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Interconversions of Phenylcarbene, Cycloheptatetraene, Fulvenallene, and Benzocyclopropene. A Theoretical Study of the C_7H_6 Energy Surface

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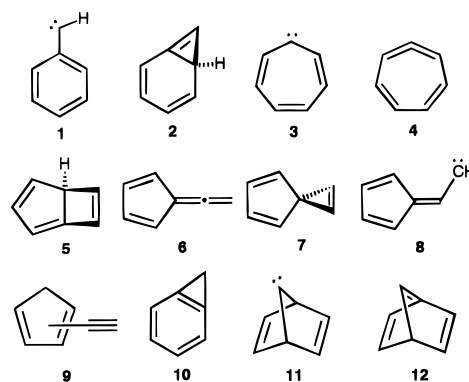
Ab initio calculations at the G2(MP2,SVP) and B-LYP/6-311+G(3df,2p)+ZPVE levels have been used to examine the potential energy surface of C_7H_6 . Fulvenallene (**6**) is the most stable C_7H_6 isomer considered in this study. 1-Ethynylcyclopentadiene (**9A**), benzocyclopropene (**10**), and 1,2,4,6-cycloheptatetraene (**4**) lie 12, 29, and 49 kJ mol^{-1} , respectively, above **6**. Phenylcarbene (**1**) is calculated to have a triplet ($^3A''$) ground state, 16 kJ mol^{-1} more stable than the singlet state ($^1A'$). Interconversion of **1** and **4** is predicted to have a moderate activation barrier, with the involvement of a stable bicyclic intermediate (bicyclo[4.1.0]hepta-2,4,6-triene, **2**). However, **2** is found to lie in a shallow potential energy well with a small barrier (8 kJ mol^{-1}) to rearrangement to **4**. At the G2(RMP2,SVP)//QCI level, the 3A_2 and 3B_1 triplet states of cycloheptatrienylidene (**3**) are predicted to lie very close in energy. The singlet "aromatic" cycloheptatrienylidene ($^1\mathbf{3}$, 1A_1) is found to be a transition structure interconverting two chiral cyclic allenes (**4**) and it lies $\sim 25 \text{ kJ mol}^{-1}$ below the triplet states. Bicyclo[3.2.0]hepta-1,3,6-triene (**5**) is predicted to be a stable equilibrium structure, lying in a significant energy well. Rearrangement of **4** to **5** constitutes the rate-determining step for the rearrangement of phenylcarbene to fulvenallene (**6**), the ethynylcyclopentadienes (**9**), and spiro[2.4]heptatriene (**7**). Rearrangement of **9A** to **6**, via a 1,4-H shift, requires a large barrier of 325 kJ mol^{-1} . Rearrangement of benzocyclopropene (**10**) to **6** involves a methylenecyclohexadienylidene intermediate (**27**) and is associated with an energy barrier of 223 kJ mol^{-1} . The calculated mechanisms and energetics for the interconversions of various C_7H_6 isomers are in good accord with experimental results to date.

Introduction

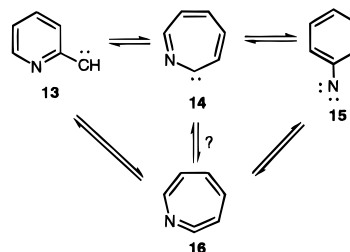
The rearrangements and interconversions of arylcarbenes and arylnitrenes have fascinated chemists since their discovery in 1968–1970,^{1–5} and they have been the subject of intensive investigation as documented in several reviews.⁶

The major species of interest on the C_7H_6 energy surface (**1**–**12**) are shown in Chart 1. The ring expansion of phenylcarbene (**1**), taking place on flash vacuum thermolysis (FVT) of phenyldiazomethane, was originally formulated in terms of (singlet) cycloheptatrienylidene (**3**), and this reaction was shown to be reversible in the gas phase.^{4,5} Work on FVT^{7,8} (and later also matrix photolysis)⁹ of the tolylcarbenes further documented the reversibility of reactions analogous to $\mathbf{1} \rightleftharpoons \mathbf{3}$. An analo-

Chart 1



gous FVT reaction interconverts 2-pyridylcarbene (**13**) and phenylnitrene (**15**) via an intermediate or transition state that has the geometry of 2-azacycloheptatrienylidene (**14**).^{1,2}



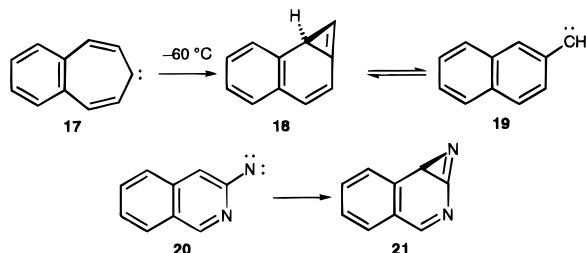
However, Chapman and co-workers showed in elegant Ar matrix isolation studies that the seven-membered ring

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formed on either FVT or matrix photolysis of **1** (or phenyldiazomethane) is not the carbene **3** but the allene **4**.¹⁰ and likewise, the species interrelating **13** and **15** is not carbene **14** but ketenimine **16**.^{11,12} MNDO calculations by Waali indicated that the planar seven-membered ring singlet carbene (**3**) is in fact a transition state for the inversion of the nonplanar allene **4**.¹³

In neither of the experimental studies cited so far was there any evidence for the existence of a bicyclo[4.1.0]-hepta-2,4,7-triene intermediate (**2**).^{10,14} If formed, it cannot be detected by matrix isolation IR spectroscopy. On the other hand, there is no doubt of the existence of benzannelated analogs, e.g. **18**, which is formed by rearrangement of **17** (from the diazo compound) at -60



°C and can be trapped in a Diels–Alder reaction with cyclopentadiene.¹⁵ The dibenzo analog behaves similarly.¹⁵ Furthermore, Ar matrix photolysis of **19** gives **18**, and this reaction is photochemically reversible.¹⁶ Analogous evidence for bicyclic azirines in the Ar matrix photolysis of naphthyl azides¹⁷ and 3-azidoisoquinoline (**20** → **21**)^{6f} has also been reported.

