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Rearrangements of C_7H_6 Isomers: Computational Studies of the Interconversions of Bicyclo[3.2.0]hepta-1,3,6-triene, Bicyclo[3.2.0]hepta-3,6-diene-2-ylidene, Bicyclo[3.2.0]hepta-2,3,6-triene, and Cyclohepta-1,2,4,6-tetraene

Eric V. Patterson and Robert J. McMahon*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706-1396

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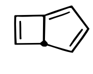
The structures of several bicyclo[3.2.0] isomers on the C_7H_6 potential energy surface, and the transition states which interconnect them, have been fully optimized using density functional theory (BLYP/6-31G*). Relative energies were determined using single-point calculations at higher levels of theory (CCSD(T), CASPT2N). These calculations show that bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**) readily undergoes ring opening to cycloheptatetraene (**4**) with a barrier of 5 kcal/mol. The rearrangement of **2** to **4** occurs without intervention of bicyclo[3.2.0]hepta-1,3,6-triene (**1**). Triene **1** is much more stable than carbene **2**, but faces a much higher barrier (35 kcal/mol) to rearrangement to cycloheptatetraene (**4**). The singlet and triplet states of carbene **2**, along with the triplet state of triene **1** and the singlet state of bicyclo[3.2.0]hepta-2,3,6-triene (**3**), lie very close in energy, ca. 55 kcal/mol higher than the singlet state of **4**. The computed transition states for the electrocyclic ring closure of cycloheptatetraene (**4**) to bicyclo[3.2.0]hepta-1,3,6-triene (**1**) and for the degenerate 1,5-sigmatropic H-shift in triene **1** occur at very similar energy. This finding provides a rationalization for the experimental observation of ^{13}C-label scrambling upon high-temperature pyrolysis of various C_7H_6 isomers. The calculated IR frequencies and intensities for **1**, ^{1}**2**, ^{3}**2**, and **3** may aid future identification of these species.

Introduction

Carbene rearrangements, particularly those occurring on the C_7H_6 potential energy surface, have long been of interest.[1−4] The ring expansion of phenylcarbene to cycloheptatetraene (**4**) has been studied extensively,[5−7] and many of the intricacies of this potential energy surface are now understood. The high-temperature ring contraction from phenylcarbene to fulvenallene and the isomeric ethynylcyclopentadienes has also been studied in some detail.[3,8,9] Bicyclo[3.2.0]hepta-1,3,6-triene (**1**) has been proposed as an intermediate in this ring-contraction mechanism (Scheme 1);[9] although **1** has been trapped, it has never been observed directly. The role of bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**) is even more elusive. Attempts to generate bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**) via photolysis of the corresponding diazo compound in an argon matrix led to the unexpected observation of cycloheptatetraene (**4**) as the sole product; no evidence was obtained for carbene **2** or triene **1** (Scheme 2).[10] While several semiempirical[11−14] and ab initio[15−21] studies have been carried out on the C_7H_6 potential energy surface, bicyclo[3.2.0]hepta-1,3,6-triene (**1**) has been investigated only once.[19] Neither bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**) nor bicyclo[3.2.0]hepta-2,3,6-triene (**3**) has been investigated computationally. We now report a detailed computational investigation that provides new insight into this portion of the C_7H_6 surface. Our results indicate that carbene **2** may possess a singlet ground state, contrary to expectation, and that carbene **2** faces a barrier of only 5 kcal/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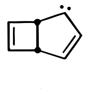
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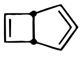
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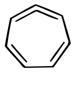
4

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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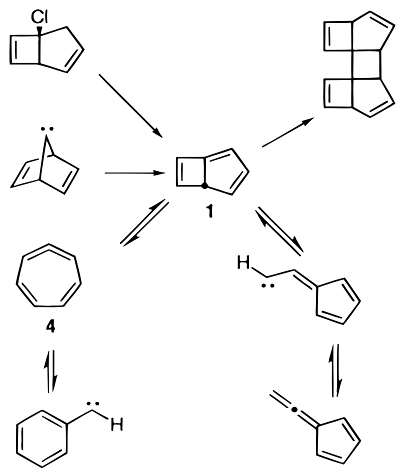
Scheme 1



