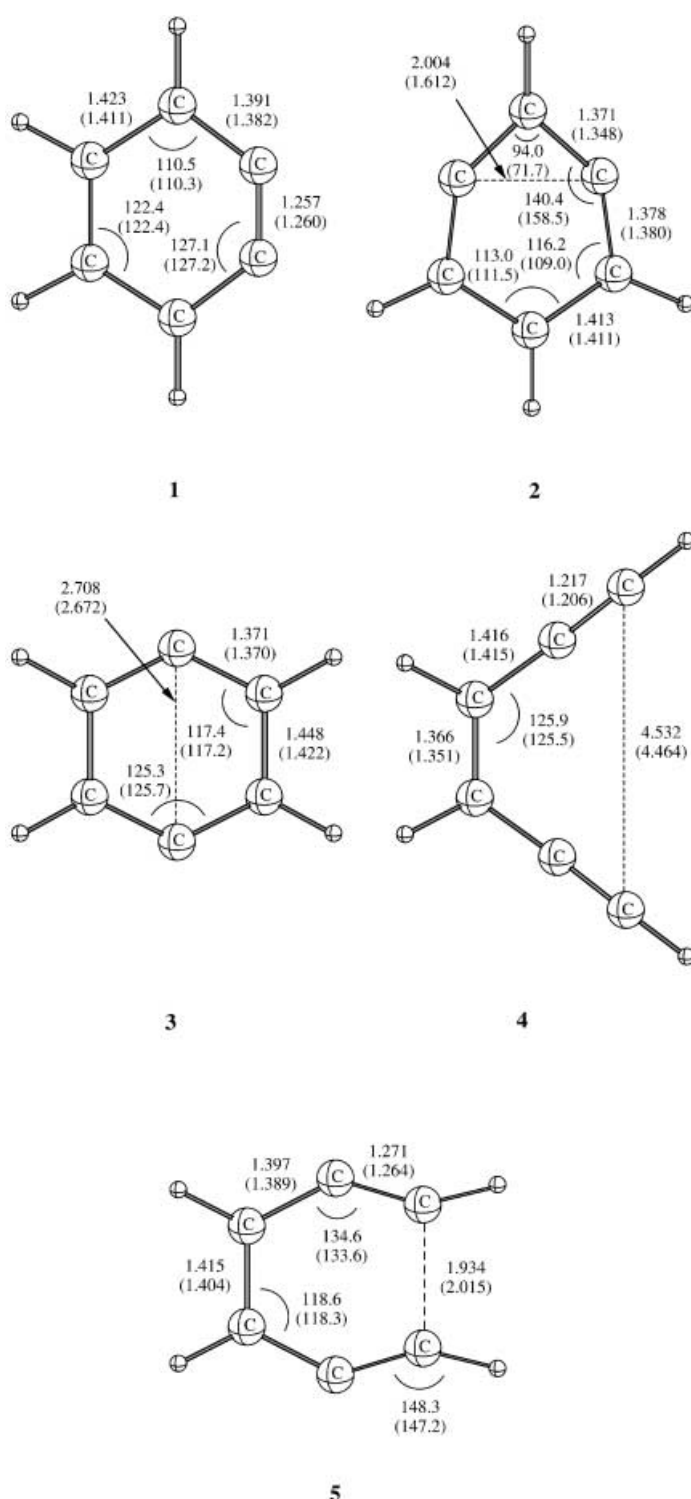

Figure 1. Geometries of the *o*- (**1**), *m*- (**2**), and *p*-benzyne (**3**) isomers, the (*Z*)-hexa-1,5-diyn-3-ene (**4**), and the transition state of the Bergman cyclization of this compound (**5**), together with some relevant geometrical parameters determined at the BLYP/6–311 + G** level (values in brackets are obtained at the B3LYP/6–311 + G** level; see also Supporting Information).

species and leads to line broadening. This makes NMR experiments meaningless for most of these species.[81] In computations, however, the magnetic field is applied as a perturbation after the determination of the electronic structure; moreover, the open-shell NMR calculations in Gaussian[71] consider only terms which do not include the effects caused by the unpaired electron. In addition, CASSCF(8,8)/cc-pVDZ magnetic

susceptibilities and susceptibility anisotropies were obtained with the Dalton program.[82] In these calculations, eight valence electrons were distributed among all symmetry-allowed configurations that involve the six π and π* and the two nonbonding σ orbitals.

Finally, valence-bond (VB) calculations of the Pauling resonance energies were performed with the TURTLE program,[83] as implemented in the GAMESS-UK[84] program system, with the 6–31G basis set.

