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The reaction of benzene with a ground state carbon atom, C(^3P_j)

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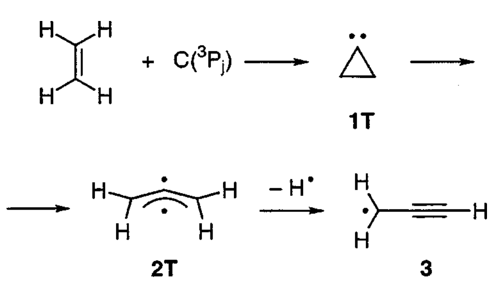
The reaction between benzene and a single ground state carbon atom, C(^3P_j), which yields a C_7H_5 radical without a barrier in the exit channel, has been studied using density functional theory (B3LYP), Møller–Plesset perturbation theory, and the G2(B3LYP/MP2) and complete basis set (CBS) model chemistries. Comparing the computed reaction energies for the formation of various C_7H_5 radicals with experimental data suggests that the 1,2-didehydrocycloheptatrienyl radical (**15**) is observed in crossed-beams experiments at collision energies between 2 and 12 kcal mol^{-1}. The carbon atom attacks the π-electron density of benzene and forms without entrance barrier a C_s symmetric complex (**17T**) in which the carbon atom is bound to the edge of benzene. From **17T**, the insertion of the C atom into a benzene CC bond to yield triplet cycloheptatrienylidene (**9T**) is associated with a much lower barrier than the insertion into a CH bond to give triplet phenylcarbene (**7T**). As both steps are strongly exothermic, high energy vinyl carbene rearrangements on the triplet C_7H_6 potential energy surface provide pathways between **9T** and **7T** below the energy of separated reactants. In addition, intersystem crossing in the vicinity of **17T** and **9T** might give rise to singlet cycloheptatetraene (**12S**). The monocyclic seven-membered ring compounds **9T** or **12S** are precursors of the 1,2-didehydrocycloheptatrienyl radical: the dissociation of a CH bond α to the divalent carbon atom proceeds without an exit barrier, in agreement with experiment. In contrast, a direct carbon–hydrogen exchange reaction pathway analogous to the aromatic electrophilic substitution followed by rearrangement of phenylcarbyne (**13**) to **15** involves high barriers (39 kcal mol^{-1} with respect to separated reactants) and is thus not viable under the experimental conditions. [S0021-9606(00)31028-5]

I. INTRODUCTION

Gas phase reactions of various unsaturated hydrocarbons, like acetylene, methyl acetylene, ethylene, or perdeuterobenzene with ground-state carbon atoms, C(^3P_j), have been studied under the single collision conditions provided by crossed-molecular beam experiments.[1–5] These reactions are dominated by a carbon–hydrogen exchange channel, i.e., a carbon atom is incorporated into the molecule and a hydrogen atom is ejected. With ethylene, the incoming triplet carbon atom is known to attack the π electrons to form triplet cyclopropylidene (**1T**) without an entrance barrier (Scheme 1).[3] Two micro channels, rotation around the *C*- and the *A*-axes (which are orthogonal to the C_2 symmetry axis) of cyclopropylidene, lead to C_{2v} symmetric triplet allene (**2T**).[3] As **2T** cannot dissipate the energy accumulated throughout the reaction under the single collision conditions, a C–H bond rupture and H atom release gives the C_{2v} symmetric propargyl radical (**3**).[3]



Scheme 1. Mechanism for the reaction of ^{3}P$_j$ carbon atom with ethylene, according to crossed beams experiments.

Reactions of carbon atoms with π systems have been investigated systematically since the 1950s. But as all these investigations were performed under bulk conditions, differ-

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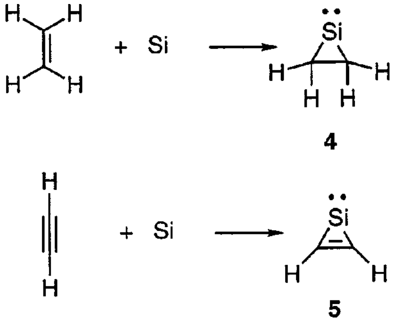
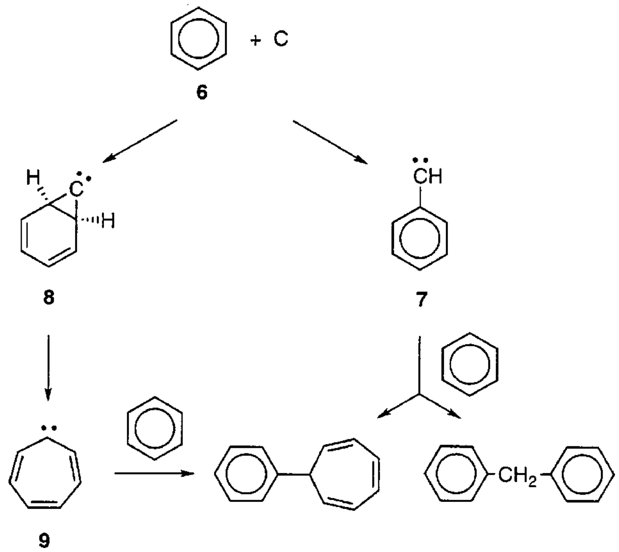
ent products are obtained than under single collision conditions. When thermal ground state carbon atoms are condensed in noble gas–ethylene matrices, various products, like acetylene, allene, methylacetylene, propene, and cyclopropane, arise from secondary bimolecular reactions of C_3H_4 or from matrix stabilization effects.[6] Skell and co-workers found earlier that ^3P carbon atoms add stereospecifically to *cis*- and *trans*-butene in an inert gas matrix at −196 °C.[7–10] Note that silicon atoms also add to the π system of ethylene or acetylene under matrix conditions as silacyclopropylidene (**4**) and silacyclopropenylidene (**5**), respectively, and have been identified as reaction products by Maier *et al.* recently (Scheme 2).[11]



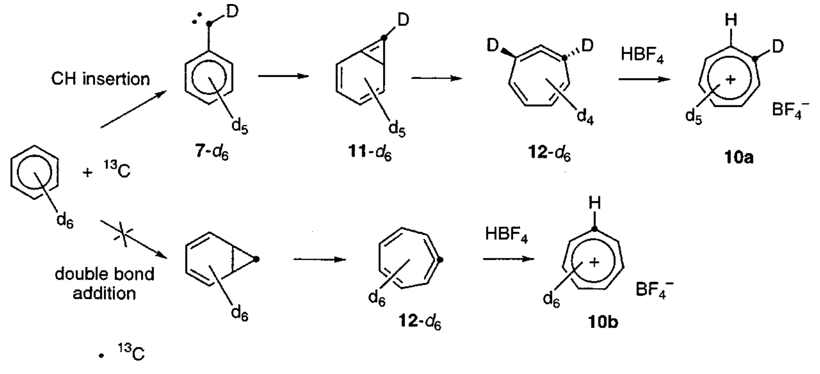
Scheme 2. Co-deposition of ethylene or acetylene and silicon atoms in inert gas matrices results in silacyclopropylidene (**4**) and silacyclopropenylidene (**5**), respectively.

''Hot'' carbon atoms formed with kinetic energies of several keV in nuclear reactions and accelerated carbon ions (C^+) react with benzene (**6**), in solid (−196 °C), liquid, or gaseous form, under bulk conditions to produce various larger molecules.[12–16] The formation of diphenylmethane and 7-phenyl-1,3,5-cycloheptatriene is explained by secondary reactions of the C_7 carbenes, phenylcarbene (**7**), bicyclo[4.1.0]hepta-2,4-diene-7-ylidene (**8**), and cycloheptatrienylidene (**9**) (Scheme 3).[14,15] The product distribution depends not only on the physical state of benzene[12,13] but also on the kinetic energy (2 to 5000 eV) of the carbon atoms.[14–16]



Scheme 3. Mechanism proposed by Lemmon and co-workers[15,16] for the formation of diphenylmethane and 7-phenyl-1,3,5-cycloheptatriene from benzene and ''hot'' atomic carbon. The spin states of the carbon atom and carbene intermediates were not discussed by Lemmon and co-workers.