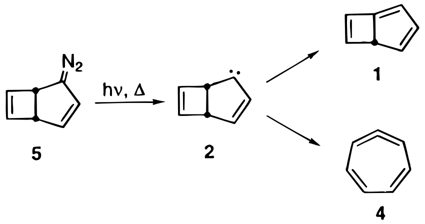
mol for ring opening to cycloheptatetraene (**4**). Computed infrared spectra for bicyclo[3.2.0]hepta-1,3,6-triene (**1**), singlet and triplet bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**), and bicyclo[3.2.0]hepta-2,3,6-triene (**3**) may aid in the future identification of these species.

Background

Breslow and co-workers generated bicyclo[3.2.0]hepta-1,3,6-triene (**1**) by dehydrohalogenation of the corresponding chloride (Scheme 1).[22] The triene itself could not be isolated, but was trapped with diphenylisobenzofuran. Bauld and co-workers established that, in the absence of a trapping agent, triene **1** dimerizes by a 2 + 2 addition across the bridgehead double bond.[23] Further trapping studies demonstrated that **1** serves as a good dienophile but a relatively poor diene in 4 + 2 cycloadditions.[23]

In 1977, Wentrup and co-workers proposed bicyclo[3.2.0]hepta-1,3,6-triene (**1**) as an intermediate in the high-temperature rearrangement of phenylcarbene to fulvenallene.[9a] Their mechanism postulates the electrocyclic ring-closure of cycloheptatrienylidene (now known to be cycloheptatetraene) to form triene **1**, followed by C−C bond homolysis and hydrogen migration to form fulvenallene (Scheme 1). The authors also proposed that triene **1** is formed by the "foiled methylene" rearrangement of 7-norbornadienylidene.[9] Brown and Jones provided firm evidence for the formation of bicyclo[3.2.0]hepta-1,3,6-triene (**1**) upon pyrolysis of a precursor to 7-norbornadienylidene by isolating the expected dimers (Scheme 1).[24]

Scheme 2



Chapman and Abelt attempted to generate bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**) by photolysis or thermolysis of the corresponding diazo compound **5**.[10] Surprisingly, they observed exclusive formation of cycloheptatetraene (**4**); they obtained no evidence for formation of either carbene **2** or triene **1**. The authors suggested two mechanisms to explain the formation of **4** (Scheme 2). In the first mechanism, decomposition of diazo compound **5** yields carbene **2**, which rapidly opens to cycloheptatetraene (**4**) because the barrier to ring opening is extremely low.[25] In the second mechanism, ring opening of the diazo compound **5** occurs concomitantly with loss of nitrogen so that cycloheptatetraene (**4**) is formed directly without intervention of carbene **2**. Both mechanisms account for the failure to observe triene **1** or carbene **2**.

Our present work undertakes to clarify some of the unresolved issues concerning bicyclo[3.2.0]hepta-1,3,6-triene (**1**) and bicyclo[3.2.0]hepta-2,6-diene-4-ylidene (**2**). Recent advances in computational hardware and software now make it possible for reliable quantum chemical calculations to be carried out on systems of this size. Our results provide a clearer understanding of this portion of the C_7H_6 potential energy surface and will aid in future attempts to observe the elusive triene **1** and carbene **2**.

Methods

Initially, we optimized the geometries of **1**−**4** at the UHF and UMP2 level[26] using the 6-31G* basis set.[27] The triplet species displayed substantial spin contamination,[28] which establishes that neither theoretical treatment (UHF or UMP2) provides reliable geometries or relative energies. We therefore turned to density functional theory. In particular, we employed Becke's gradient-corrected exchange functional[29] in

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combination with the correlation functional of Lee, Yang, and Parr[30] (commonly referred to as BLYP). This combination gives reliable geometries and harmonic frequencies when used with a good double-ζ basis set.[18,31,32] Therefore, all geometries reported here were optimized at the BLYP/6-31G* level of theory.