Results and Discussion

Relative aromaticities of *o*-, *m*- and *p*-benzyne from NICS and dissected NICS: The relative aromaticity of the three benzyne isomers was derived from the total nucleus-independent chemical shifts. The total GIAO NICS values for the three isomers (BLYP/6–311 + G** level) are given in Table 1, for a series of points located at the geometrical ring centers and at

Table 1. BLYP/6–311 + G** nucleus-independent chemical shifts [ppm] at different positions z above the geometrical center of the *o*-, *m*-, and *p*-benzyne ring.

z [Å]	*o*-benzyne	*m*-benzyne	*p*-benzyne		benzene
			RBLYP	UBLYP	
0.0	− 17.8	− 15.4	− 26.4	− 19.3	− 7.6
0.5	− 16.4	− 14.6	− 24.0	− 18.1	− 9.4
1.0	− 12.5	− 11.7	− 17.5	− 14.0	− 9.8
1.5	− 8.1	− 7.8	− 10.8	− 9.0	− 7.3
2.0	− 4.9	− 4.8	− 6.4	− 5.4	− 4.7
2.5	− 2.9	− 2.9	− 3.8	− 3.3	− 3.0
3.0	− 1.8	− 1.8	− 2.4	− 2.1	− 1.9

points located above these ring centers, equally spaced by 0.5 Å. For the *para* isomer, both the RBLYP and UBLYP values are listed. The data in Table 1 confirm that all three of the isomers are aromatic, as they possess large negative NICS values at the ring center. Unlike benzene, the most negative NICS value is in the ring planes of the benzynes, which might indicate that the largest diamagnetic ring current is in the molecular plane.[48] However, the NICS values away from the center decrease much less rapidly than in the case of, for example, the transition state of the acetylene trimerization. While Cossio et al. claimed this transition state lacked π aromaticity, Jiao and Schleyer found that the σ contributions of this transition state only constituted approximately half of

the total NICS values.[64] While the in-plane contribution is larger, the out-of-plane π contribution is significant as well. From Table 1, the aromaticity order of the benzyne isomers is proposed to be *m*-benzyne < *o*-benzyne < *p*-benzyne. It should, however, be noted that the RBLYP NICS values for the *p*-benzyne isomer are even larger than the UBLYP values.

The magnetic properties of *o*-benzyne and its aromaticity have already been studied separately and in more detail in a previous study.[18] However, the nucleus-independent chemical shifts were not separated into σ and π contributions.

The results of dissected NICS calculations, employing the Pipek–Mezey orbital localization procedure, on the three isomers in Table 2 list data in the ring center and 1 Å above the ring. The results for benzene[65] have been included for comparison. Also listed in Table 2 are the values for the (*Z*)-hexa-1,5-diyn-3-ene and the TS of the Bergman cyclization, depicted in Scheme 2. Note that these dissected NICS calculations are based on a restricted solution of the Kohn–Sham equations and that an unrestricted solution of *p*-benzyne exists at a lower energy.
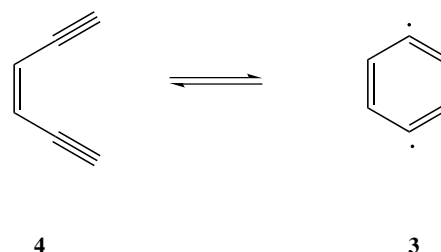
Scheme 2. Bergman cyclization of the (*Z*)-hexa-1,5-diyn-3-ene, yielding *p*-benzyne.

At the PW91/IGLO III level, the total NICS(0) values in the geometrical center of the *o*-benzyne ring (− 18.4 ppm) and NICS(1), 1 Å above the ring plane (− 13.3 ppm; Table 2), are in very good agreement with the BLYP/6–311 + G** values of − 17.8 and − 12.5 ppm, respectively. The π contributions to these values are − 22.2 and − 9.7 ppm, respectively, whereas the in-plane component of the triple bond contributes − 2.7 and − 2.1 ppm. For *m*-benzyne, the agreement is less satisfactory for the NICS in the center of the ring plane. The π contributions are − 23.0 ppm in the ring plane and − 9.3 ppm 1 Å above the ring plane. The through-space "bond" between

Table 2. Dissected NICS [ppm] at the ring centers and 1 Å above at the PW91/IGLO III level on BLYP/6–311 + G** geometries for the benzynes and the B3LYP/6–311 + G** geometry of benzene.