The activation energies for the carbene (or nitrene) rearrangements, e.g. **1** ⇌ **2**, **2** ⇌ **4**, or **1** ⇌ **4**, etc. are not known, and they are not easily amenable to experiment. The thermal reaction **1** ⇌ **4** only takes place in the gas phase under FVT conditions (> ca. 300 °C). The reaction can, however, be made observable in solution by introduction of sterical hindrance in the 1,3-positions flanking the allene moiety in **4** (or the 2,7-positions in **3**), thereby suppressing intermolecular reactivity.¹⁸ This suggests that there is only a modest barrier between **1** and **4**.

The ground state of **1** is known from ESR studies¹⁹ to be the triplet (³**1**) but the singlet-triplet splitting is small

(4–5 kcal/mol), and the chemistry observed in solution is frequently that of the reactive singlet (¹**1**).^{20,6g} The interconversions on the C₇H₆ energy surface presumably involve (primarily) the singlet species. ³**1** cannot be directly observed by ESR in the FVT of phenyldiazomethane or of precursors of **4**. However, ³**15** is more long-lived and has been successfully matrix isolated and observed by ESR following FVT of both phenyl azide and 2-(diazomethyl)pyridine.²¹

As mentioned above, singlet cycloheptatrienylidene (¹**3**) is now thought to be the transition state (TS) between invertomers of **4**.¹³ Two groups have reported ESR spectra ascribed to Ar matrix-isolated ³**3**.^{21,22} Unfortunately, the two spectra are quite different, and it is clear that two different species were produced. The problem lies in the instability of diazocycloheptatriene, which can be generated by thermolysis of the sodium or lithium salts of tropone tosylhydrazone at 90–100 °C and directly isolated in Ar matrices at 10 K. Subsequent photolysis of the Ar matrix provided Kuzai, Lüerssen, and Wentrup with the ESR spectrum of cycloheptatrienylidene, ³**3**.²¹ The ESR spectrum reported by the Chapman group was obtained by irradiation of a diazo compound generated from the reaction of tropone tosylhydrazone with butyllithium,²² a reaction giving an unknown but apparently butylated diazo compound. Control experiments demonstrated that the tropone tosylhydrazone salt prepared by the BuLi method did not regenerate the free tosylhydrazone on hydrolysis; nor did it reproduce an appreciable quantity of heptafulvalene on thermolysis.²³ The salts prepared with LiH or NaH did regenerate the free tosylhydrazone on hydrolysis, and they gave almost quantitative yields of heptafulvalene on thermolysis.²³ It is now clear that the spectrum reported by the Chapman group was incorrectly assigned.²⁴

The ESR and UV spectrum of ³**17** is known,²⁵ and the naphtho-,²¹ dibenzo-, and tribenzo-analogs^{26,27} are relatively stable species, the latter two being observable by ESR and UV at 77 K.^{26,27} ³**3**, in contrast, is not observable by ESR at 77 K, and the Ar matrix-isolated species does not obey the Curie law.²¹ An intriguing but unproven possibility is that ³**3** exists in a shallow minimum, where it can be populated directly on photochemical generation from the diazo precursor. On warming, it crosses to the singlet surface and hence **4**. More experimental work is required in this area, but the scenario just mentioned would be in agreement with ab initio calculations at the DZ+d SCF/TCSCF level.²⁸

If the interconversion of **1** and **4** is complicated enough, it becomes worse when we enquire about the mechanism

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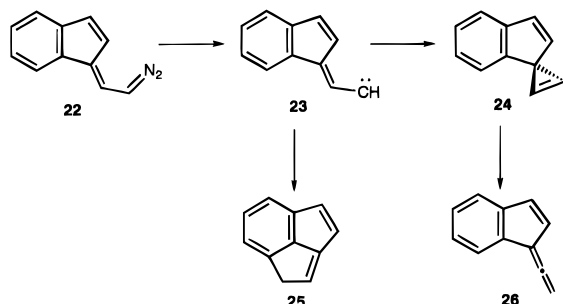
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of ring contraction to the final thermal product on the C_7H_6 energy surface, viz. "fulvenallene" (vinylidenecyclopentadiene) (**6**). Extensive labeling studies have revealed the route **1** \rightarrow **4** \rightarrow **5** \rightarrow **6**.²⁹ The path from **5** to **6** likely involves spiro compound **7** and/or vinylcarbene **8**.²⁹ There is direct experimental evidence for benzoanalogues of **7** and **8** in the FVT of 1-(diazooethylidene)indene (**22**), which yields **24**–**26** as isolable/observable products.³⁰



There are several more C_7H_6 species of interest. Benzocyclopropene (**10**) gives fulvenallene (**6**) in high yield on FVT.³¹ Generation of **11** results in the formation of a dimer of **5** as well as rearrangement to **4** and **6**.³² Generation of **12** results in **4** and **6**.^{33,10b} Some of these species as well as *N*-containing analogs of **1**–**10** will be the subjects of future publications.

In this paper we investigate the C_7H_6 potential energy surface, in particular that part involving species **1**–**10**, using modern ab initio molecular orbital theory. Previous calculations confined to species **1**–**4** at the INDO,³⁴ MINDO/3,³⁵ MNDO,¹³ and ab initio (4–31G//STO-3G),³⁶ or DZ+d SCF/TCSCF²⁸ levels of theory as well as combined force field-SCF calculations¹⁴ have been reported. With the availability of ever faster computers, it is now feasible to study this relatively large system at a reliable level of theory. We have employed the G2-(MP2,SVP)³⁷ theory as well as density functional theory³⁸ to investigate the mechanisms of the interconversions of the highly reactive C_7H_6 intermediates. We note that the rearrangements and energy levels of **1**–**4** have been examined in great details very recently by Matzinger *et al.*³⁹ and Schreiner *et al.*⁴⁰ using high level CCSD(T) and CASPT2N calculations.