Transition states were located using the synchronous transit-guided quasi-Newton (STQN) method.[33] The nature of each stationary point was confirmed with harmonic frequency calculations, i.e. minima have zero imaginary frequencies, while transition states have exactly one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations[34] were carried out to ensure that each transition state smoothly connects the expected minima.

In order to obtain more reliable estimates for the relative energies of the various isomers, we carried out single-point CCSD(T) calculations[35,36] using Dunning's correlation-consistent polarized valence double-ζ (cc-pVDZ) basis set.[37] We further investigated the effect of enlarging the basis set to triple-ζ quality by performing single-point HF and MP2 calculations using Dunning's cc-pVTZ basis set.[38] For the triplets, UHF and UMP2 proved to be unreliable due to spin contamination, so we relied on energies computed using restricted open-shell methods (i.e. ROHF and ROMP2). The same could not be done for the CCSD(T) calculations, since we do not have the ability to calculate restricted open-shell CCSD(T) wave functions; therefore, the UCCSD(T) method was employed for the triplets. The choice of UCCSD(T) vs RCCSD(T) for open-shell species is not crucial.[39] The effects of enlarging the basis set from double-ζ (DZ) to triple-ζ (TZ) at the CCSD(T) level were estimated by the formula 1:[40]

$$E^{\mathrm{CCSD(T)}}_{\mathrm{estim}}(\mathrm{TZ}) = E(\mathrm{HF/TZ}) + \frac{E^{\mathrm{MP2}}_{\mathrm{corr}}(\mathrm{TZ})}{E^{\mathrm{MP2}}_{\mathrm{corr}}(\mathrm{DZ})}\, E^{\mathrm{CCSD(T)}}_{\mathrm{corr}}(\mathrm{DZ}) \quad (1)$$

where $E(\mathrm{HF/TZ})$ is the (RO)HF energy, E_{corr} are the correlation energies at the (RO)MP2 or CCSD(T) levels with the DZ or TZ basis sets, and $E^{\mathrm{CCSD(T)}}_{\mathrm{estim}}(\mathrm{TZ})$ is the estimated energy at the CCSD(T)/cc-pVTZ level. This energy, after correction for zero-point energies at the BLYP/6-31G* level, serves as the basis for our discussion.[41]

Since the CCSD(T) method is based to some degree on perturbation theory, it provides reliable results only when the zero-order reference wave function is of good quality. In particular, strong nondynamic correlation effects must be absent. To check this, we examined the T_1 diagnostic for the CCSD wave function[42] which is a measure of how much reorganization occurs upon going from the HF reference to the final CCSD wave function. All T_1 diagnostics obtained from the CCSD(T) calculations (Table 1) are within acceptable limits,[43] suggesting that the single-reference CCSD(T) results are reliable.

CASSCF, the multireference analog of HF theory, accounts for nondynamic electron correlation. We performed single-point CASSCF calculations[44] with an active space of eight electrons in eight orbitals on the BLYP/6-31G* geometries.[45] It is also important to account for dynamic electron correlation when starting with a CASSCF reference.[46] We treated multireference dynamic electron correlation by utilizing the CASPT2N method.[47]

In order to compute accurate singlet−triplet energy gaps, the computational method must treat both states equally well and account for all important electron correlation effects. It has generally been accepted that a two-configuration wave function is necessary to adequately describe a singlet carbene. In principle, it is therefore necessary to include dynamic correlation starting from the multireference wave function (see above).[46] Recent work, however, demonstrates that standard single-reference CCSD(T)[48] and density functional[49] methods reproduce singlet−triplet gaps from high-level multireference techniques and experiment remarkably well.

All single-reference calculations were performed using Gaussian 94,[50] while the multireference calculations were performed using MOLCAS-3.[51]

Results

Conceptually, the key species of interest in this study can all be considered as being derived from C_7H_7 radical **A** by removal of one hydrogen atom. Removal of a

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[36] Extensive applications of the CCSD(T) method have demonstrated that this method consistently yields results very close to those obtained by full configuration interaction (cf.: Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic, Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995).