Molecule	z [Å]	NICS (Total)	CC (π)	CC (p, in plane)	CC(σ)	CH	Core
o-benzyne	0.0	− 18.4	− 22.2	− 2.7	+ 8.5	− 2.0	− 0.8
	1.0	− 13.3	− 9.7	− 2.1	+ 0.9	− 1.1	− 0.6
m-benzyne	0.0	− 17.9	− 23.0	− 3.1	+ 8.5	+ 0.4	− 0.8
	1.0	− 12.9	− 9.3	− 1.6	0.0	− 1.4	− 0.3
p-benzyne	0.0	− 28.1	− 23.1	− 3.0	+ 1.3	− 2.6	− 0.6
	1.0	− 18.6	− 11.2	− 3.8	− 1.2	− 2.3	− 0.6
benzene[a]	0.0	− 8.8	− 20.7	–	+ 13.8	− 1.3	− 0.6
	1.0	− 10.6	− 9.6	–	+ 2.3	− 3.0	− 0.3
(*Z*)-hexa-1,5-diyn-3-ene	0.0	− 2.6	− 6.9		6.1[b]	− 1.4	− 0.4
	1.0	− 1.6	− 0.7		1.1[b]	− 1.8	0.0
TS Bergman cyclization	0.0	− 20.7	− 15.8		− 1.6[b]	− 2.8	− 0.6
	1.0	− 13.2	− 6.4		− 4.3[b]	− 2.4	− 0.4

[a] The values for benzene were taken from Ref. [65]. [b] Sum of the contributions of CC(p, in plane) and CC(σ).

C1 and C3 is slightly diamagnetic and contributes −3.1 and −1.6 ppm, respectively.

Finally, for *p*-benzyne, the localization scheme assigns three Kekulé-like double bonds and a C1−C4 through-space bond. While the contributions from the C−H bonds and the core electrons appear to be quite normal, the paratropic C−C σ-bond contributions are much smaller than for the other benzyne isomers and for benzene in the center. This ultimately results in a very large NICS(0) value for *p*-benzyne. This, as we already pointed out above, has to be considered with extreme caution because of the restricted nature of the wave function. Judging from these NICS(π) values in the ring plane, the aromaticity ordering of the three benzyne isomers becomes *o*-benzyne < *m*-benzyne < *p*-benzyne, which does not entirely agree with the ordering according to BLYP/6−311 + G** NICS values 1 Å above the ring. Note that only the ordering of the *o*- and *m*-isomers changes for which dissected NICS is applicable. *p*-Benzyne, however, for which dissected NICS is questionable, displays the largest NICS values independent of the applied method. Moreover, all three benzyne isomers are more aromatic than benzene, when the NICS(π) in the ring plane is considered. Again, it must be noted that the dissected NICS values for *p*-benzyne are based on a restricted DFT calculation, which is not the lowest-energy solution.

Table 2 also contains the dissected NICS results of the (*Z*)-hexa-1,5-diyn-3-ene (**4**) and the transition state of its Bergman cyclization (**5**). In a previous study, Galbraith et al. concluded that the π-electron system of this TS is essentially reactant-like and that the large NICS value is the result of σ aromaticity.[31] In agreement with previous studies conducted on BLYP/6−31G* geometries,[62] the IGLO-NICS total value at the center of the ring is −20.7 ppm and −13.2 1 Å above the ring, and thus corroborate the transition state of the parent Bergman cyclization as aromatic. The 6π electrons contribute −15.8 ppm to the NICS(0) value; NICS(π) 1 Å above the ring is −6.4 ppm (Table 2). Thus the largest contributions to these total NICS values are attributed to the π orbitals perpendicular to the molecular plane and therefore π-delocalization is dominant. We find no evidence for cyclic electron delocalization in the σ plane.[62] The aromaticity profile of the Bergman cyclization of (*Z*)-hexa-1,5-diyn-3-ene yielding *p*-benzyne provides more insight. The reaction profile given in Figure 2 was obtained by a relaxed potential-energy surface scan as a function of the distance of the terminal acetylenic carbon atoms, while the rest of the molecule was fully optimized. It has been shown that the reaction coordinate can be approximated satisfactorily by variation of the C1−C6 carbon distance.[47] Also plotted is the evolution of the BLYP/6−311 + G** magnetic susceptibility anisotropies. The aromaticity along the reaction path of the Bergman cyclization approaches a minimum in the vicinity of the transition state, but not exactly at this structure. This is supported by the notion that the perfectly resonating state and the transition state do not precisely coincide.[31, 64, 65] The evolution of the total NICS(1, U) (obtained at the UBLYP/6−311 + G** level) along the reaction path (Figure 3) is similar to the progression of the magnetic susceptibility and susceptibility anisotropy. Plotted on the same graph is the total NICS(1,R) obtained at a spin-restricted level
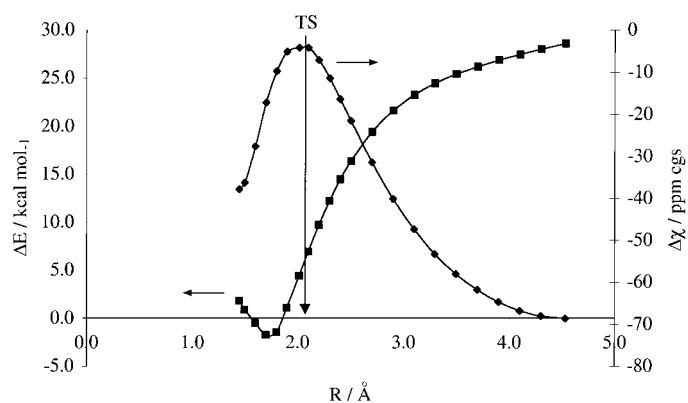