Singlet carbon atoms, produced in a low-intensity carbon arc under high vacuum, react with simple unsaturated hydrocarbons under bulk conditions to yield allenes (via **1S** derivatives) and dienes, if allylic CH bonds are present.[17–19] The formation of the latter is explained by initial $C(^1D)$ insertion into an allylic CH bond and subsequent H migration.[17–19] Shevlin's group has reported several investigations of singlet carbon atom reactions with aromatic hydrocarbons.[20–22] Armstrong *et al.* found that singlet ^{13}C atoms insert into a perdeuterobenzene (**6**-d_6) CH bond at 77 K (Scheme 4): addition of HBF_4 to the cold matrix only resulted in the tropylium fluoroborate **10a**, where the ^{13}C atom is connected to a deuterium. Only initial CH insertion yielding phenylcarbene **7**-d_6 and subsequent rearrangement to bicyclo[4.1.0]hepta-2,4,6-triene (**11**-d_6) and cycloheptatetraene (**12**-d_6) can explain the observed substitution pattern. Double bond addition to give a cyclopropylidene derivative should result ultimately in tropylium fluoroborate **10b**. Note, however, that a different reactivity towards singlet carbon atoms is observed for pyrrole (double bond addition),[20] and for thiophene (attack of the double bond, but also at sulfur and at CH bonds).[21]



Scheme 4. Reaction of ^{13}**C** atom with deuterobenzene followed by workup with HBF_4 yields tropylium tetrafluoroborate **10a** from CH insertion but not **10b** from double bond addition according to Armstrong *et al.*[22]

Parts of the singlet C_7H_6 potential energy surface (PES) have been well investigated theoretically, both at semiempirical[23–28] and at *ab initio* levels.[29–36] It was shown recently that semiempirical methods are not suitable for the study of carbene rearrangements.[35] For instance, singlet–triplet separations are generally too large and the energetic ordering of carbene vs. allene-type structures is often incorrect with the semiempirical AM1 method.[35] Most of the theoretical C_7H_6 studies were stimulated by experimental investigations of singlet phenylcarbene (**7S**) and its rearrangement,[37–50] which puzzled chemists for some time. Recently, the heat of formation for $^3A''$ phenylcarbene was determined to be $102.8\pm 3.5\,\mathrm{kcal\,mol^{-1}}$.[50] The small singlet–triplet separation of **7**, less than 3 kcal $\mathrm{mol^{-1}}$ according to experimental[51,52] and theoretical estimates,[31–33,53] is in agreement with the singlet reactivity observed in most cases. Initially, the phenylcarbene rearrangement was considered to yield cycloheptatrienylidene (**9**),[36–38,43–45,54] but theory suggested that **12** is lower in energy than **9**.[24,29] Indeed, Chapman and co-workers identified spectroscopically cycloheptatetraene (**12S**) as the product of the pyrolytic and the photochemical rearrangement reactions of phenylcarbene.[47,48] Their assignment of the infrared (IR) spectra was later confirmed computationally.[31]

Kuzaj *et al.*[55] observed a stable triplet cycloheptatrienylidene (**9T**) species via electron spin resonance (ESR) spectroscopy, but neither from experiment nor from recent theoretical work[31–33] can it be concluded beyond doubt which state of **9** has been detected. Although the recent computational investigations by Matzinger *et al.*,[31] Wong and Wentrup,[32] and Schreiner *et al.*[33] discussed the various electronic states of cycloheptatrienylidene comprehensively, the nature of the lowest state in the triplet manifold is still uncertain as the B3LYP and BLYP density functional results do not agree with complete active space self-consistent field (CASSCF) concerning the nature of $^3B_1$-**9** and $^3A_2$-**9**.[31–33] Whereas $^3B_1$-**9** is a transition structure (TS) and $^3A_2$-**9** is a minimum 0.5 kcal $\mathrm{mol^{-1}}$ lower at B3LYP/6-311+G**, the order is reversed ($E_{\mathrm{rel}}=2\,\mathrm{kcal\,mol^{-1}}$) at the CASSCF level, with $^3B_1$-**9** being a minimum.[33]

Bicyclo[4.1.0]hepta-2,4,6-triene (**11S**), suggested to be an intermediate in the phenylcarbene rearrangement,[36,37] is 3 kcal $\mathrm{mol^{-1}}$ more stable than **7S** but is separated from the latter by a barrier of 15 kcal $\mathrm{mol^{-1}}$, according to recent theoretical investigations.[31–33] Due to the small ring opening barrier (about 1 kcal $\mathrm{mol^{-1}}$) to cycloheptatetraene (**12S**), the most stable singlet C_7H_6 isomer in this region of the PES,[31–33] **11S** never could be characterized.

In contrast to the established reactivity of singlet carbon atoms towards benzene at 77 K,[22] our research groups[5] communicated recently that the reaction of a laser-ablated ground state carbon atom, $C(^3P_j)$, with perdeuterobenzene (**6**-d_6) resulted in the formation of a C_7D_5 radical under single collision conditions. Analogously, a C_7H_5 product was obtained from the slightly exothermic $C_6H_6+C(^3P_j)$ reaction ($-3.7\pm 1.1\,\mathrm{kcal\,mol^{-1}}$) in a crossed-beams experiment at collision energies as low as 2 kcal $\mathrm{mol^{-1}}$. A carbon–hydrogen exchange reaction mechanism analogous to the one outlined for ethylene under single collision conditions[3] has been proposed.[5] Although phenylcarbyne (**13**) and benzocyclopropyl radical (**14**) have been considered as reaction products, the experimental and theoretical data strongly suggest that the 1,2-didehydrocycloheptatrienyl radical (**15**) is produced in the crossed-beams reactions via double bond addition followed by ring opening (or ultimately CC insertion) to **9T** and CH bond breaking.[5]

The study of the exchange reactions of unsaturated hydrocarbons with triplet carbon atoms identified in the crossed-beams investigations significantly improves the understanding of combustion processes and soot formation[56–64] as well as interstellar chemistry.[4,65–75] The crossed beams experiments combined with the electronic structure computations on the triplet and singlet C_7H_6 intermediates and the doublet C_7H_5 product unravel the chemical dynamics and the mechanism of the reaction of benzene with $C(^3P_j)$ atoms. In addition, the limited information on the triplet C_7H_6 PES with regard to the stability and reactions of the two cycloheptatrienylidene (**9**) triplet states prompted Matzinger *et al.*[31] to call for a detailed computational investigation. Here, we present a comprehensive theoretical study of the triplet C_7H_6 and doublet C_7H_5 potential energy surfaces (PES) and provide an energy profile for the carbon atom–benzene reaction obtained with hybrid Hartree–Fock/density functional, coupled-cluster, and G2 levels of theory. In addition, we revisit the enigmatic triplet cycloheptatrienylidene and study its reactions on the triplet PES.

II. METHODS

Geometries of stationary points were optimized with the 6-31G* and 6-311+G** basis sets[76] and Becke's[77] three parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr[78] (B3LYP) as implemented[79] in GAUSSIAN 94.[80] The spin-unrestricted formalism was employed for all open-shell species; spin-contamination turned out to be negligible. Harmonic vibrational frequencies and zero-point vibrational energy (ZPVE) corrections were computed at B3LYP/6-31G* (Table I).

Selected structures were also optimized using Becke's[81] 1988 exchange functional in conjunction with the LYP correlation functional (BLYP) as well as second-order Møller-Plesset perturbation theory based on either a restricted open-shell (ROHF-MP2) or spin-unrestricted (UHF-MP2) Hartree–Fock reference. In addition, the coupled-cluster method with single and double excitations (UHF-CCSD),[82] and a perturbative treatment of triple excitations [CCSD(T)][83] was utilized for geometry optimizations and single-point energy computations, respectively. A DZP basis set constructed from Dunning's[84] double-ζ contraction and augmented with one set of d (for C) and p (for H) polarization functions with orbital exponents of $\alpha_d(\mathrm{C})=0.75$ and $\alpha_p(\mathrm{H})=0.75$ was employed for the CCSD computations. The TZ2P basis set, obtained from Dunning's triple-ζ C $(10s6p/5s3p)$, H $(5s/3s)$ contraction and augmented with two sets of polarization functions with orbital exponents $\alpha_d(\mathrm{C})=1.5$ and 0.375 and $\alpha_p(\mathrm{H})=1.5$ and 0.375, was utilized in the CCSD(T) computations.

Single-point energies were also determined for selected structures at the G2(B3LYP/MP2) level (Table II).[85] The

TABLE I. Energies of C_7H_6 and C_7H_5+H species relative to separated benzene (**6**) plus $C(^3P_j)$ at the B3LYP/6-311+G** level of theory. Zero-point vibrational energies were obtained at the B3LYP/6-31G* level.

Species	$E_{rel}/\mathrm{kcal\,mol^{-1}}$
6$+C(^3P_j)$, separated reactants	0
7T	−81.8
8S	−36.3
9T, $^3B_1$	−69.3
9T, $^3A_2$	−70.4
11T	−33.5
12S	−89.9
13+H	+6.5
14+H	−10.8
15+H	−2.7
16$(^2B_1)$+H	−2.7
17T	−14.9
18T	−0.7
19T	+0.2
20T	−25.4
21T	−9.9
22T	−22.6
23T	−39.4
TS1+H	+38.6
TS2+H	+22.0
TS3	−8.1
TS4	−14.0
TS5	−3.8
TS6	−29.8
TS7	−30.7
TS8	−36.1
TS9	+3.6
TS10	−10.0
TS11	+13.5
TS12	+5.0
TS13	−5.7
TS14	+1.4

B3LYP modification of the G2(MP2)[86,87] model chemistry uses B3LYP/6-31G* geometries and ZPVEs scaled by 0.98, instead of HF/6-31G* ZPVE corrections and MP2(fu)/6-31G* geometries, to approximate the QCISD(T)/6-311+G$(3df,2p)$ energy. The G2(B3LYP/MP2) approach is more reliable for open-shell species where MP2 geometries and HF harmonic vibrational frequencies may be significantly in error due to spin-contamination of the UHF reference wave function.[85] We also employed the CBS-Q complete basis set extrapolation scheme of Petersson and co-workers (Table III).[88] Energies referred to in the text were obtained at the B3LYP/6-311+G** level with B3LYP/6-31G* zero-point vibrational energy (ZPVE) corrections unless noted otherwise.

TABLE II. Energies of selected C_7H_6 and C_7H_5+H species relative to separated benzene (**6**) and $C(^3P_j)$ at the G2(B3LYP/MP2) level of theory.

Species	$E_{rel}/\mathrm{kcal\,mol^{-1}}$
6$+C(^3P_j)$, separated reactants	0
13+H	+9.8
15+H	−1.9
TS2+H	+24.2
TS5+H	−0.3

TABLE III. Reaction enthalpies at 0 K for the formation of the 1,2-didehydrocycloheptatrienyl radical **15**+H from C_6H_6 benzene (**6**) and $C(^3P_j)$ at various levels of theory.