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$$E^{\mathrm{CCSD(T)}}_{\mathrm{estim}}(\mathrm{TZ}) = E^{\mathrm{CCSD(T)}}(\mathrm{DZ}) + [E^{\mathrm{MP2}}(\mathrm{TZ}) - E^{\mathrm{MP2}}(\mathrm{DZ})]$$

[41] The full complement of single-point energies for all species is available as Supporting Information.

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[43] For closed-shell systems, it has been suggested that a T_1 value less than 0.02 indicates that the system is well described by a single-reference wave function. However, for open-shell species, values as high as 0.04 may be acceptable (see Taylor, P. R. In *Lecture Notes in Quantum Chemistry II*; Roos, B. O., Ed.; Springer-Verlag: Berlin, 1994; pp 125−202).

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[45] In order to allow proper comparison of total and relative energies, a consistent active space size of CAS(8,8) was chosen for all molecules. In some instances, the choice of four occupied orbitals to include in the active space was straightforward. In other instances, the choice of the fourth orbital was not obvious. In the latter cases, the fourth orbital was selected automatically by the MOLCAS program. The appropriateness of the chosen orbital was checked in the case of triene ^{1}**1**, and no better set of orbitals could be found.

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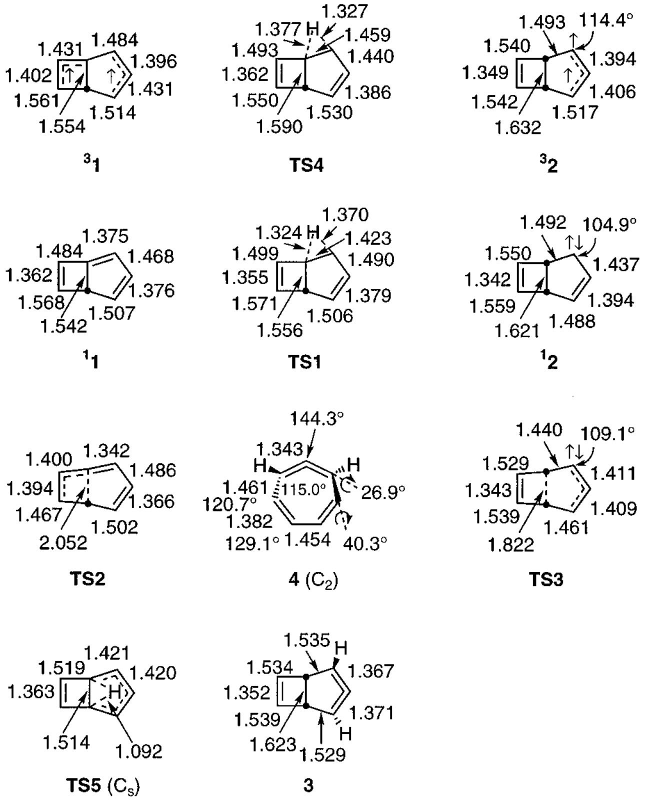
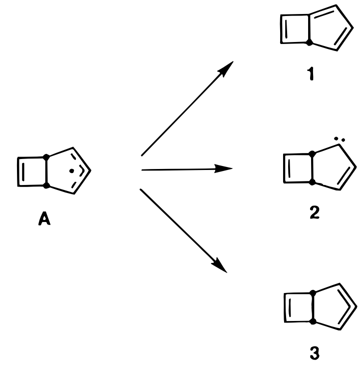


Figure 1. Important geometrical parameters of C_7H_6 structures considered in the present study, BLYP/6-31G* optimized.