Computational Methods and Results

Standard ab initio molecular orbital calculations⁴¹ were carried out with the GAUSSIAN 92/DFT⁴² series of programs. The structures and energies of the C_7H_6 species were examined at the G2(MP2,SVP) level of theory.³⁷ This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* energies together with zero-point vibrational and isogyric corrections. The G2(MP2,-SVP) theory is different from the standard G2 theory⁴³ in two aspects: (1) the basis-set extension energy contributions are obtained at the MP2 level and (2) the QCISD(T) energies are evaluated using the 6-31G* basis set. It has been shown that the accuracy of the G2(MP2,-SVP) method is comparable to that of the G2(MP2) theory⁴⁴ but computationally more efficient.³⁷ Harmonic vibrational frequencies were computed at the HF/6-31G* and MP2/6-31G* levels in order to characterize the stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point vibrational energies (ZPVEs). The frozen-core approximation was used for all MP2 and QCISD(T) calculations. Unless otherwise noted, the relative energies discussed below correspond to the G2(MP2,SVP) values.

Significant spin contaminations were found for the open-shell species examined in this paper. Thus, it is not advisable to use the UMP2 procedure for geometry optimizations and energy calculations. We have modified the G2(MP2,SVP)³⁷ method slightly to obtain more reliable energies for the singlet and triplet states of phenylcarbene and cycloheptatrienylidene: (1) geometry optimizations were carried out at QCISD/6-31G* level and (2) basis-set extension energy contributions were calculated using the restricted Møller–Plesset (RMP) theory.⁴⁵ We designate this method G2(RMP2,SVP)/QCI.

In recent years, density functional theory (DFT)³⁸ has emerged as a promising approach for investigating organic reaction mechanisms. Here, we have employed the B-LYP formulation⁴⁶ of DFT, i.e. the Becke exchange functional^{46a} and the Lee–Yang–Parr correlation functional.^{46b} Geometry optimizations of all structures were carried out at the B-LYP/6-31G* level. Harmonic vibrational frequencies and infrared intensities were computed at these equilibrium geometries. A recent study has shown that the unscaled B-LYP/6-31G* frequencies are suitable for reliable prediction of experimental frequencies.⁴⁷ The calculated IR spectra for all C_7H_6 equilibrium structures are given in the supporting information. Improved relative energies were obtained through B-LYP/

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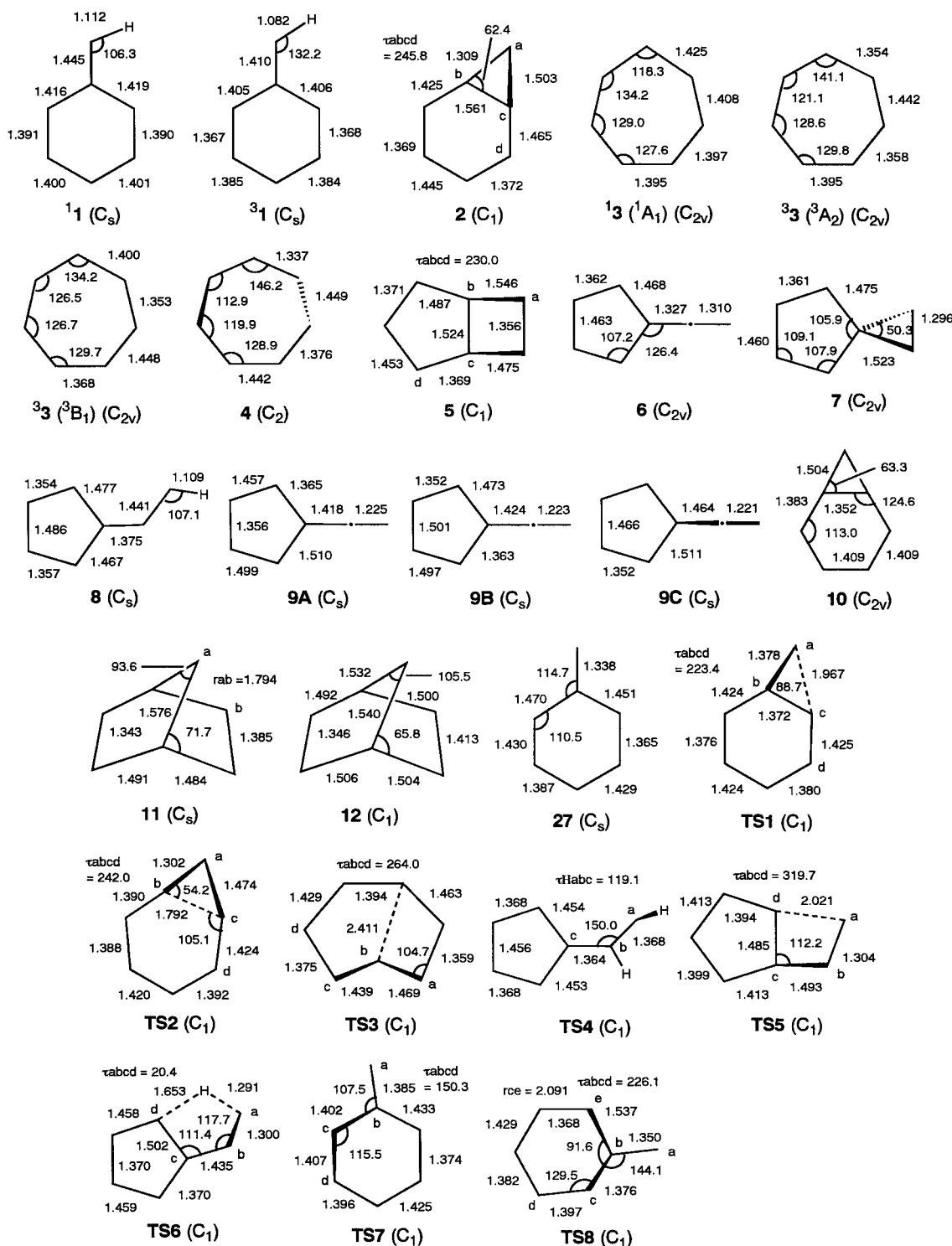


Figure 1. Optimized geometries (MP2/6-31G*) for the equilibrium and transition structures of C₇H₆. **9A**, **9B**, and **9C** = 1-ethynyl-, 2-ethynyl-, and 5-ethynylcyclopenta-1,3-diene, respectively.