Level of theory	$\Delta H_R(0\ \mathrm{K})/\mathrm{kcal\,mol^{-1}}$
UHF-MP/DZP[a]	+15.6
UHF-MP2/TZ2P[a]	+10.5
UHF-MP2/TZ2Pf[a]	+7.8
UHF-CCSD/DZP[b]	+12.1
UHF-CCSD(T)/DZP[b]	+8.3
UHF-CCSD(T)/TZ2P[b]	+4.4
B3LYP/6-311+G**	−2.7
G2(B3LYP/MP2)	−1.9
CBS-Q	−6.2
Experiment	−3.7±1.1

[a] Using the B3LYP/6-311+G** geometries and the B3LYP/6-31G* zero-point vibrational energy corrections.
[b] Using the UHF-CCSD/DZP geometries and B3LYP/6-31G* zero-point vibrational energy corrections.

In addition, we computed the ‘‘nucleus independent chemical shifts’’ (NICS)[89] for various cyclic open-shell[90] π systems in the center of rings at HF/6-311+G**//B3LYP/6-311+G** using the GIAO approach[91] as implemented in GAUSSIAN 94.[80] The NICS values allow an assessment of the aromatic or antiaromatic character of molecules as they provide information about ring currents. By convention, aromatic molecules have negative NICS values, while antiaromatic molecules have positive values. All DFT, MP2, and G2 computations were performed with GAUSSIAN 94.[80] The coupled-cluster results were obtained with ACES II.[92] Absolute energies and geometries of all stationary points are available from the Electronic Physics Auxiliary Publication Service.[93]

III. RESULTS AND DISCUSSION

A. The thermochemistry of the carbon–benzene reaction

Whereas the formation of phenylcarbyne **13**+H from benzene and $C(^3P_j)$ is endothermic, the formation of all other C_7H_5 isomers discussed above is exothermic at the B3LYP/6-311+G** level of theory (Table I). Best agreement with the $-3.7\pm1.1\,\mathrm{kcal\,mol^{-1}}$ exothermicity derived from the crossed-beams experiments is obtained for formation of **15**+H and **16**+H. However, the formation of **16**+H can be excluded: the final C–H bond breaking step towards **16** involves a barrier, but the experimental data suggest a barrierless exit channel. In order to determine the reaction energies more reliably, several higher-level computations, including the G2(B3LYP/MP2) and CBS-Q extrapolation schemes, were performed for the **15**+H and **13**+H formation (Tables II and III).

First, we stress that the B3LYP/6-311+G** reaction energies (Table I) agree well with the significantly more demanding G2(B3LYP/MP2) data given in Table II. In addition, we find that the energy for the **15**+H formation strongly depends on the level of theory employed (Table III). Even with the relatively large TZ2P basis set, UHF-MP2 (using the B3LYP/6-311+G** geometries) underestimates the stability of **15** considerably. The higher-level CCSD(T)/

TZ2P approach reduces the reaction energy significantly (+4.4 kcal mol^{-1}). From the effect of the *f*-basis functions on the UHF-MP2 energies, one can assume that CCSD(T) also benefits significantly from additional higher-angular momentum functions. However, CCSD(T)/TZ2P*f* computations for **15** are currently beyond our capabilities. The ''complete basis set'' CBS-Q extrapolation scheme of Petersson and co-workers[88] overestimates (−6.2 kcal mol^{-1}) the stability of **15** somewhat.

In contrast to the formation of **15**+H, the direct C/H exchange to **13**+H is endothermic. Therefore, we conclude that the reaction to **13**+H has not been observed under single-collision conditions by Kaiser *et al.*[5] The following sections present possible pathways for the $C_6H_6+C(^3P_j)\rightarrow$**15**+H reaction and a rationalization why this product is formed and not the thermodynamically competitive structures **14** or **16**.

B. The C_7H_5 potential energy surface

The formal C/H substitution product, phenylcarbyne (**13**), has two low-lying electronic states, $^2B_1$ and $^2B_2$, in C_{2v} symmetry. The unpaired electron in the $^2B_1$ state is described by a π-symmetric (with respect to the molecular plane) singly-occupied molecular orbital (SOMO) localized on the exocyclic carbon atom. In contrast, the SOMO is σ-symmetric in the $^2B_2$ state (Chart 1)

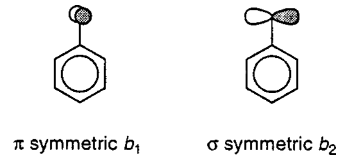

π symmetric b_1 σ symmetric b_2

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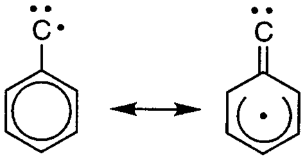
Chart 1. The π and σ symmetric singly occupied molecular orbitals (SOMO) of the $^2B_1$ and $^2B_2$ states of phenylcarbyne (**13**).

Both states are subject to the second-order Jahn–Teller (SOJT) effect,[94] as they can interact vibronically via an a_2 normal mode, i.e., the $^2B_1$ and $^2B_2$ states can mix under an a_2 distortion as then both transform as ^2B. The SOJT effect is strong enough to distort the more stable $^2B_1$ state (0.6 kcal mol^{-1} below the $^2B_2$ minimum) to C_2 symmetry as one imaginary vibrational frequency (99*i* cm^{-1}) is obtained at the B3LYP/6-31G* level of theory. However, both the energy and the geometry of the C_2 minimum (but *not* the vibrational frequencies, the lowest is 145 cm^{-1}) are identical to that of the $^2B_1$ state within the numerical accuracy of the computations. In order to assess if the double-minimum potential energy curve predicted for the ground state of the phenylcarbyne radical (**13**) by B3LYP/6-31G* is artifactual or not, we performed BLYP/6-31G* and UHF-MP2/6-31G* computations for the $^2B_1$ state of **13**. The UHF reference suffers from high spin-contamination ($\langle S^2\rangle=1.3$), which renders the UHF-MP2/6-31G* prediction of a $^2B_1$ minimum unreliable. However, the C_{2v} symmetric $^2B_1$ state is also found to be a minimum at BLYP/6-31G*. Hence, it cannot be concluded beyond doubt whether the $^2B_1$ state distorts to C_2 symmetry due to the SOJT effect or not; but the flatness of the ground state PES in the vicinity of **13** has been established. We use the B3LYP/6-311+G**C_2 structure and energy of **13** for the following discussions.

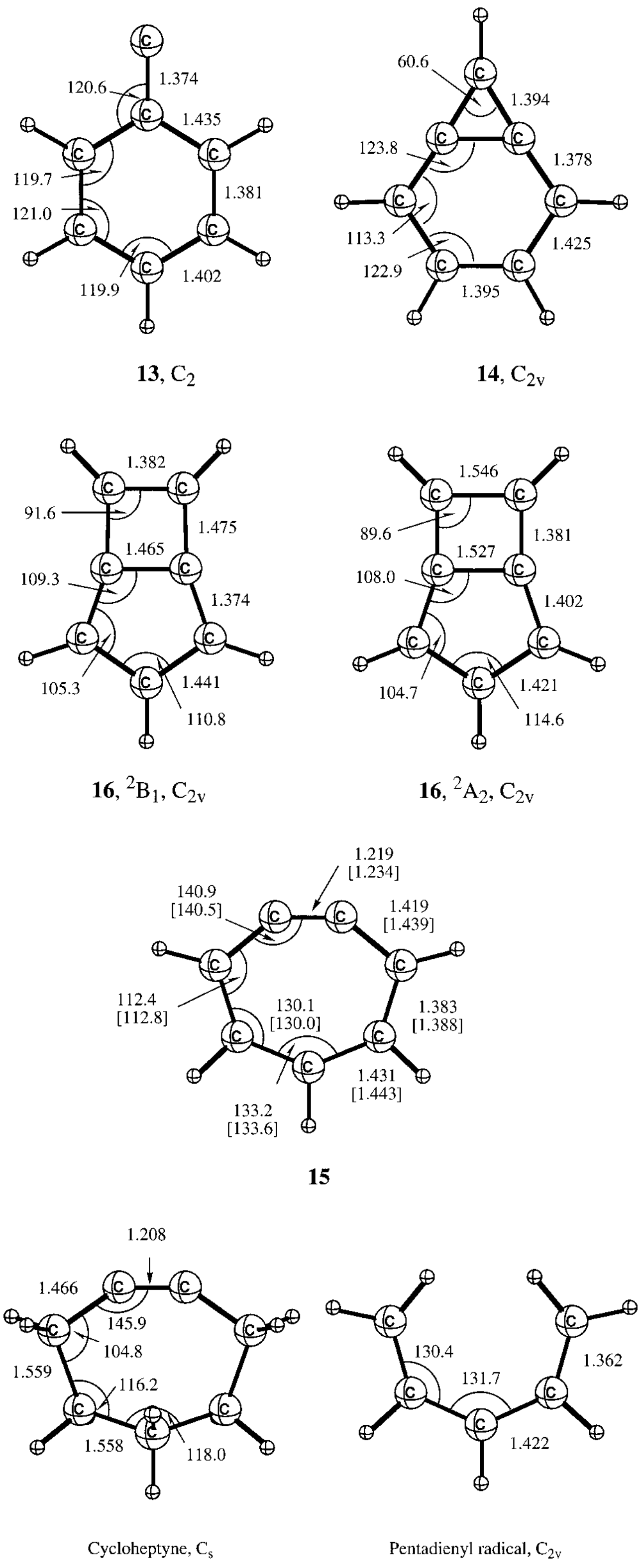
The alternating bond lengths in the benzene ring and the rather short 1.374 Å exocyclic CC bond (Fig. 1) indicate the participation of methylene carbene resonance forms in the electronic structure of **13** (Scheme 5). The small NICS[89,90] value of **13** (−2.4) with respect to benzene (−9.5) confirms that the aromaticity of the six-membered ring is reduced due to the contributions from the vinylidene form. Such behavior has also been reported for the benzyl cation, first by Dewar and Landman[24] and then by others,[95–98] as well as for the phenolate anion.[99] We also deduce a substantial degree of quinoid character for triplet phenylcarbene (**7T**) from its low −2.3 NICS value. In contrast, the quinoid valence structure for singlet phenylcarbene (**7S**) is less favorable due to charge separation and therefore is not as important as in **7T**.[24] Indeed, the NICS value for **7S** (−6.6) is significantly larger than for **7T** (−2.3). Nonetheless, the singlet–triplet splittings of carbenes depend on the π-donor ability of the substituents, as investigated recently.[100]


13

Scheme 5. The conventional and vinylidene resonance structures for phenylcarbyne (**13**).