Scheme 3



hydrogen atom from C1 affords triene **1**, from C2 affords carbene **2**, and from C3 affords allene **3** (Scheme 3). Figure 1 presents important geometrical parameters of all stationary points, while Figure 2 illustrates the structures using ball-and-stick renditions. Table 1 lists the relative energies of these species at the BLYP/6-31G* geometries as obtained by the various single-reference methods (BLYP, CCSD(T)(est.)) and multireference methods (CAS(8,8), CASPT2N), along with the zero-point vibrational energies and various computational diagnostics. Table 2 lists the harmonic frequencies calculated at the BLYP/6-31G* level for ^{1}**1**, ^{1}**2**, ^{3}**2**, and **3**. Finally, the potential energy surface connecting the C_7H_6 isomers studied in this work is presented in Figure 3.

Discussion

Bicyclo[3.2.0]hepta-1,3,6-triene (1). The strain in triene ^{1}**1** is reflected in the slightly elongated single bond between C5 and C6 (1.568 Å) compared to what would be expected for a normal single bond (1.51 Å),[52] and in the marked deviation from planarity at C1 (sum of angles = 336.8°). The dihedral angles formed between the two rings at each bridgehead carbon are 141° (C7−C1−C5−C2) and 127° (C6−C1−C5−C4). Despite the significant degree of pyramidalization, the double bond at the bridgehead is not elongated and the double bonds in ^{1}**1** are clearly localized. Triene ^{1}**1** lies only 9 kcal/mol higher in energy than cycloheptatetraene (**4**). The computed infrared frequencies and intensities for bicyclo[3.2.0]hepta-1,3,6-triene (^{1}**1**) are presented in Table 2.

Since bicyclo[3.2.0]hepta-1,3,6-triene (^{1}**1**) is a highly strained type-B bridgehead olefin,[53,54] we sought to examine whether a low-lying triplet state exists. Accordingly, we optimized triplet bicyclo[3.2.0]hepta-1,3,6-triene (^{3}**1**) at the BLYP/6-31G* level. The dihedral angles at the bridgehead carbons are virtually identical in the singlet and the triplet. The singlet is best described as a triene with a strained double bond, while the triplet is best described as having two noninteracting allyl radicals, one in each ring (Figure 1). At the CCSD(T)/TZ-(estim)//BLYP/6-31G* + ZPVE level ^{3}**1** lies 42.7 kcal/mol above ^{1}**1**. Compared to other conjugated hydrocarbons of comparable size, this is indeed a low triplet energy.[55] Thus, the strain inherent in the ground state of triene **1** manifests itself in terms of a rather low triplet energy. According to Wentrup's recent calculations,[19] ^{1}**1** thermally rearranges to spiro[2.4]heptatriene with a barrier of ca. 40 kcal/mol and to fulvenallene with a barrier of ca. 47 kcal/mol. Our results suggest that, under the conditions of these rearrangements (>600 °C), ^{3}**1** will also be thermally accessible.

Bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (2). The geometries of ^{1}**2** and ^{3}**2** display only small differences. The carbene angle in ^{1}**2** is 104.9°, while in ^{3}**2** it is 114.4°. In the case of ^{1}**2**, the dihedral angles which define the ring fusion are rather different (112° for C7−C1−C5−C2 and 120° for C6−C1−C5−C2), while in ^{3}**2** these angles are equivalent (117°). In both cases, delocalization of the π bond in the five-membered ring is evident. This effect is more pronounced in ^{3}**2**, which clearly shows the (nearly) equivalent bond lengths expected of an allyl radical. Both electronic states exhibit a C1−C5 bond which is significantly longer (0.08−0.09 Å) than that in ^{1}**1**. The computed infrared frequencies and intensities for both ^{1}**2** and ^{3}**2** are presented in Table 2. In general, there are no remarkable features. The triplet shows a strong absorption at 1256 cm^{-1} which is absent in the singlet, and also from triene ^{1}**1**. The spectra of ^{1}**1**, ^{1}**2**, and ^{3}**2** show enough unique features to make spectroscopic differentiation feasible.