Figure 2. Evolution of the BLYP/6−311 + G** magnetic susceptibility anisotropy along the reaction path of the Bergman cyclization of (*Z*)-hexa-1,5-diyn-3-ene (see text).
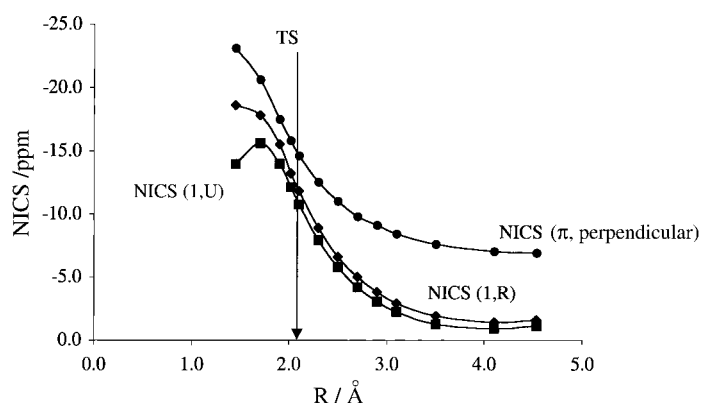

Figure 3. Evolution of the UBLYP/6−311 + G** NICS(1,U), RPW91/IGLO III NICS(1,R), and RPW91/IGLO III NICS(π,perpendicular) in the ring plane, along the reaction path of the Bergman cyclization of (*Z*)-hexa-1,5-diyn-3-ene (see text).

(PW91/IGLO III). Although this treatment is not strictly valid for the biradical species along the reaction path, both plots are similar. Also plotted is the perpendicular π component of the PW91/IGLO III NICS(π, perpendicular), which varies significantly past the TS, in accord with its behavior in the trimerization of acetylene.[64]

Relative aromaticities of *o*-, *m*- and *p*-benzyne from global magnetic aromaticity indices: The aromaticity of the benzyne isomers was also assessed with global magnetic aromaticity indicators, such as the magnetic susceptibility exaltation[85] (see below) and anisotropy.[86, 87] The latter is defined [Eq. (1)] as the difference between the out-of-plane and the average in-plane diamagnetic susceptibilities ($\Delta\chi$) for a ring lying in the (*xy*) plane.

$$\Delta\chi = \chi_{zz} - \tfrac{1}{2}[\chi_{xx} + \chi_{yy}] \tag{1}$$

An advantage of this index is the independence from a reference system, in contrast to the magnetic susceptibility exaltation Λ [Eq. (2)], namely, the difference between the magnetic susceptibility of the system χ and that of a reference value derived from atom or bond increments.

$$\Lambda = \chi - \chi' \tag{2}$$

The estimates of the magnetic susceptibility and magnetic susceptibility anisotropies at the different quantum-mechanical levels can be found in Table 3. Also listed in Table 3 are the values for benzene, for the enediyne, and for the transition state of the Bergman cyclization reaction studied in the section on NCIS relative aromaticities, and for the non-aromatic cyclic isomer of benzene, fulvene. At all levels of theory, the aromaticity ordering is *o*-benzyne < *m*-benzyne < *p*-benzyne, that is, the aromaticity increases with increasing separation of the divalent carbon atoms within the aromatic ring. At the B3LYP/6 – 311 + G** level, the difference between *o*-benzyne and *m*-benzyne becomes larger. This is confirmed at the CASSCF(8,8)/cc-pVDZ level. The anisotropies of the benzyne isomers are somewhat less negative compared to benzene, indicating a somewhat lower aromaticity. The anisotropies of the benzyne isomers, however, are definitely larger than those of fulvene, clearly establishing their aromatic character. In addition, the proton chemical shifts for the isomers are all shifted downfield into the aromatic region.