The influence of the vinylidene valence structure also is reflected in the two possible intramolecular reactions of **13**. The insertion into an ortho-CH bond (**TS1**, Fig. 2) yields the planar C_{2v} symmetric benzocyclopropyl radical (**14**, Fig. 1), which is the most stable C_7H_5 isomer studied, 17.3 kcal mol^{-1} lower in energy than **13**. However, the barrier for the CH insertion (32.1 kcal mol^{-1}) is higher than the barrier for insertion into the adjacent CC bond (**TS2**, Fig. 2) via [1,2]-C shift [15.5 kcal mol^{-1}; 14.4 kcal mol^{-1} at G2(B3LYP/MP2)]. This [1,2]-C shift of **13** is an exothermic reaction [−9.2 kcal mol^{-1}, −11.7 kcal mol^{-1} at G2(B3LYP/MP2)] with the C_{2v} symmetric $^2B_1$ state of the 1,2-didehydrocycloheptatrienyl radical (**15**) as the product. In contrast, the ortho-CH insertion reaction of **7S** to **11S** (Scheme 4) has a lower barrier (15 kcal mol^{-1} at B3LYP/6-311+G**//B3LYP/6-31G*)[33] than the [1,2]-C shift. The preference of **7S** to preserve the six-membered ring system reflects the larger aromaticity (NICS: −6.6) as compared to **13** (NICS: −2.4).

The bond lengths and bond angles in the 1,2-didehydrocycloheptatrienyl radical (**15**) are very similar to those in the pentadienyl radical (Fig. 1). The distance between the dehydro atoms (1.219 Å at B3LYP/6-311+G**, but 1.234 Å at UHF-CCSD/DZP) is close to the C≡C triple bond in cycloheptyne (1.208 Å) and in 3,3,6,6-tetramethyl-1-thiacycloheptyne (1.209 Å from electron diffraction).[101] Note that the C≡C triple bond in **15** is significantly shorter than that in *o*-benzyne [1.245 Å at B3LYP/6-311+G** (Ref.



13, C_2

14, C_{2v}

16, $^2B_1$, C_{2v}

16, $^2A_2$, C_{2v}

15

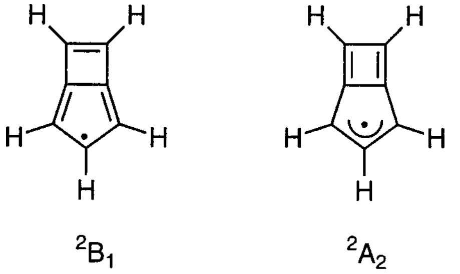
Cycloheptyne, C_s

Pentadienyl radical, C_{2v}

FIG. 1. Geometries of C_7H_5 isomers at the B3LYP/6-311+G** level of theory. The UHF-CCSD/DZP values for **15** are given in brackets. Bond lengths are in Å, bond angles are in degrees.

102) and 1.24±0.02 Å from the dipolar ^{13}C-NMR spectra],[103] and 1,2,4,5-tetradehydrobenzene [1.269 Å at CCSD(T)/TZ2P].[104] The geometry of **15** resembles that of a pentadienyl radical whose terminal ends interact with the connecting triple bond. Although other isomers of **15** (the 1,3- and 1,4-dehydro forms) are possible, the analogy to the dehydrobenzenes[105–111] strongly suggests that the 1,2-dehydro isomer is the lowest in energy. Note that anions derived from **13** and **15** have been observed and studied by the flowing afterglow technique recently.[112] We found that the $^2A_2$ state of **15** is 9 kcal mol^{-1} above the $^2B_1$ state (*vide supra*).

Another minimum located on the C_7H_5 PES is the planar C_{2v} symmetric bicyclo[3.2.0]hepta-1,4,6-triene-3-yl radical (**16**). The geometry of the five-membered ring resembles the $^2B_1$ cyclopentadienyl radical,[113–118] which has a butadiene π-system in the five membered ring. The second Jahn–Teller[119] distorted form of the cyclopentadienyl radical is the $^2A_2$ state, which has an allyl radical system incorporated into the five-membered ring, and is almost isoenergetic with the $^2B_1$ state.[117,118] Similarly, the radical center of $^2B_1$-**16** connects the terminal ends of the butadiene system (Chart 2). However, the $^2A_2$ state of **16** is an energetically higher-lying transition structure (13.5 kcal mol^{-1}) on the C_7H_5 PES.



16

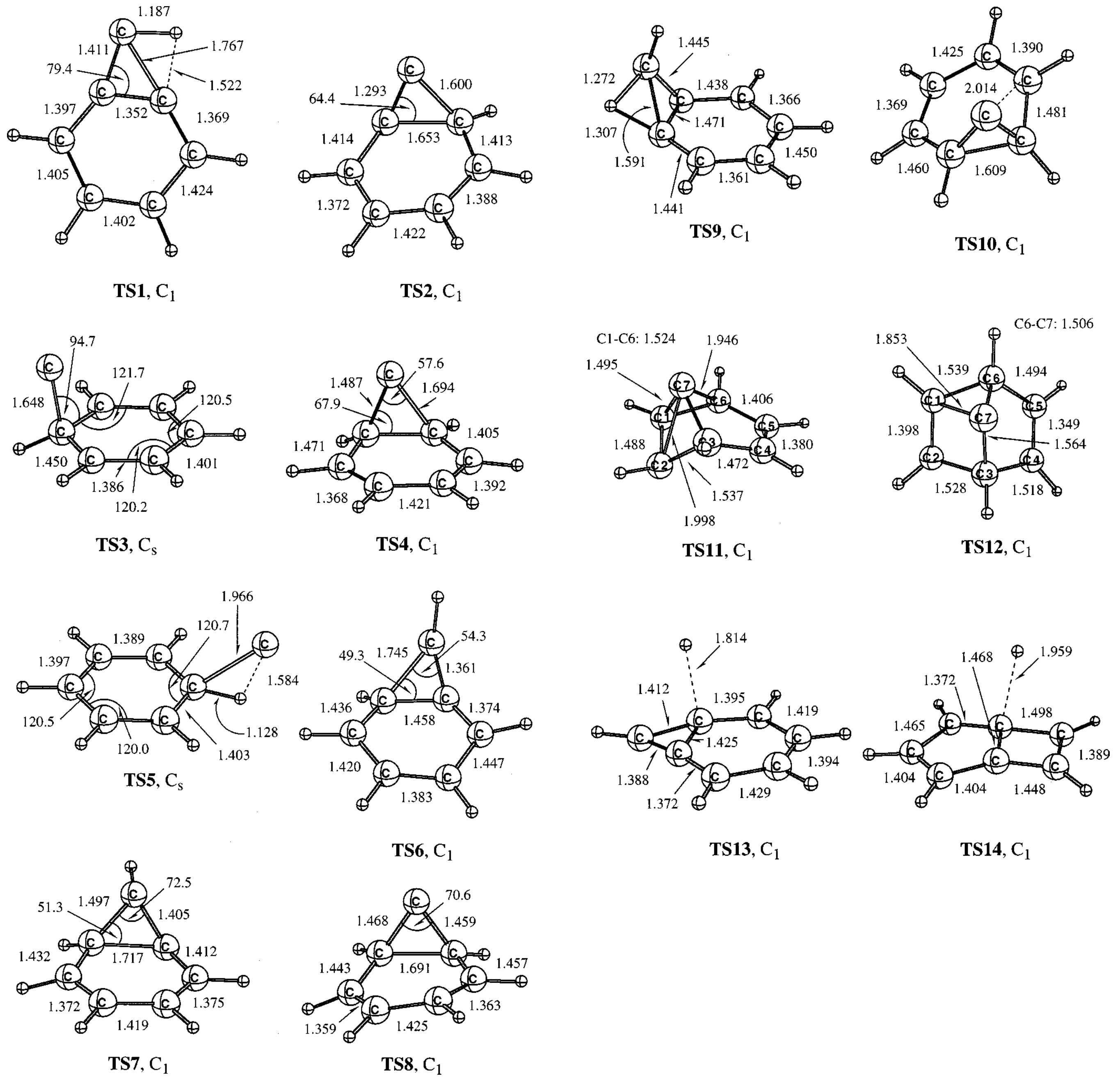
Chart 2. The $^2B_1$ state of **16** with a cisoid butadiene system is lower in energy than the $^2A_1$ state with an antiaromatic cyclobutadiene ring.