6-311+G(3df,2p) calculations, based on the B-LYP/6-31G* optimized geometries. The best DFT energies correspond to the B-LYP/6-311+G(3df,2p)/B-LYP/6-31G* values, with zero-point energy contributions (evaluated from the B-LYP/6-31G* vibrational frequencies).

The full set of optimized (MP2(FC)/6-31G*) C₇H₆ equilibrium and transition structures is displayed in Figure 1. Calculated G2(MP2,SVP) and B-LYP/6-311+G(3df,2p) total energies and ZPVE (B-LYP/6-31G*) for all species are collected in Table 1. Schematic potential energy profiles for interconversions of C₇H₆ isomers are shown in Figure 2. Calculated (B-LYP/6-31G*) IR spec-

tra of the C₇H₆ equilibrium structures are summarized in Table 2 (supporting information). Throughout this paper, bond lengths are given in angstroms and bond angles in degrees, and refer, unless otherwise noted, to the MP2/6-31G* values.

Discussion

Phenylcarbene (1). Consistent with earlier STO-3G³⁶ and 3-21G⁴⁸ calculations, both singlet (¹1, ¹A') and triplet (³1, ³A') phenylcarbene are predicted to have a planar geometry. The triplet state has a wider carbenic bond angle (132.2°) than the singlet (106.3°). As in the case

Table 1. Calculated Total Energies (hartrees) and ZPVE (kJ mol⁻¹)

species	state	symmetry	G2	B-LYP/6-311+	ZPVE ^b
			(MP2,SVP)	G(3df,2p) ^a	
1	¹ A'	C _s	-269.68487	-270.18925	260.0
3	³ A''	C _s	-269.68720	-270.19575	260.5
2	¹ A	C ₁	-269.69017	-270.18909	261.4
13	¹ A ₁	C _{2v}	-269.66913	-270.18230	260.2
33 (³ A ₂)	³ A ₂	C _{2v}	-269.66220	-270.17969	256.4
33 (³ B ₁) ^c	³ B ₁	C _{2v}	-269.65483	-270.17660	253.8
4	¹ A	C ₂	-269.71258	-270.21760	264.2
5	¹ A	C ₁	-269.69879	-270.19235	263.7
6	¹ A ₁	C _{2v}	-269.73132	-270.23502	260.7
7	¹ A ₁	C _{2v}	-269.69603	-270.19110	258.7
8	¹ A'	C _s	-269.63282	-270.13367	252.4
9A	¹ A'	C _s	-269.72677	-270.22350	258.3
9B	¹ A'	C _s	-269.72509	-270.21931	258.8
9C	¹ A'	C _s	-269.71575	-270.20880	258.7
10	¹ A ₁	C _{2v}	-269.72010	-270.22365	267.2
11	¹ A'	C _s	-269.65190	-270.13171	262.2
12	¹ A	C ₁	-269.61379	-270.09775	256.9
27	¹ A'	C _s	-269.66814	-270.18145	260.3
TS1	¹ A	C ₁	-269.66367	-270.16899	258.6
TS2	¹ A	C ₁	-269.68692	-270.18844	259.1
TS3	¹ A	C ₁	-269.62384	-270.12700	251.5
TS4	¹ A	C ₁	-269.63097	-270.13927	246.5
TS5	¹ A	C ₁	-269.65344	-270.15181	253.9
TS6	¹ A	C ₁	-269.60280	-270.09941	241.5
TS7	¹ A	C ₁	-269.66730	-270.18140	260.0
TS8	¹ A	C ₁	-269.63519	-270.14204	248.3

^a Based on B-LYP/6-31G* geometry ^b B-LYP/6-31G* (unscaled) values. ^c The ³B₁ state is calculated to be a first-order saddle point at the B-LYP/6-31G* level.

of methylene, the triplet is the ground state of phenylcarbene. At both the G2(MP2,SVP) and G2(RMP2,SVP)/QCI levels, the singlet lies 6 kJ mol⁻¹ above the triplet. For the parent methylene, the G2(RMP2,SVP)/QCI singlet–triplet separation (Δ_{ST} gap) is 28 kJ mol⁻¹ compared to the experimental value of 38 kJ mol⁻¹.⁴⁹ If we assume that there is a similar error of about 10 kJ mol⁻¹ in the G2(RMP2,SVP)/QCI prediction for phenylcarbene, this leads to our best predicted singlet–triplet separation of 16 kJ mol⁻¹, in good agreement with experimental²⁰ and recent theoretical^{39,40} findings. This small energy difference between the two spin states of phenylcarbene is consistent with the fact that both singlet and triplet types of reactions have been observed.²⁰ The smaller Δ_{ST} gap in phenylcarbene compared with methylene may be explained in terms of the orbital interaction between a phenyl substituent and a carbene center (Figure 3). In the planar structure of **1**, the spⁿ orbital of the carbene lies in the nodal plane of the π orbital (HOMO) of the phenyl substituent. Thus, the spⁿ orbital is unperturbed by the phenyl substituent. On the other hand, the 2p (i.e. 2p_z) orbital of the carbene is raised in energy by the phenyl substituent due to the favorable overlap between the carbene 2p orbital and the aromatic π orbital. This conjugation is reflected in the shorter C(ring)–C(exocyclic) bond length (1.410 Å) in **31** (Figure 1). As a consequence, the separation of the 2p and spⁿ orbitals is increased and the triplet state is destabilized.