Aromaticity of the benzyne isomers as derived from energetic properties: A major difficulty encountered in the evaluation of the aromatic stabilization energy (ASE) by the use of homodesmotic reactions is the correct incorporation of the biradical coupling in the benzyne isomers. An elegant way to avoid this problem is the evaluation of the ASE by means of an isomerization method[88]: the ASE is approximated by the energy difference of the methyl-substituted compound and the isomeric compound with a exocyclic double bond (Scheme 3 and Figure 4). The ASE for benzene calculated with this method, is approximated by the energy difference
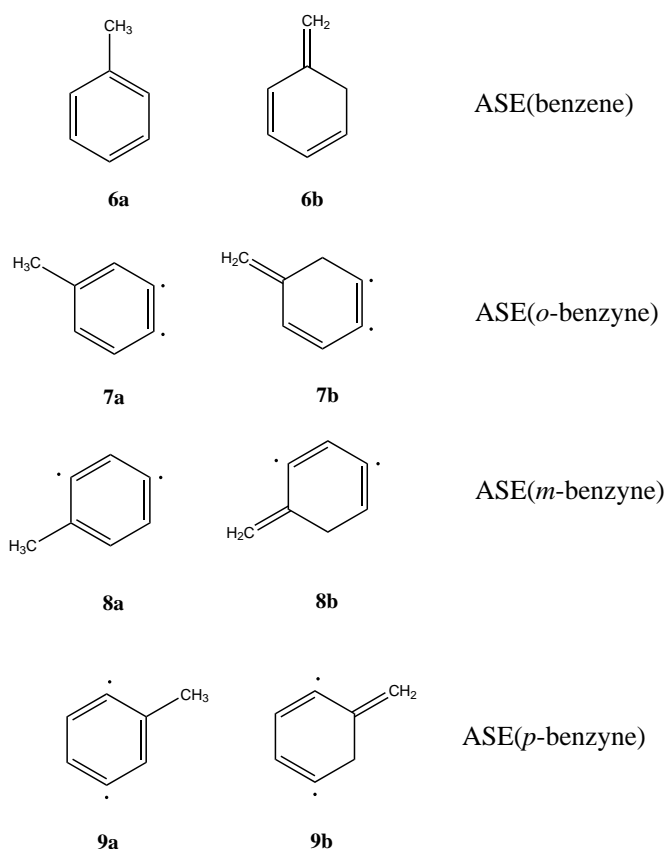
Scheme 3. Structures considered in the computation of the aromatic stabilization with the isomerization methods described in the text.

between toluene (**6a**) and 5-methylene-1,3-cyclohexadiene (**6b**). In addition, the difference between the magnetic

Table 3. Magnetic susceptibilities, susceptibility anisotropies and chemical shifts (δ) of the protons (numbering corresponds to the carbon atom to which they are attached) at two levels of theory for the *o*-, *m*-, and *p*-benzyne isomers. Level (1) corresponds to CSGT/BLYP/6 – 311 + G**//BLYP/6 – 311 + G** whereas level (2) corresponds to CSGT/B3LYP/6 – 311 + G**//B3LYP/6 – 311 + G**. The values in level (3) correspond to the CASSCF(8,8)/cc-pVDZ// BLYP/6 – 311 + G** values for the benzynes. Values for benzene, fulvene, (*Z*)-hexa-1,5-diyn-3-ene, and the TS of its Bergman cyclization are given for comparison.

| | Level (1) | | | Level (2) | | | Level (3) | |
Molecule	$\Delta\chi$ [ppm cgs]	χ [ppm cgs]	δ	$\Delta\chi$ [ppm cgs]	χ [ppm cgs]	δ	$\Delta\chi$ [ppm cgs]	χ [ppm cgs]
o-benzyne	− 56.35	− 50.89	6.67 (H3) 7.53 (H4)	− 56.95	− 51.49	6.83 (H3) 7.59 (H4)	− 52.28	− 56.89
m-benzyne	− 56.55	− 45.71	7.50 (H2) 6.92 (H4) 8.47 (H5)	− 61.23	− 47.97	8.05 (H2) 6.53 (H4) 8.88 (H5)	− 55.29	− 54.30
p-benzyne	− 64.42	− 49.18	7.33	− 65.04	− 50.71	7.43	− 58.81	− 55.68
benzene	− 66.45	− 52.09	7.64	− 67.47	− 52.88	7.61		
fulvene	− 37.34	− 41.55	6.94 (HA) 6.41 (HB) 6.35 (HC)	− 37.90	− 42.26	6.72 (Ha) 6.42 (Hb) 6.03 (Hc)		
(*Z*)-hexa-1,5-diyn-3-ene	− 3.15	− 43.37	5.97 (Hv) 3.47 (Ha)	− 3.11	− 44.08	6.00 (Hv) 3.35 (Ha)		
TS Bergman cyclization	− 58.50	− 56.30	7.15 (Hv) 6.04 (Ha)	− 59.89	− 57.05	7.35 (Hv) 5.78 (Ha)		
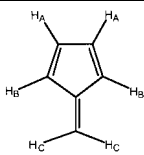
[a] Numbering for the protons in fulvene corresponds to: . [b] For the protons in (*Z*)-hexa-1,5-diyn-3-ene and the TS of its Bergman