In the case of bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**), the singlet−triplet gap proves to be very sensitive to the level of theory employed. At our best single-reference level (CCSD(T)/TZ (estim)//BLYP/6-31G* + ZPVE) the *singlet* is favored by 4.4 kcal/mol. This number is reproduced well at the BLYP/6-31G* level, which gives

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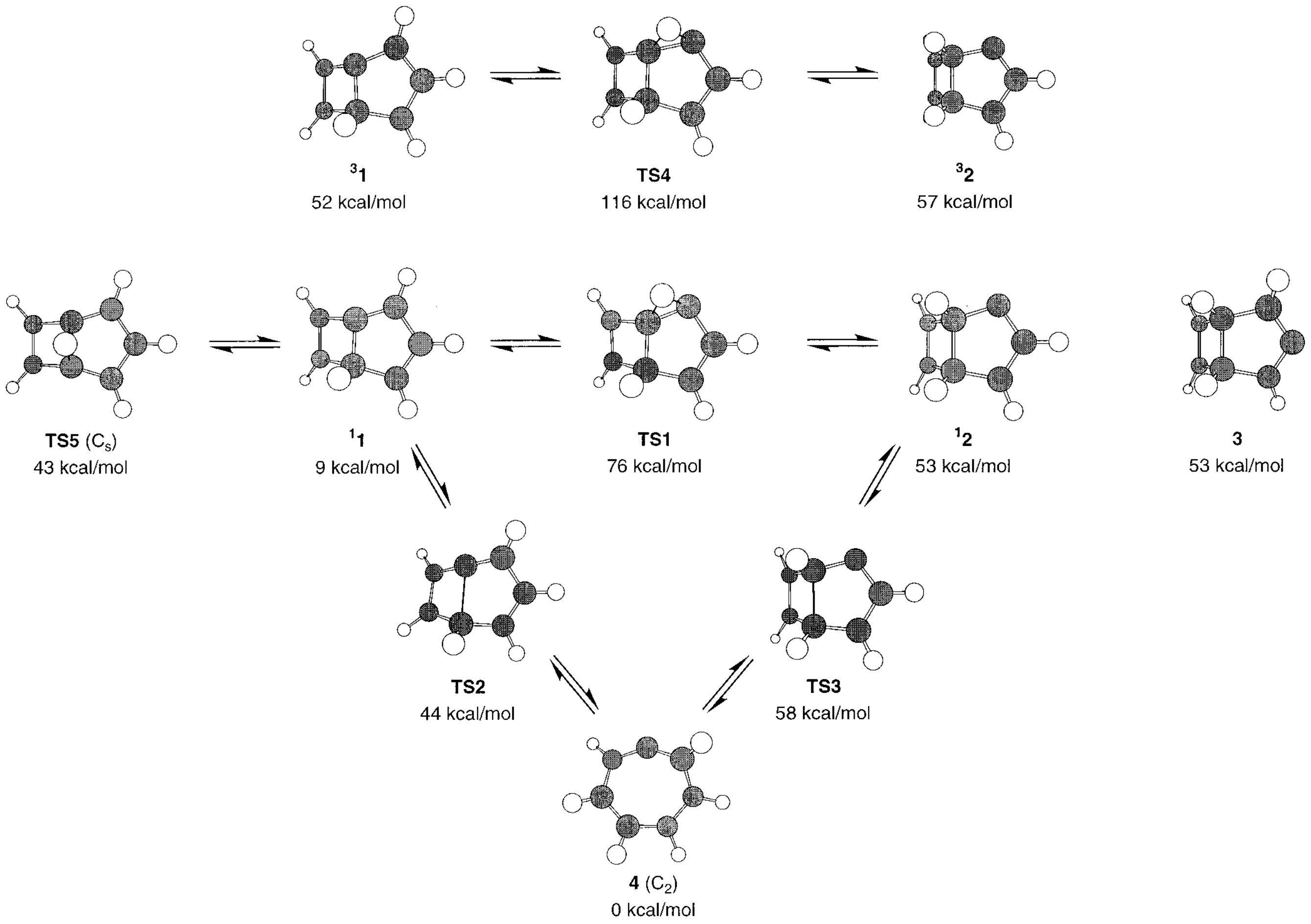

Figure 2. Ball-and-stick models of the C_7H_6 structures presented in Figure 1.