This energetic order of isomers is in agreement with the nucleus independent chemical shift (NICS) values obtained at the UHF/6-311+G**//UB3LYP/6-311+G** level. Large positive values in the centers of the four- and five-membered rings (+11.6 and +8.1, respectively) of $^2A_2$-**16** indicate unfavorable antiaromaticity. In contrast, the antiaromatic character is the much smaller in $^2B_1$-**16** according to the NICS: it is close to zero (+0.2) in the five-membered ring, and +6.3 in the four-membered ring. Accordingly, $^2B_1$-**16** is found to be significantly lower in energy than its $^2A_2$ isomer.

C. The triplet C_7H_6 potential energy surface

1. Attack of C(^3P_j) on benzene

The approach of the electron deficient triplet carbon atom on benzene results in the formation of a $^3A''C_s$ symmetric minimum (**17T**) with the attacking carbon atom bound to the ''edge'' of benzene by −14.9 kcal mol^{-1} with respect to the reactants. The ring bond bridged by the carbon atom in **17T** is elongated (1.460 Å) compared to benzene (1.395 Å), but is much too short to describe **17T** as a cyclopropylidene derivative (**8T**). Furthermore, the CC bonds to the triplet carbon atom, which are oriented almost perpendicular to the ring plane, are very long (1.714 Å, Fig. 3). Note that **8T** does not exist as a stationary point on the triplet



TS1, C_1 **TS2**, C_1 **TS9**, C_1 **TS10**, C_1

TS3, C_s **TS4**, C_1 **TS11**, C_1 **TS12**, C_1

TS5, C_s **TS6**, C_1 **TS13**, C_1 **TS14**, C_1

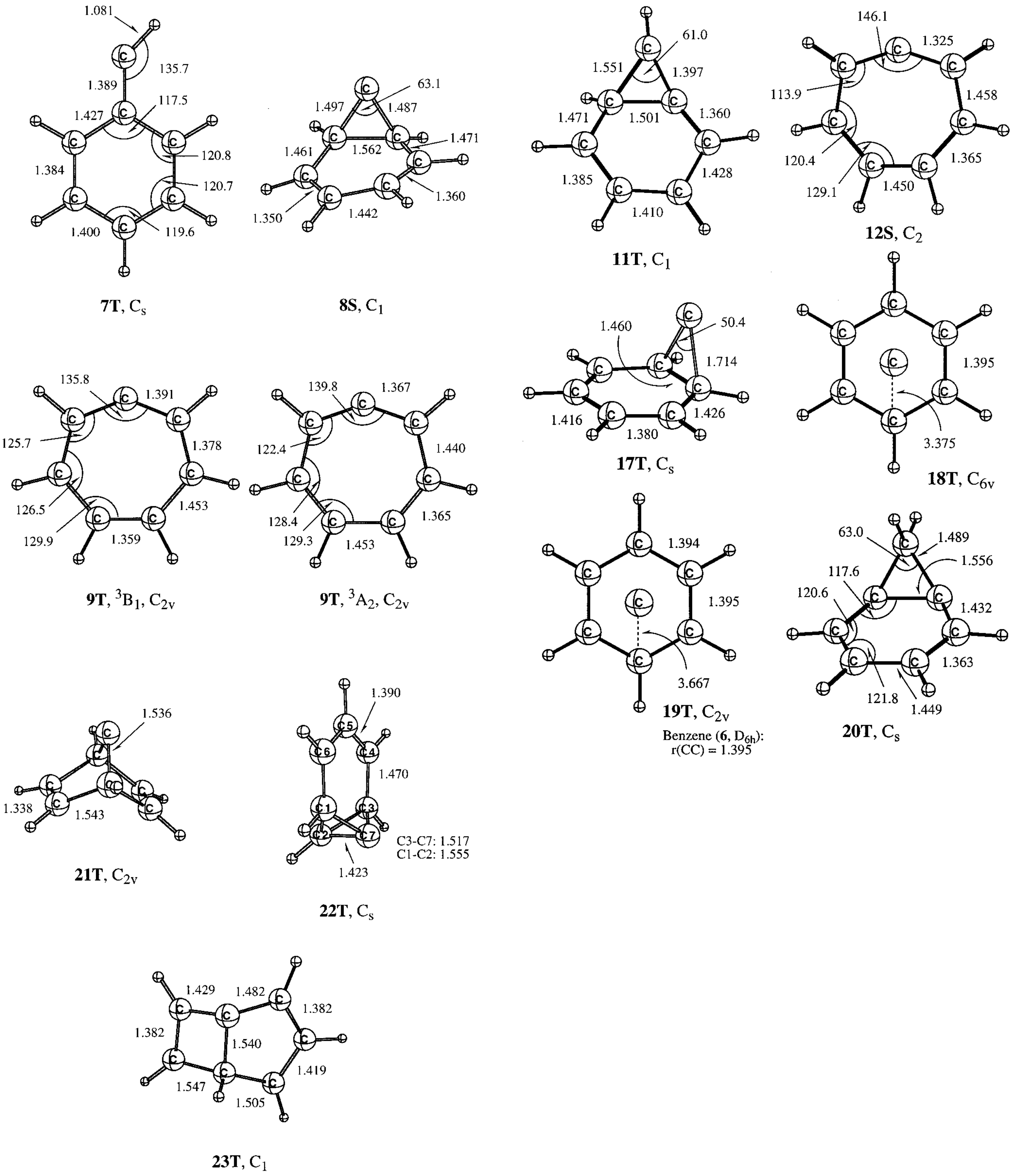
TS7, C_1 **TS8**, C_1

FIG. 2. Transition structures on the C_7H_5 and C_7H_6 potential energy surfaces at the B3LYP/6-311+G** level of theory. Bond lengths are in Å, bond angles are in degrees.

C_7H_6 PES at B3LYP/6-311+G**, as all attempts to optimize to **8T** resulted in the ring opening product cycloheptatrienylidene, **9T**. To make sure that the nonexistence of **8T** is not an artifact of the DFT treatment, **8T** also was studied with the MP2 method. Whereas $^3A'$ **8T** still corresponds to a minimum at UHF-MP2/6-31G*($\langle S^2\rangle = 2.1$), the distance between bridgehead carbons is increased to 2.290 Å. The even larger 6-311+G** basis set does not give a minimum for **8T**, in agreement with B3LYP. As triplet carbenes prefer large angles at the carbene carbon atom, long distances between bridgehead carbons are anticipated for bicyclic triplet cyclopropylidenes.[120–123] The corresponding bond in parent **1T** is 1.629 Å, significantly longer than in singlet cyclopropylidene (1.491 Å at B3LYP/TZP).[121]

As indicated by the structure of **17T**, there is only a weak interaction between the C(^3P_j) and the benzene molecule. As a consequence, the two unpaired electrons occupy orbitals of a' and a'' symmetry resulting in a $^3A''$ state for **17T**. The unpaired electrons of triplet cyclopropylidenes reside in two a' orbitals when the C_s plane is oriented as in **17T**. The energy (14.9 kcal mol^{-1} below separated educts), the geometry, and the $^3A''$ electronic state suggest that **17T** is a complex between singlet benzene and the triplet carbon atom. Computing the energy as a function of the distance between the benzene and C(^3P_j) reveals that there is no barrier to **17T** formation, as the potential is attractive even at large distances.

Besides the ''edge'' adduct between benzene and triplet



7T, C_s

8S, C_1

11T, C_1

12S, C_2

9T, $^3B_1$, C_{2v}

9T, $^3A_2$, C_{2v}

17T, C_s

18T, C_{6v}

19T, C_{2v}

Benzene (**6**, D_{6h}): r(CC) = 1.395

20T, C_s

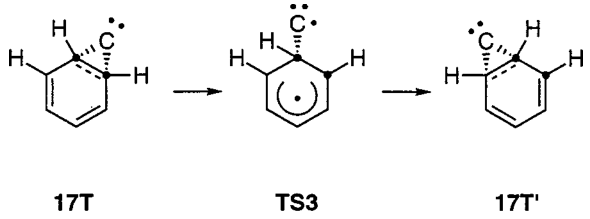
21T, C_{2v}

22T, C_s

23T, C_1

FIG. 3. Geometries of C_7H_6 isomers at the B3LYP/6-311+G** level of theory. Bond lengths are in Å, bond angles are in degrees.

carbon, there also exists a $^3A''$ C_7H_6 stationary point (**TS3**) with the C atom loosely bound (-8.1 kcal mol^{-1}) to the ''corner'' of benzene. However, this structure is not the biradical intermediate of an addition–elimination mechanism analogous to the aromatic electrophilic substitution. Rather, it is a TS (504i cm^{-1}, a'') for degenerate isomerization (barrier of 6.8 kcal mol^{-1}) of **17T** forms (Scheme 6). Note, however, that the ''aromatic radical substitution'' has been observed recently for the reaction of CN with benzene under single collision conditions in crossed-beams experiments.[124]

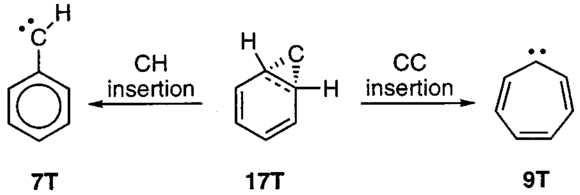


Scheme 6. Degenerate rearrangement of **17T** *via* **TS3**.