cyclization, Hv corresponds to the vinylic protons and Ha to the acetylenic protons.
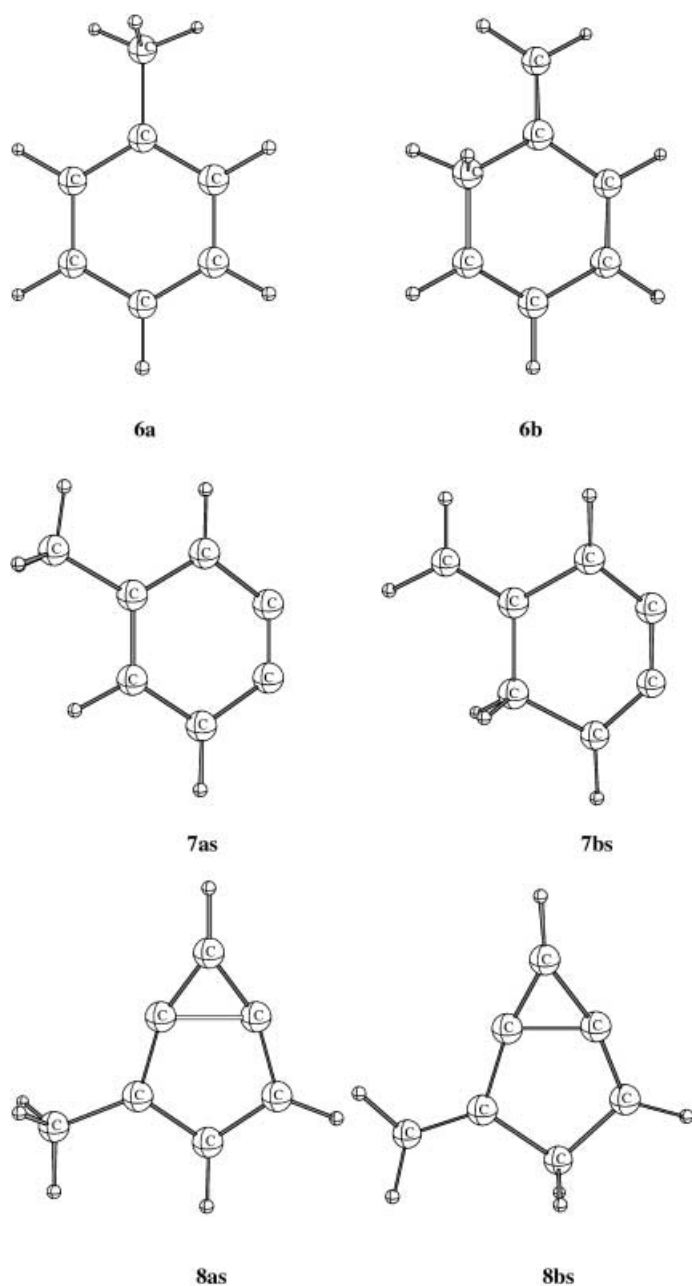
6a

6b

7as

7bs

8as

8bs

Figure 4. B3LYP/6–311+G** equilibrium structures of the compounds (**6a**,**6b**, **7as**,**7bs**, and **8as**,**8bs**) used in the evaluation of the aromatic stabilization energies of benzene and the singlet benzynes (see also Supporting Information).

Table 4. Aromatic stabilization energies (ASE) for benzene, *o*- and *m*-benzyne (without and with zero-point vibrational energies (ZPVE)), as calculated from the isomerization method described in the text. Also given are the magnetic susceptibility exaltations Λ derived with the same method.

Molecule	ASE [kcal mol^{-1}]	ASE (+ ZPVE) [kcal mol^{-1}]	Λ [ppm cgs]
benzene	33.9	33.2	– 16.4
o-benzyne	34.9	34.0	– 16.9
m-benzyne	28.2	27.9	– 13.8

with the aromaticity ordering as given by the NICS(π), measured 1 Å above the ring center.