Bicyclo[4.1.0]hepta-2,4,6-triene (2) is 14 kJ mol⁻¹ more stable than the singlet phenylcarbene (**1**), but lies 59 kJ mol⁻¹ above the cycloheptatetraene (**4**). The stability of **2** depends on the barriers for intramolecular rearrangements to **1** and **4**. Rearrangement of **2** to

singlet phenylcarbene (**1**), via transition structure **TS1**, has a significant barrier of 69 kJ mol⁻¹, while ring expansion of **2** to **4**, via transition structure **TS2**, has a barrier of just 8 kJ mol⁻¹. Therefore, an experimental observation of **2** will be virtually impossible. Similar computational conclusions have been reached by recent CCSD(T) and CASSCF calculations.^{39,40} This result is in accord with experimental studies to date which found no evidence for the existence of bicyclo[4.1.0]hepta-2,4,6-triene.^{10,14} However, as mentioned in the introduction, the bicyclic intermediates **18** and **21** are clearly involved in the carbene and nitrene rearrangements of the benzannelated derivatives (**17**, **19**, and **20**). Preliminary calculations at the MP2/6-31G* level indicate that the cyclic allenes are destabilized by annelation.⁵⁰ In both cases, the bicyclic intermediates (**18** and **21**) are significantly more stable than the corresponding seven-membered ring allenes.

Since **TS1** is the highest energy point of the reaction sequence **1** → **TS1** → **2** → **TS2** → **4**, the predicted barrier for the rearrangement of **1** to **4** is 55 kJ mol⁻¹ (128 kJ mol⁻¹ for the reverse reaction). The calculated moderate barriers are consistent with the experimental finding that the **1** ⇌ **4** interconversion is rapid in the gas phase.

1,2,4,6-Cycloheptatetraene (4). This strained cyclic allene is calculated to have a chiral equilibrium geometry (C₂ symmetry), in agreement with experimental evidence for chirality.⁵¹ The strong nonplanar distortion in **4** is due to the presence of the allenic moiety. The calculated C=C bond length and CCC angle of the allene moiety in **4** are 1.337 Å and 146.2°, respectively (Figure 1). This cyclic allene is 67 kJ mol⁻¹ more stable than phenylcarbene (**1**). Chapman and co-workers have generated **4** by matrix irradiation of phenylcarbene at 10 K.¹⁰ The observed IR absorptions (1824 and 1816 cm⁻¹) are consistent with the allenic structure. The assignment is readily confirmed by B-LYP/6-31G* frequency calculation which predict a C=C=C stretching frequency of 1813 cm⁻¹.³⁹

Cycloheptatrienylidene (3). Contrary to the earlier STO-3G results,³⁶ the 6 π -electrons in singlet **3** (**3**, ¹A₁) are strongly delocalized, with C–C bond lengths in the range 1.395–1.408 Å (Figure 1). At the HF/6-31G* level, this closed-shell singlet carbene is calculated to be a local minimum on the C₇H₆ potential energy surface. However, at the correlated MP2/6-31G* level, **3** is a transition structure for interconversion of two chiral cyclic allenes **4**. This is readily confirmed by higher level frequency calculations at the MP2/6-311G** and QCISD/6-31G* levels. It is important to note that Matzinger *et al.*³⁹ and Schreiner *et al.*⁴⁰ have examined the open-shell singlet states (¹A₂ and ¹B₁) of **3** and found that the ¹A₂ state is significantly more stable than the ¹A₁ state.⁵²

We have considered two triplet states of **3** (**33**), ³A₂, and ³B₁. At the G2(MP2,SVP) level, both triplet states lie reasonably close in energy, with ³A₂ favored by 19 kJ mol⁻¹. ³A₂ is also calculated to lie 19 kJ mol⁻¹ above the singlet ¹A₁ (**3**) state. Both triplet states were found to have significant spin contamination, $\langle S^2 \rangle = 2.20$ (³A₂) or 2.41 (³B₁). Therefore, we have calculated the singlet and triplet states of cycloheptatrienylidene with the G2-

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(52) These open-shell systems cannot be calculated by the single-configuration methods employed in this study. Further work is required to provide a definitive answer as to the stability of the open-shell singlet of cycloheptatrienylidene.

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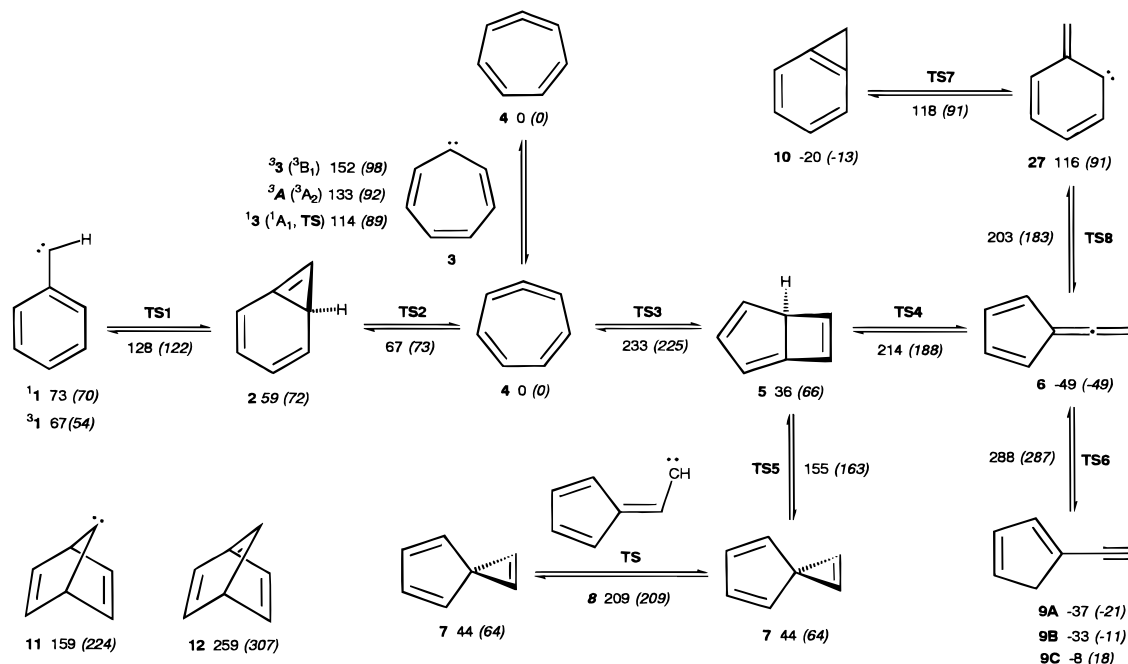