The hypothetical C_{6v} form (**18T**) with the C(^3P_j) atom 3.073 Å above the center of the benzene ring is a second order stationary point only 0.7 kcal mol^{-1} lower than the separated reactant species. Following the two imaginary vibrational modes downhill leads to **TS3** and to **17T**. Likewise, a C_{2v} minimum **19T** with the C(^3P_j) atom 3.392 Å above the benzene ring is 0.2 kcal mol^{-1} less stable than the reactants. To summarize, the benzene–C(^3P_j) complex **17T** marks the entry to the triplet C_7H_6 PES for the reactants, as no other complex of competitive stability exists.

2. Rearrangements on the triplet C_7H_6 potential energy surface

Cycloheptatrienylidene (**9T**) and triplet phenylcarbene (**7T**) are accessible from **17T** through exothermic CC (−55.5 kcal mol^{-1}) and CH insertions (−66.9 kcal mol^{-1}), respectively (Scheme 7). The **TS4** for the non-least-motion carbon atom insertion yielding **9T** from **17T** lies very early along the reaction coordinate and is characterized by two extremely different separations between the divalent carbon atom and the closest benzene carbons (1.694 Å vs. 1.487 Å). The bridged CC bond is elongated by 0.084 Å to 1.544 Å. In spite of the considerable geometry changes, **TS4** is only 0.9 kcal mol^{-1} higher in energy than **17T**.

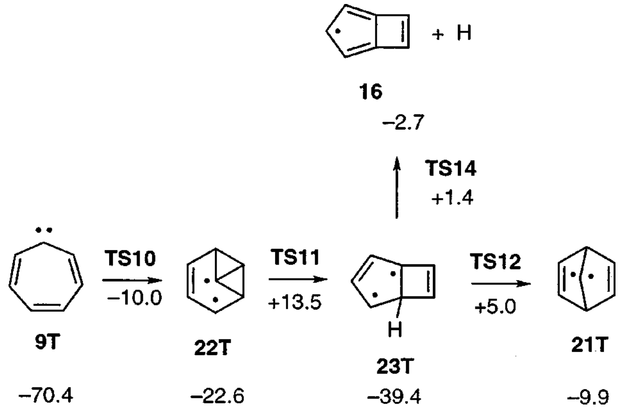


Scheme 7. CC-insertion (or ring opening) to **9T** and CH-insertion to **7T** are possible reactions of **17T**.

Besides the insertion into a benzene CC bond, we identified the insertion into a CH bond as a possible reaction of **17T** (Scheme 7). The **TS5** for this process has C_s symmetry with distances of 1.966 Å and 1.584 Å to the benzene C and H, respectively (Fig. 2). Intrinsic reaction coordinate (IRC) analysis confirms that **TS5** connects **17T** with **7T**. The barrier for the CH-insertion is 11.1 kcal mol^{-1} with respect to **17T**, and thus is 3.8 kcal mol^{-1} below the separated reactants at B3LYP/6-311+G**. However, at G2(B3LYP/MP2) **TS5** is only 0.3 kcal mol^{-1} below the separated reactants.

Similar to singlet phenylcarbene (**7S**),[31–33] triplet phenylcarbene **7T** can undergo a rearrangement to bicyclo[4.1.0]hepta-2,4,6-triene (**11T**). However, the barrier for the 48.3 kcal mol^{-1} endothermic reaction from **7T** to **11T** is considerably higher (52.0 kcal mol^{-1} via **TS6**) than the barrier on the singlet surface (12–15 kcal mol^{-1}),[31–33] but nonetheless 29.8 kcal mol^{-1} below the separated reactants. According to the spin density analysis, the single electrons are located on C3 and C7 in **11T** giving rise to a pyramidal cyclopropyl C7 and an allyl system incorporated into the six-membered ring. Ring opening of **11T** to **9T** is exothermic by −36.9 kcal mol^{-1} and requires only 2.8 kcal mol^{-1} activation via **TS7**. Alternatively, a [1,2]-H shift transforms **11T** into the bent, C_s symmetric triplet benzocyclopropene (**20T**) in a 8.1 kcal mol^{-1} endothermic reaction. The bridgehead carbon atoms bear the single electrons and are therefore pyramidal (Fig. 3). The barrier for the **11T**→**20T** rearrangement is large (37.1 kcal mol^{-1} via **TS9**) compared to ring opening to **9T**. As **TS9** lies energetically above the reactants (3.6 kcal mol^{-1}), this pathway is not viable when very low collision energies are employed in the crossed-beams experiments.

We were also searching for a reaction pathway which would directly interconnect **17T** and the 5.0 kcal mol^{-1} higher-lying triplet norbornadienylidene **21T** (see Scheme 8). However, no TS for such a path could be found at the B3LYP/6-31G* level of theory. We were able to locate a transition state (**TS10**), which at first glance might be connecting **17T** and tricyclo[4.1.0.0^{2,7}]heptendiyl **22T**. But according to IRC calculations one of the paths downhill from **TS10** leads to **9T** (Scheme 8). The barrier for the reaction from **9T** to the 47.8 kcal mol^{-1} higher-lying **22T** is as large as 60.4 kcal mol^{-1}. A complex rearrangement of **22T**, breaking of the C7–C2 and C1–C6 bonds and formation of the C7–C6 bond (Fig. 2), provides a pathway to **23T** via **TS11**. The barrier for this exothermic reaction (−16.8 kcal mol^{-1}) is 36.1 kcal mol^{-1}. Finally, another transition structure (**TS12**) connects **23T** to **21T**.



Scheme 8. Reaction pathways from **9T** to **21T** and **16**+H. Energies are given in kcal mol^{-1} with respect to separated reactants at B3LYP/6-311+G**(B3LYP/6-31G* ZPVE) level of theory. Note that these reactions are not important experimentally as **TS11** is very high in energy.

Again, a complex molecular rearrangement is needed for this reaction and accordingly the barrier for this endothermic process (+29.5 kcal mol^{-1}) is a sizable 44.4 kcal mol^{-1}. Note that both **TS11** and **TS12** have geometries which suggest that they connect to a triplet tricyclo[4.1.0.0^{3,7}]heptendiyl rather than to **23T**. But in spite of extensive searches at B3LYP/6-31G*, no minimum could be located for tricyclo[4.1.0.0^{3,7}]heptane as all attempts yielded bicyclic **23T**. As both **TS11** and **TS12** are energetically high-lying with respect to reactants, formation of **23T** is not viable at the low collision energy employed in the crossed-beams experiments.

3. Cycloheptatrienylidene

The presence of the cyclic conjugated π-system adjacent to the carbene center allows the existence of two triplet and three singlet states which all lie energetically within 20 kcal mol^{-1}. Recently, Matzinger *et al.*[31] and Schreiner *et al.*[33] identified the lowest-lying singlet state ($^1A_2$) of **9** as the TS for the enantiomerization of C_2 symmetric **12** [^1A state, $\Delta E^{\ddagger}=21\,\mathrm{kcal\,mol}^{-1}$ at CASPT2N/cc-pVDZ//CASSCF(8,8)/6-31G* and two-determinant CCSD/cc-pVDZ levels of theory]. The closed-shell $^1A_1$ state, which resembles the usually-depicted cycloheptatrienylidene structure,[23–30] and the open-shell $^1B_1$ states are higher in energy (10 and 14 kcal mol^{-1}, respectively) than $^1A_2$-**9**.[33] There exist two almost degenerate states in the triplet manifold, $^3B_1$ and $^3A_2$, which lie slightly above $^1A_2$-**9**.[31,33] At the density functional BLYP/6-31G* or B3LYP/6-31G* levels the $^3B_1$ state is a TS and the $^3A_2$ state is a minimum.[31–33] However, the nature of the stationary points is reversed at the CASSCF level, i.e., the $^3B_1$ state corresponds to a minimum and the $^3A_2$ state is a TS.[33]

It has been argued that intersystem crossing from $^3A_2$ to $^1A_2$ should rapidly depopulate the $^3A_2$ state since these two states of **9** are almost degenerate at very similar geometries.[32,33] An analogous situation does not exist for the $^3B_1$ and $^1B_1$ states, and furthermore, the $^1A_2$ state is found to be higher in energy than $^3B_1$ when computed at the $^3B_1$-**9** geometry. Hence, it has been assumed[32,33] that the $^3B_1$ state of **9** was detected in ESR experiments.[55,125]

Spin–orbit coupling is the most important mechanism for intersystem crossing, but the $^3A_2 \rightarrow {}^1A_2$ transition is spin–orbit forbidden. The direct product of $A_2 \times A_2 = A_1$ does not transform as a rotation and therefore spin–orbit coupling between $^1A_2$ and $^3A_2$ states is zero according to the spin–orbit coupling selection rules.[126] Consequently, the intersystem crossing between these two states might be very slow at very low temperatures, as only vibrational coupling provides a mechanism for theses states to interact. In addition, triplet cycloheptatrienylidene (**9T**) is expected to be kinetically stable towards rearrangement to the energetically lower-lying **7T** via **11T** at 12 K as the barriers for this reaction are as large as 40 kcal mol^{-1} (*vide supra*). These arguments might explain the 1986 ESR observation of a stable **9T** species at 12 K.[55]