In addition, the aromatic stabilization energies for the triplets were obtained at the B3LYP/6–311+G**//B3LYP/6–311+G** level. The respective structures (**7at**,**7bt**, **8at**,**8bt**, and **9at**,**9bt**) are shown in Figure 5, energies are listed in Table 5, together with the GIAO/B3LYP/6–311+G**//B3LYP/6–311+G** NICS(1) values. The aromatic stabiliza-

7at

7bt

8at

8bt

9at

9bt
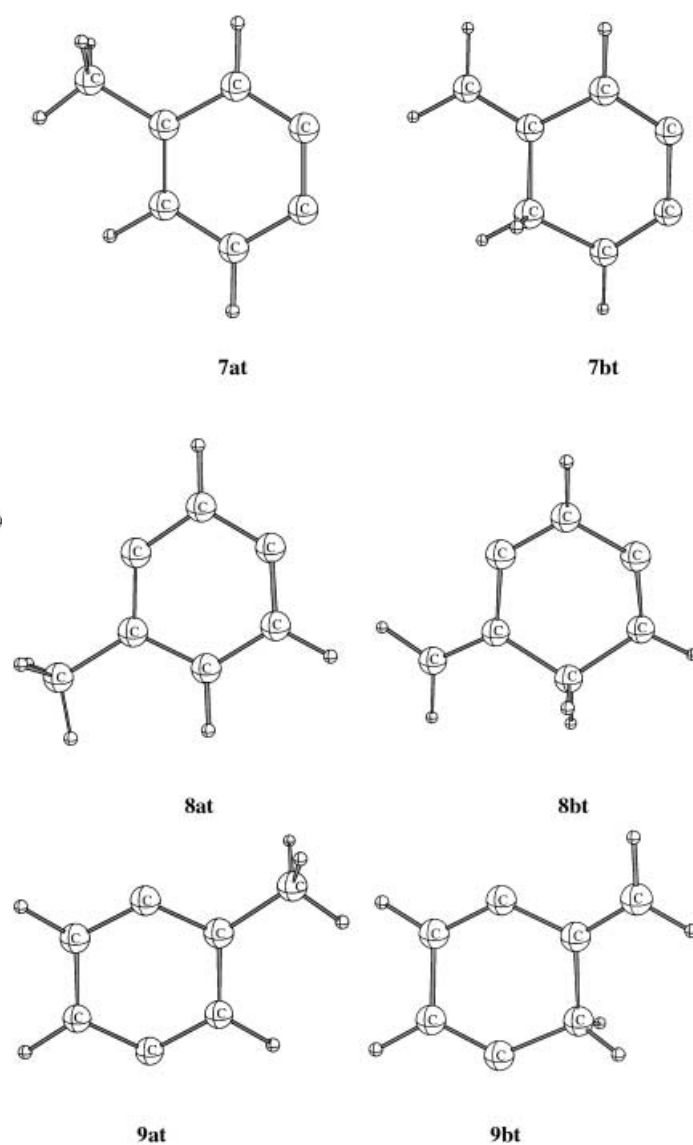
Figure 5. B3LYP/6–311+G** equilibrium structures of the compounds (**7at**,**7bt**, **8at**,**8bt**, and **9at**,**9bt**) used in the evaluation of the aromatic stabilization energies of the triplet benzynes (see also Supporting Information).

susceptiblities of the two isomers provides a good estimate for the magnetic susceptibility exaltation Λ of these compounds. Scheme 3 contains the structures constructed for the evaluation of the ASE of the benzyne isomers; ball-and-stick models are shown in Figure 4. Table 4 lists the ASEs obtained at the B3LYP/6–311+G**//B3LYP/6–311+G** level. No entries are given for *p*-benzyne, since no equilibrium structures for the *p*-benzyne isomers listed in Scheme 3 could be obtained as a result of ring-opening during optimization. *o*-Benzyne is slightly more aromatic than benzene, in agreement with the NICS data, whereas *m*-benzyne is less aromatic than *o*-benzyne; a trend that is confirmed by the magnetic susceptibility exaltations Λ (Table 4). Note that these trends agree

Table 5. Aromatic stabilization energies (ASE) for the triplet *o*-, *m*-, and *p*-benzyne (without and with zero-point vibrational energies (ZPVE)), as calculated from the isomerization method described in the text. Also given are the magnetic susceptibility exaltations Λ derived with the same method and the GIAO/B3LYP/6–311+G** NICS values in the center of the ring NICS(0) and 1 Å above the ring center NICS(1) [ppm].

Molecule	ASE [kcal mol^{-1}]	ASE (+ZPVE) [kcal mol^{-1}]	Λ [ppm cgs]	NICS(0) [ppm]	NICS(1) [ppm]
o-benzyne	30.1	29.1	− 13.4	− 14.7	− 12.4
m-benzyne	31.1	30.2	− 14.8	− 14.7	− 11.4
p-benzyne	32.3	31.6	− 15.9	− 14.0	− 11.4

tion energy increases from *o*- to *p*-benzyne. This does not correlate with the total NICS(1), indicating that dissecting the different NICS contributions is necessary (but is not yet implemented in the GIAO method).