Figure 2. Schematic energy diagram showing the interconversions of the C₇H₆ isomers (G2(MP2,SVP) values with B-LYP/6-311+G(3df,2p)+ZPVE values in parentheses, energy unit: kJ mol⁻¹). Calculated G2(RMP2,SVP)//QCI (*E_c*) relative energies for ¹A₁, ³A₂, and ³B₁ states of **3** are 0, 23, and 25 kJ mol⁻¹, respectively. **9A**, **9B**, and **9C** = 1-ethynyl-, 2-ethynyl-, and 5-ethynylcyclopenta-1,3-diene, respectively.

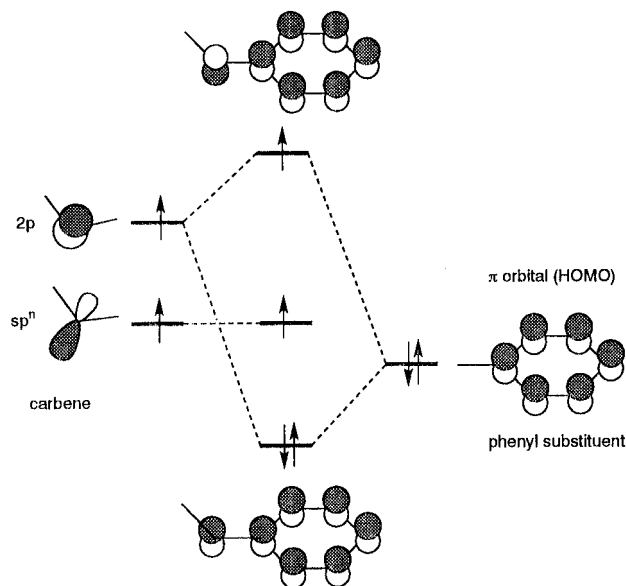


Figure 3. Orbital interaction diagram for phenylcarbene.

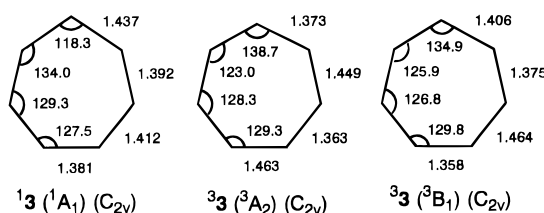


Figure 4. QCISD/6-31G* geometries for ¹A₁, ³A₂, and ³B₁ of cycloheptatrienyldiene (**3**).

(RMP2,SVP)//QCI method. First, we note that the QCISD-optimized geometry of ³A₂ (Figure 4) is significantly different from the UMP2 structure (Figure 1). The use of RMP2 (instead of the standard UMP2) energies for additivity approximation is justified by comparison of

Table 2. Calculated Relative Energies (kJ mol⁻¹) of Singlet and Triplet States of Cycloheptatrienyldiene (**3**)

level ^a	³ B ₁	³ A ₂	¹ A ₁
UMP2/6-31G*	0.0	1.8	-77.5
PMP2/6-31G*	0.0	21.7	-21.2
RMP2/6-31G*	0.0	-3.8	-8.0
QCISD/6-31G*	0.0	7.6	15.1
QCISD(T)/6-31G*	0.0	2.4	-0.9
UMP2/6-311+G(3df,2p)	0.0	-3.2	-88.7
RMP2/6-311+G(3df,2p)	0.0	-8.4	-22.6
G2(RMP2,SVP)//QCI ^b	0.0	-2.2	-24.8

^a Based on QCISD/6-31G* optimized geometries. ^b *E_c* values.

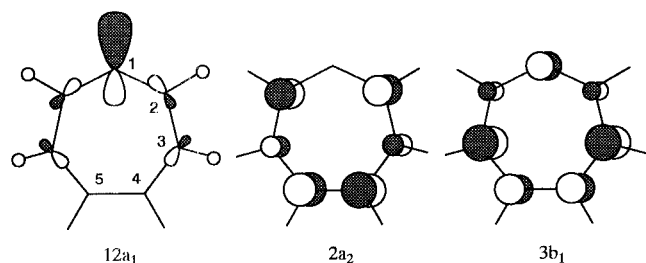
UMP2 and RMP2 energies with higher level QCISD(T) results. As evidenced in Table 2, the UMP2 relative energies are in serious disagreement with the QCISD(T) values. The RMP2 energies, on the other hand, are in better agreement with the QCISD(T) results. Note that the projected Møller–Plesset method (PMP2)⁵³ also gives a poor prediction of the relative energies of **3** (Table 2). At the QCISD(T)/6-31G*//QCISD/6-31G* level, the triplets ³A₂ and ³B₁ are very close in energy, with ³B₁ slightly favored by 2 kJ mol⁻¹ (Table 2). There is a reversal of energy ordering at the G2(RMP2,SVP)//QCI (*E_c*) level,⁵⁴ with ³A₂ preferred by 2 kJ mol⁻¹. This result is in agreement with recent CASPT2N calculations of Schreiner *et al.*⁴⁰ The prediction of a stable triplet state of **3** is in agreement with the observation of cycloheptatrienyldiene by ESR spectroscopy,²¹ although current calculations do not permit a clear conclusion as to which state is being observed. Since the singlet ¹A₂ state is calculated to lie lower in energy than the closely related ³A₂ state,^{39,40} the ³A₂ carbene may be expected to easily