As there is a discrepancy between the CASSCF(8,8)/6-31G* and B3LYP/6-311+G** methods concerning the nature of the triplet states of **9**, we tried to resolve this by additional UHF-MP2 computations. In agreement with earlier results, we find large spin-contamination of the UHF reference wave functions in the UHF-MP2 computations. But even more disastrous is the finding of an exceedingly large (more than $10\,000i\ \mathrm{cm}^{-1}$) imaginary vibrational frequency for the $^3A_2$ state at UHF-MP2/DZP. At this level of theory, an unusually large vibrational frequency (4151 cm^{-1}) is also obtained for the $^3B_1$ state. Such unphysical vibrational frequencies indicate an instability of the molecular orbital Hessian of the reference wave function, as discussed by Crawford *et al.*[127] recently. The instability in a certain symmetry block (for **9T** states it is the b_2 block) causes a singularity and a pole of second order, vividly called an ''instability volcano,'' in a correlated-level force constant of the same symmetry block. Among the correlated methods studied by Crawford *et al.*,[127] MP2 showed the poorest performance as the instability volcanoes were exceptionally wide. This causes the MP2 force constants to blow up even at geometries somewhat away from the singularity. Crawford *et al.*[127] concluded that the magnitude of the eigenvalues of the molecular orbital Hessian is a valuable diagnostic to determine the reliability of a vibrational frequency computation. If one of the eigenvalues is exceedingly small, either positive or negative, an unphysically large vibrational frequency results, due to the proximity to the singularity. Note that the sign of this eigenvalue is not important in this context; even a wave function that is found to be stable under certain perturbations (all positive eigenvalues of the molecular orbital Hessian; negative eigenvalues indicate unstable wave functions)[128] can produce unphysical vibrational frequencies.

We find instabilities in the b_2 symmetry block of the molecular orbital Hessian of the UHF reference wave function at the UHF-MP2/DZP geometries of $^3B_1$-**9** and $^3A_2$-**9** with associated eigenvalues of -0.0176 and -0.0021, respectively. The force constants are 111 and 5054 aJ $\mathrm{\AA}^{-2}$ resulting in the 4151 cm^{-1} and $>10\,000i\ \mathrm{cm}^{-1}$ b_2 vibrations for the $^3B_1$-**9** and $^3A_2$-**9** states, respectively. Clearly, the UHF-MP2/DZP method produces physically unrealistic results for the b_2 symmetry block.

The UB3LYP/6-31G* and UBLYP/6-31G* wave functions are stable at the optimized geometries and the smallest eigenvalues of the molecular orbital Hessians in the b_2 symmetry block are $+0.0181$ and $+0.0204$ for the $^3B_1$-**9** and $^3A_2$-**9** states, respectively. The formal analogy between Kohn–Sham (KS) and HF theory suggests that KS wave functions can in principle suffer from molecular orbital instabilities as well.[129] But there is no indication that the DFT vibrational frequencies of the triplet states of **9** are corrupt.

We therefore assumed that the B3LYP and BLYP predictions of a $^3A_2$ minimum as the most stable triplet state of **9** are correct. This is also supported by the finding[31–33] that both triplet states of **9** are extremely similar in energy (less than 1 kcal mol^{-1} at highly correlated levels as well as at B3LYP/6-311+G**) with the $^3A_2$ state being somewhat lower.[130] We note that the final answer on the nature of the triplet states of **9** awaits the results of higher-level computations.

To summarize, the reaction of C(^3P_j) with benzene on the C_7H_6 PES to **9T** is a highly-exothermic (-70.4 kcal mol^{-1}) reaction involving the very unstable intermediate **17T**. Triplet cycloheptatrienylidene (**9T**) is directly accessible from **17T** by ring opening or via **7T** and **11T** by CH-insertion. Both routes to **9T** involve barriers below the energy of the separated reactants, but the CC-insertion pathway is energetically more favorable, as it involves a much lower barrier.

D. The singlet C_7H_6 potential energy surface

Single point energy computations at the B3LYP/6-311+G** geometry of **17T** reveal that the $^1A'$ state is

1.3 kcal mol^{-1} more stable than the $^3A''$ state. Thus, an intersystem crossing from $^3A''$ to $^1A'$ might be possible for the C_7H_6 molecule in the vicinity of **17T**, although this transition is spin-forbidden and might be slow in the gas phase.

If intersystem crossing were possible from $^3A''$ to $^1A'$ in the vicinity of **17T**, the reacting species would fall onto a ridge rather than into a valley, as the $^1A'$ C_7H_6 surface has a negative curvature at the geometry of **17T**. Hence, slight perturbations should cause the downhill reaction path on the $^1A'$ C_7H_6 PES to bifurcate, leading to the two enantiomeric forms of the C_1 bicyclo[4.1.0]hexa-2,5-diene-7-ylidene singlet (**8S**). The reaction from **17T** to **8S**, whose energy is 36.3 kcal mol^{-1} below separated benzene and a carbon atom, is exothermic by -21.4 kcal mol^{-1}. The bridgehead bond in **8S** (1.562 Å) is significantly longer than in **17T** (1.460) In addition, the **8S** CC bond lengths alternate more than in **17T** (Fig. 3). Ring opening of **8S** to the cyclic allene **12S**, the most stable C_7H_6 isomer investigated in this study (-90 kcal mol^{-1}), via **TS8** is almost barrierless (0.2 kcal mol^{-1}). Low barriers were also found for opening of the parent and the dimethyl-substituted cyclopropylidenes (0 to 5 kcal mol^{-1}).[121,131,132] In contrast, the barrier is 15 kcal mol^{-1} for the ring opening reaction of the saturated bicyclo[4.1.0]hepta-7-ylidene to 1,2-cycloheptadiene due to conformational strain.[132]

E. Pathways from the C_7H_6 PESs to the doublet C_7H_5 PES

None of the C_7H_6 species produced from benzene and a $C(^3P_j)$ atom can dissipate the sizable reaction energy, since the molecular crossed-beams experiment were performed under single collision conditions. Three body reactions, which might stabilize the C_7H_6 intermediates by diverting the internal energy, were eliminated.[5] The species formed will be highly excited and thus can undergo endothermic CH bond dissociation reactions.

Despite thorough searches of the PESs, no TSs could be located for the formation of **13**+H from **7T** or **17T**. In all attempts, the H atom moved more than 5 Å away from the ring system while the remaining C_7H_5 moieties approached the geometry of **13**. In addition, the energies of the systems were close to that of separated **13**+H. This suggests that there are barrierless, but nonetheless uphill reaction paths from **17T** and **7T** to **13**+H. As mentioned already above, the reaction to **13**+H is not important experimentally due to its endothermicity.

The CH bond dissociation of **11T** and **20T** results in the formation of **14**, which is the most stable C_7H_5 species studied. However, this isomer most probably has not been observed, as the computed reaction energy (-10.8 kcal mol^{-1}) is not in agreement with experiment (*vide supra*). In addition, the loss of the bridgehead H atom in **11T** involves a transition state (**TS13**) which is found to lie 5.7 kcal mol^{-1} below the reactants, but the experimental results suggest that there is no barrier in the exit channel of the $C_6H_6+C(^3P_j) \rightarrow C_7H_5+H$ reaction.[5] On the other hand, formation of **20T** from **11T** proceeds through a very high barrier (**TS9**, +3.6 kcal mol^{-1} with respect to reactants). Although the CH dissociation of **20T** proceeds without TS, the finding that the reaction product is unchanged at collision energies below 3.6 kcal mol^{-1} suggests that a pathway involving **20T** is not detected in the crossed-beams experiments.

The same arguments can be employed to exclude **16** (via hydrogen loss from **23T**) as possible reaction product. The pathway to its precursor **23T** involves the very high-lying **TS11** (+13.5 kcal mol^{-1}), and the C–H bond breaking of **23T** is not barrierless but proceeds through **TS14**. Thus, this pathway is not in agreement with experimental data.

The only remaining possibility is the formation of **15** +H from **9T** or from **12S**. As both α-CH dissociation reactions do not involve any transition states, and as both monocyclic seven-membered ring compounds are expected to have lifetimes longer than their rotational periods, it cannot be concluded beyond doubt which of the two species is the precursor of **15**. To shed light on this point, variational RRKM calculations are to be performed.

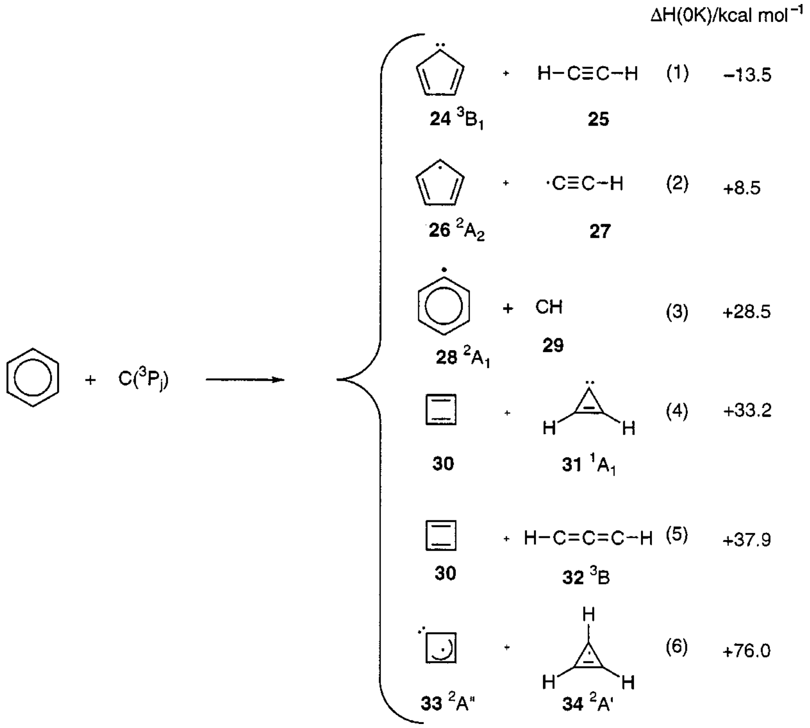
We conclude that the α-CH dissociations of **9T** and **12S** yield radical **15**, which has been observed in the crossed-beams experiments,[5] in barrierless but highly endothermic reactions. Hence, this C_7H_5 PES only pertains to single collision experiments and not reaction conditions, where typical bimolecular carbene (or allene) chemistry would dissipate the reaction energy (Scheme 3).[12–16]