Valence-bond resonance energies of the benzyne isomers: A natural way to study aromaticity would be to use Kekulé's concept of two resonating structures[89] for benzene. This was applied later by Pauling and Wheland,[90] employing an approximate form of the valence bond (VB) method developed by Heitler and London,[91] to describe the aromaticity of benzene. Classical VB calculations that use fixed orbitals and contain all possible covalent and ionic structures for the π-system were reported by Norbeck and Gallup[92] and by Tantardini et al.,[93] both used σ-orbitals from an SCF calculation. They defined the resonance energy as the energy difference between benzene (described with all the structures) and 1,3,5-cyclohexatriene (described with a subset of structures) at a certain geometry. These calculations give large resonance energies of − 61.4 and − 67.4 kcal mol^{-1} for benzene. The first calculations on benzene that used optimized orbitals were performed by Cooper et al.,[94] with his spin-coupled VB method,[95] yielding a resonance energy of 20 kcal mol^{-1}.

The Pauling resonance energies for the three benzyne isomers were obtained with the valence-bond method. In a first step, the wave function used consisted only of the two Kekulé structures. The three Dewar structures were not taken into account, since earlier calculations[95, 96] showed that they only have a weight of about 6–7% each. Because these weights are relatively small and since they obscure the view of the resonance, they were excluded from our computations.

The σ cores consist of completely optimized, doubly occupied, delocalized orbitals. The singly occupied p-π orbitals used in the Kekulé structures are allowed to delocalize over all atoms, but remain essentially localized (cf.[94]).

Strictly adhering to the Pauling definition,[90] the resonance energy (E_{res}) of an aromatic hydrocarbon is calculated from the difference between the total VB energy and the energy of the most stable structure ($E_{res} = E_{tot} - E_{lowest}$). This gives a resonance energy of 19.8 kcal mol^{-1} for benzene,[97] which compares well with the 20 kcal mol^{-1} calculated with five structures by Cooper et al.[95] If the orbitals are strictly confined to their respective atoms, the resonance energy is given as 25.4 kcal mol^{-1}. This result is, however, more basis set-dependent as the origin of an atomic orbital becomes less meaningful as the basis set is increased. At the limit of an

infinite (complete) basis set, the origin of all the orbitals may be chosen on a single center. Then, a restriction to an atom is impossible and meaningless. We thus report the results for delocalized orbitals. Note that some resonance energies reported in the literature are significantly higher.[98–101] Since we only compare the relative resonance energies of different molecules; the absolute value of the resonance energy is less important (cf. ref. [102]). The resonance energies obtained in this way with the 6–31G basis set can be found in Table 6, in

Table 6. Valence-bond Pauling resonance energies, obtained at the 6–31G level, by means of the two models described in the text.

Molecule	RE(1) [kcal mol^{-1}]	RE(2) [kcal mol^{-1}]
o-benzyne	11.87	11.63
m-benzyne	20.44	20.37
p-benzyne	20.12	20.17

the column RE(1). The Pauling resonance energy of *o*-benzyne at the 6–31G* level was 11.4 kcal mol^{-1}, which compares well with the 6–31G value (11.9 kcal mol^{-1}). We used the 6–31G basis set for all VB calculations. In a second step, the two structure VB calculations were repeated with an added GVB pair for the in-plane bond of the benzyne isomers. The resulting Pauling resonance energies RE(2) are also given. The resonance energy decreases slightly when the extra GVB pair is added. From these VB calculations, we concluded that both *m*- and *p*-benzyne are slightly more aromatic than benzene. In these molecules, analogous to benzene, the two Kekulé structures are equivalent. In *o*-benzyne one structure is significantly more favored with respect to the other because of the shorter bond length of the "triple" bond. This energy difference reduces the resonance, consequently *o*-benzyne is considerably less aromatic.

Conclusion

The relative aromaticities of the *o*-, *m*-, and *p*-benzyne isomers have been probed with diverse aromaticity indicators. Most of the results point to the relative ordering *o*-benzyne < *m*-benzyne < *p*-benzyne, that is, the aromaticity increases with increasing distance between the divalent carbon atoms in the molecule. Only the aromatic stabilization energies based on the "isomerization method" predict *m*-benzyne to be less aromatic than *o*-benzyne. The relative aromaticity of the isomers with respect to benzene was found to differ depending on the aromaticity criterion used. The total NICS values for the three isomers are larger than those of benzene. The NICS(π) values based on the dissected π contributions 1 Å above the rings also indicate the three isomers to be more aromatic than benzene. VB calculations, however, indicate that the aromaticity of *o*-benzyne is less than that of benzene. The aromaticity evolution during the Bergman cyclization of (Z)-hexa-1,5-diyn-3-ene was investigated by means of magnetic aromaticity criteria. The aromaticity profile approaches a maximum around the transition state, which, based on dissected NICS calculations, is classified as being π aromatic to a large extent.

Acknowledgement

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