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(54) The calculated UHF/6-31G* zero-point energy difference between ³B₁ and ³A₂ of **3** is 19 kJ mol⁻¹, in serious disagreement with the UB-LYP/6-31G* values (-3 kJ mol⁻¹, Table 1). We believe the UHF/6-31G* calculated frequencies are very poor because of spin contamination problem, and the zero-point energies for these closely related species should have similar values.

undergo intersystem crossing to 1A_2 . Hence, it is likely that 3B_1 is the triplet observed in the ESR experiment. The triplets are calculated to lie above the singlet 1A_1 state (by ~ 25 kJ mol $^{-1}$, Table 2). Note that both the singlet and the triplets of **3** are significantly higher in energy (>100 kJ mol $^{-1}$) than cycloheptatetraene (**4**).

Triplets 3A_2 and 3B_1 have wider CCC angles than the singlet state (1A_1) at the carbenic center. Furthermore, both triplets have significantly different C–C bond lengths (Figure 4). The interesting structural features may be readily understood by considering their electronic structures. The highest occupied molecular orbitals of the two triplets are $12a_1$, $2a_2$, and $3b_1$.



The singlet 1A_1 state has two electrons occupying the $12a_1$ orbital. Excitation of one electron from the $12a_1$ orbital to the $3b_1$ orbital leads to the 3B_1 triplet state. The $3b_1$ orbital is C_2 – C_3 and C_4 – C_5 bonding but C_1 – C_2 and C_3 – C_4 antibonding. As a consequence, there is shortening of the C_2 – C_3 and C_4 – C_5 bonds but lengthening of the C_1 – C_2 and C_3 – C_4 bonds in going from the singlet 1A_1 to the triplet 3B_1 state (Figure 4). For the triplet 3A_2 state, the highest occupied molecular orbitals are $12a_1$ and $2a_2$. The $2a_2$ orbital is C_3 – C_4 bonding but C_2 – C_3 and C_4 – C_5 antibonding. Hence, 3A_2 has shorter C_3 – C_4 and C_4 – C_5 bond and a longer C_2 – C_3 bond (Figure 4).

Fulvenallene (6) and Bicyclo[3.2.0]hepta-1,3,6-triene (5). Fulvenallene is the lowest-energy species among all the C_7H_6 isomers considered in this study. It is 49 kJ mol $^{-1}$ more stable than cycloheptatetraene (**4**). The rearrangement of **4** to **6** involves the sequence of reactions **4** \rightarrow **TS3** \rightarrow **5** \rightarrow **TS4** \rightarrow **6** (Figure 2). The bicyclic structure, bicyclo[3.2.0]hepta-1,3,6-triene (**5**), is found to be a stable intermediate in the transformation of **4** to **6**. It lies 36 kJ mol $^{-1}$ higher in energy than **4**. Rearrangement of **5** to **4**, via transition structure **TS3**, has a large barrier of 197 kJ mol $^{-1}$, while ring opening of **5** to **6**, via transition structure **TS4**, has a similar barrier of 178 kJ mol $^{-1}$. Since **TS3** corresponds to the highest energy point on the reaction profile, the predicted overall barrier for the rearrangement of **4** to **6** is 233 kJ mol $^{-1}$. This result is in accord with the experimental observations that the formation of **6** from phenylcarbene (**1**) requires high-temperature FVT conditions.^{4,5,10,14}

Spiro[2.4]heptatriene (7). The spiro compound is predicted to be a stable equilibrium structure on the C_7H_6 potential energy surface; it lies 44 kJ mol $^{-1}$ higher in energy than **4**. **7** can be formed from the cyclic allene **4** via the bicyclic intermediate **5**. Rearrangement of **7** to **5**, via transition structure **TS5**, requires an energy barrier of 111 kJ mol $^{-1}$. However, **TS3** lies higher in energy than **TS5** (by 78 kJ mol $^{-1}$). Thus, similar to the **4** \rightleftharpoons **6** interconversion, the formation of **5** is the rate-determining step for the interconversion of **4** and **7**. Although bicyclo[3.2.0]hepta-1,3,6-triene (**5**) is calculated to lie in a moderate potential well (119 kJ mol $^{-1}$), it is

relatively easily traversed under high-temperature FVT conditions. Hence, the direct observation of **5** will not be straightforward.^{32a}

It has been postulated that the interconversion of **1** and **6** may involve the vinylcarbene intermediate **8**.²⁹ Our calculations indicate that this planar vinylcarbene is not a stable equilibrium structure, but corresponds to a transition structure interconverting two spiro compounds (**7**). Note that the triplet state of **8** is predicted to be a stable species on the C_7H_6 potential energy surface and is more stable than the singlet state.