F. Formation of species other than C_7H_5+H

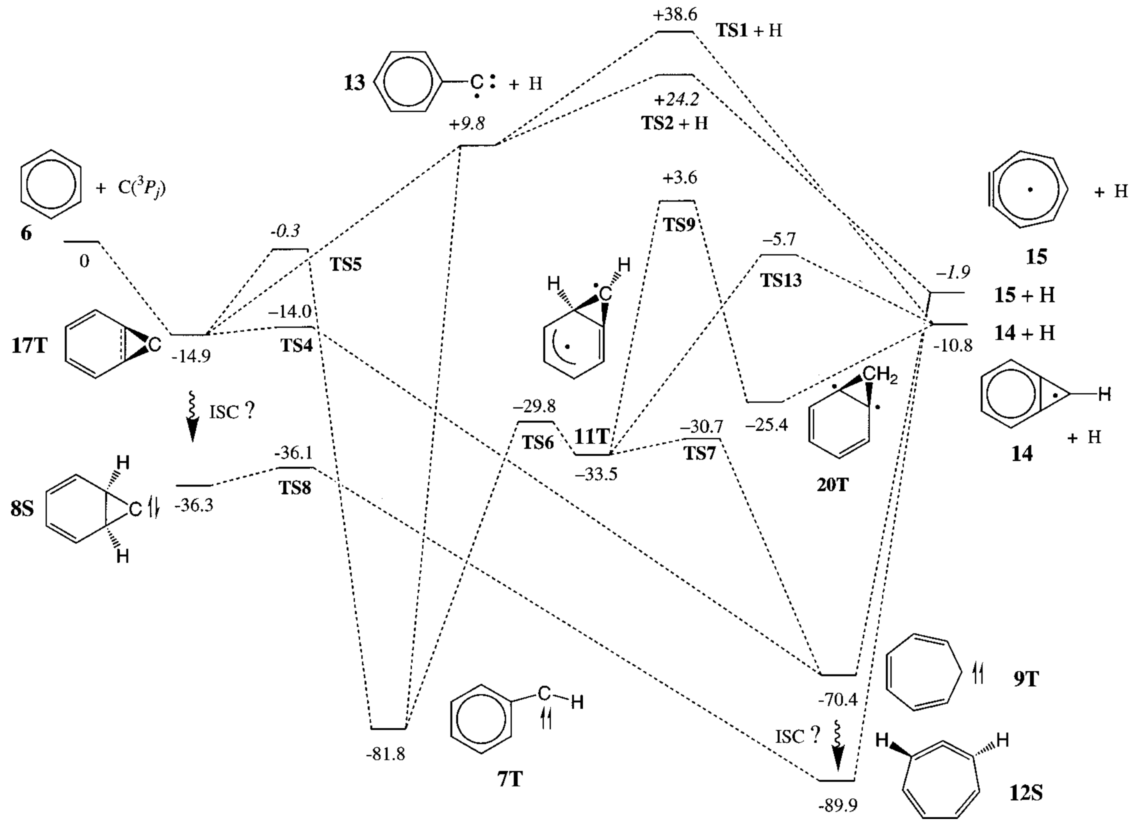
Although the crossed-beams reaction of benzene and $C(^3P_j)$ yields C_7H_5+H, we nonetheless determined the reaction enthalpies for the formation of smaller cyclic and linear hydrocarbons (see Scheme 9). Note that the linear geometry of the C_2H radical is falsely predicted to be a second order stationary point ($233i$ cm^{-1}, Π) at the B3LYP/6-31G* level; the linear $^2\Sigma$ state is a minimum at B3LYP/6-311+G** in agreement with experiment.[133] Consequently, the +8.5 kcal mol^{-1} endothermicity for the reaction to C_2H and the cyclopentadienyl radical was obtained by using the B3LYP/6-311+G** zero-point vibrational energies. However, we also encountered problems in the vibrational analysis of the two almost isoenergetic states ($^2B_1$ and $^2A_2$) of the cyclopentadienyl radical due to the limited numeric accuracy of the B3LYP approach. Recent work at B3LYP with a double-ζ quality basis set suggests that either the $^2B_1$ or the $^2A_2$ state of the cyclopentadienyl radical is a minimum.[118,134] Both states are minima at B3LYP/6-311+G**. Reducing the criteria for SCF convergence to 10^{-12} a.u., and using the fine integration grid (99 radial shells with 590 angular points per shell) employed by Rienstra-Kiracofe *et al.*,[118] the $^2B_1$ state is found to be a TS with the 6-311+G** basis set. However, the $^2B_1$ state is found to be a TS with the larger 6-311+G** basis set. Hence, we used the energy and ZPVE of the $^2A_2$ minimum for the evaluation of the reaction enthalpy of Eq. (2).

The abstraction of a hydrogen from benzene by the carbon atom to give the phenyl and CH radicals is endothermic by 29 kcal mol^{-1}. Even more endothermic are the reactions leading to the antiaromatic cyclobutadiene and cyclic (singlet cyclopropenylidene) or linear (triplet propargylene) C_3H_2.

Formation of the two radicals C_4H_3 and C_3H_3 are the least favorable processes investigated here. The geometry of C_4H_3, which has a singlet carbene center bridged by an allyl radical moiety, is intriguing and resembles that of cyclobutylidene (Fig. 4). Both carbenes have a puckered geometry with rather short transannular C1–C3 distances due to hyperconjugation involving the formally empty *p* orbital at the carbene center.



Scheme 9. Reaction enthalpies at 0K [B3LYP/6-311+G** with B3LYP/6-31G* ZPVE's except for equation (2) where B3LYP/6-311+G**ZPVE's were employed, see text] for the formation of various C_1 to C_6 species from the reaction of benzene and C(^3P_j).



Scheme 10. Schematic representation of the C_7H_6 potential energy surfaces obtained at the B3LYP6-311+G** level of theory. Where available, G2(B3LYP/MP2) data is given in italics.

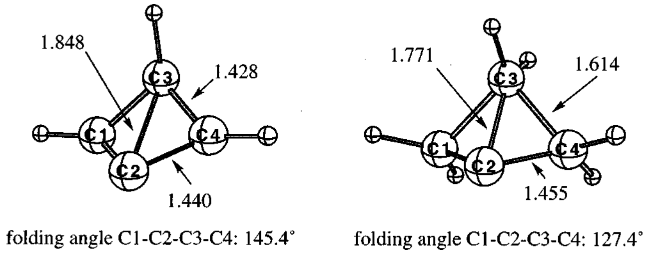


FIG. 4. Geometries of C_s symmetric singlet cyclobutylidene (right, from Ref. 120) and c-C_4H_3 (left) at the B3LYP/6-311+G** level of theory. Bond lengths are in Å, bond angles are in degrees.

The only exothermic reaction found is the formation of triplet cyclopentadienylidene and acetylene. These products could formally arise from either **9T** or **12S** by an acetylene elimination. Although we did not determine the barrier for this reaction (which presumably is not concerted), such a process surely requires a much higher exit barrier than the simple C–H cleavage. Hence, this reaction pathway is most likely not observed experimentally in spite of its overall favorable thermodynamics.

IV. CONCLUSIONS

The potential energy surface obtained and discussed in this work is given in Scheme 10. The theoretical investigations of the reaction of benzene with a single $C(^3P_j)$ atom clearly demonstrate that the complex **17T** is the decisive intermediate on the C_7H_6 potential energy surface. From **17T** three pathways are feasible: (a) ring opening via **TS4** to cycloheptatrienylidene (**9T**); (b) intersystem crossing to singlet bicyclo[4.1.0]hepta-2,4-diene-7-ylidene (**8S**) followed by ring opening to cycloheptatetraene (**12S**); and (c) intramolecular CH insertion to triplet phenylcarbene (**7T**) followed by a rearrangement via triplet bicyclo[4.1.0]hepta-1,4,6-triene (**11T**) to **9T**. The last reaction path involves a significantly higher barrier than path (a). In addition, $^3A_2$-**9T** could undergo intersystem crossing (ISC) to $^1A_2$-**9T** and finally relax to **12S**. But this ISC might be slower than observed for other carbenes, as the spin–orbit coupling between the $^3A_2$ and $^1A_2$ states is zero.

The formation of the seven-membered rings **9T** and **12S** is highly exothermic (-70 and -90 kcal mol^{-1}) and, as this reaction energy cannot be dissipated under the experimental single collision conditions, a hydrogen atom in the α-position to the dicoordinated carbon atom can be eliminated. Our analysis indicates that either **9T** or **12S** are the precursors of the seven-membered ring C_7H_5 radical **15**. Combining all available experimental and theoretical data suggests that the $C_6H_6+C(^3P_j)$ reaction yields **15** under single collision conditions.

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