Ethynylcyclopentadiene (9). We have considered all three possible structures of **9**, namely, 1- (**9A**), 2- (**9B**), and 5-ethynylcyclopentadiene (**9C**). **9A** is the most stable form of **9**, while **9B** and **9C** lie 4 and 29 kJ mol $^{-1}$, respectively, above **9A**. **9A** is the next most stable C_7H_6 isomer considered in this study; it lies 12 kJ mol $^{-1}$ higher in energy than fulvenallene (**6**). **9A** can interconvert with **6** via a 1,4-H shift (transition structure **TS6**). The calculated barrier for this rearrangement is 325 kJ mol $^{-1}$, and it is likely that it takes place via a wall-catalyzed reaction. Thus, the formation of **9** from phenylcarbene may involve the following C_7H_6 isomers: **1** \rightarrow **4** \rightarrow **5** \rightarrow **6** \rightarrow **9**.^{6a} Experimental studies have shown that **9** can be generated from **1** under high-temperature FVP conditions.^{4,5,6a,10,14}

Benzocyclopropene (10). This bicyclic compound has been the subject of considerable attention because it represents the simplest annelated system involving an aromatic nucleus and a cyclopropene ring. The deformation of the benzene moiety in **10** has been discussed in terms of the Mills–Nixon effect.⁵⁵ The MP2/6-31G* geometry (Figure 1) readily reproduces the X-ray structure of **10**,⁵⁶ with the calculated bond lengths uniformly longer by ~ 0.02 Å. The annelated C–C bond and the adjacent bonds are shortened while the rest of the C–C bonds are elongated. Benzocyclopropene is 29 kJ mol $^{-1}$ higher in energy than fulvenallene (**6**). Interconversion of **10** and **6** is predicted to involve a six-membered ring carbene intermediate, 6-methylenecyclohexa-2,4-dienylidene (**27**), and the reaction sequence **10** \rightarrow **TS7** \rightarrow **27** \rightarrow **TS8** \rightarrow **6**. **27** is calculated to lie in a shallow potential well with a small barrier (2 kJ mol $^{-1}$) to rearrangement to **10**. The calculated overall activation barrier for the **10** \rightarrow **6** rearrangement is 223 kJ mol $^{-1}$. The reaction is quantitative under FVT conditions.³¹

7-Norbornadienylidene (11). Gleiter and Hoffman have previously examined the stability of the so-called foiled methylene (**11**) using extended Hückel calculations.⁵⁷ Our calculations confirmed the existence of this nonclassical minimum in the singlet configuration. The optimized structure of this carbene has C_s symmetry, rather than C_{2v} symmetry (Figure 1). The unusual geometry of **11** can be understood in terms of the intramolecular addition of the carbene center to one of the C=C double bonds.⁵⁷ However, such interaction would lead to a highly strained system, with one carbon having four bonds on one side of the plane. The optimal structure, therefore, represents an intermediate geometry. This foiled carbene is predicted to lie 159 kJ mol $^{-1}$ above the cyclic allene **4**. Interestingly, **11** is significantly

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(56) Neidlein, R.; Christen, D.; Poignee, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Perez, C.; Hübner, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 295.

(57) Gleiter, R.; Hoffman, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457.

more stable (by 100 kJ mol⁻¹) than the related alkene, bicyclo[2.2.1]cyclohepta-1⁷,2,5-triene (**12**).^{10b,33} Brown and Jones have reported evidence for the existence of the carbene **11** and they postulated that **11** can interconvert with **4** via the bicyclic intermediate **5**.^{32a}

DFT Energies. As seen in Figure 2, the calculated B-LYP/6-311+G(3df,2p)+ZPVE relative energies are in good qualitative agreement with the G2(MP2,SVP) results except for compounds **11** and **12**. In both cases, B-LYP calculations significantly underestimate the stabilities of the bridged bicyclic molecules. It also appears that the B-LYP theory overestimates the stabilities of the singlet and triplet states of cycloheptatrienylidene (**3**). Finally, we note that the calculated B-LYP/6-31G* relative energies are close to the results obtained using the larger 6-311+G(3df,2p) basis set (± 4 kJ mol⁻¹), suggesting that the basis set effect is small for the DFT calculations.

Conclusions

In this paper, we have presented the results of a comprehensive study of the C₇H₆ potential energy surface. The calculated mechanisms and energetics for the interconversions of various C₇H₆ isomers are in good agreement with experimental observations.⁶ Interconversion of phenylcarbene (**1**) and cycloheptatetraene (**4**) is a facile process in the gas phase, requiring only a moderate activation barrier, and the absence of this process in solution is due to rapid intermolecular reactions of the carbenes. The bicyclic intermediate **2** is involved in the interconversion of **1** and **4** but is predicted to lie a shallow potential energy well of only ca. 8 kJ mol⁻¹ depth, and is therefore unlikely to be observed experimentally. In contrast, suitable benzoannulation destabilizes the seven-membered ring allene relative to the cyclopropene, making such intermediates readily

observable (**18** and **21**). The ultimate rearrangement of **1** to fulvenallene **6** requires high temperatures under FVT conditions (600–1000 °C), in agreement with the high calculated barriers (233 kJ mol⁻¹). The electrocyclic ring closure of **4** to bicyclo[3.2.0]heptatriene **5** is the rate-determining step for the rearrangements of **1** to **6** and spiroheptatriene **7**. Rearrangement of benzocyclopropene **10** to **6**, via the six-membered ring carbene **27**, has a calculated overall barrier of 223 kJ mol⁻¹. The reaction is very efficient under FVT conditions (≥ 515 °C) because once the carbene **27** is formed, only a modest barrier (87 kJ mol⁻¹) separates it from fulvenallene (**6**). Isomerization of fulvenallene (**6**) to ethynylcyclopentadienes (**9**) requires a high barrier (calculated 337 kJ mol⁻¹ for **6** → **9A**); the yield of **9** is always low, and its formation may well be due to wall-catalyzed tautomerization in some cases.

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Supporting Information Available: Computed (B-LYP/6-31G*) IR spectra for the C₇H₆ equilibrium structures (¹**1**, ³**1**, **2**, ³**3** (³A₂), ³**3** (³B₁), **4**, **5**, **6**, **7**, **9A**, **9B**, **9C**, **10**, **11**, **12** and **27**) (Table 2) (4 pages). IR spectra of **2** and **4** have also been reported in ref 39. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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