Table 1. Relative Energies (kcal/mol) and Diagnostic Information for Various Single-Point Energy Calculations at BLYP/6-31G* Geometries

species	BLYP/6-31G*	CCSD(T)/TZ (estim)[a]	T_1[b]	CAS(8,8)/DZ[c]	CAS weightings[d]	CASPT2N/DZ[e]	CASPT2N weighting[f]	ZPE[g]
4	−270.120752	−269.748478	0.0128	−268.584613	81.6, 2.0	−269.406573	77.4	63.09
^{1}**1**	14.84	9.16	0.0118	17.14	84.9, 3.2	11.57	77.3	−0.12
^{3}**1**	55.24	53.99	0.036	26.13	82.5, 1.5	54.70	78.5	−2.25
^{1}**2**	61.36	54.15	0.0193	61.21	86.6, 4.3	61.38	77.5	−1.51
^{3}**2**	64.66	58.23	0.0286	56.63	88.2, 1.8	56.49	77.1	−1.22
3	63.81	54.66	0.031	58.26	78.4, 8.9	57.68	77.2	−1.22
TS1	87.15	80.44	0.0154	96.90	87.5, 1.8	84.59	76.9	−3.95
TS2	46.27	46.05	0.0141	55.52	89.3, 3.1	43.80	76.6	−1.86
TS3	63.15	60.10	0.0237	72.34	84.5, 4.7	64.98	77.0	−2.14
TS4	121.58	120.54	0.041	103.20	83.9, 2.1	118.91	77.7	−5.04
TS5	48.69	45.91	0.011					−2.53

[a] Estimated using formula 1 in text. [b] T_1 diagnostic from CCSD(T)/DZ calculations. See text for discussion. [c] Calculations with Dunning's cc-pVDZ basis set; absolute energy in hartrees given for cycloheptatetraene (**4**), which serves as the reference. [d] Weightings, in percent, for the ground configuration and the largest contributing excited configuration in the CASSCF wave function. [e] Calculations with Dunning's cc-pVDZ basis set, using the CAS(8,8) wave function as the reference; absolute energy in hartrees given for cycloheptatetraene (**4**), which serves as the reference. [f] Weighting, in percent, of the CAS(8,8) reference in the CASPT2N wave function. See text for discussion. [g] Relative zero-point energies (ZPE) in kcal/mol at the BLYP/6-31G* level; the absolute value in kcal/mol is given for **4**, which serves as the reference.

the singlet 3.6 kcal/mol lower than the triplet. Upon moving to a multireference treatment, the *triplet* becomes the ground state by 4.3 kcal/mol (CAS(8,8)/DZ//BLYP/6-31G* + ZPVE). Inclusion of the CASPT2N dynamic correlation correction has little effect, giving the triplet 4.6 kcal/mol lower than the singlet. It is particularly troubling that the CASPT2N and CCSD(T) results are so different. One possible explanation is the known tendency of CASPT2N to overstabilize open-shell species relative to their closed-shell counterparts unless a CASSCF reference is used which includes all valence electrons.[47,48] With a system as large as C_7H_6, a full valence active space is not possible at the current time.

The possibility of a singlet ground state for carbene **2** is contrary to our initial expectation. In assessing the ground state multiplicity of **2**, we considered the following factors: effect of a vinyl substituent, effect of an alkyl substituent, and effect of the ring size.[56] Vinyl substituents favor a triplet ground state, and vinyl carbene itself

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Table 2. Computed Infrared Frequencies (cm^{-1}) and Intensities (km/mol)[a]

^{1}**1**	^{1}**2**	^{3}**2**	**3**
236 (5)	224 (7)	239 (1)	238 (0)
302 (3)	248 (2)	254 (2)	278 (3)
445 (8)	388 (7)	432 (3)	442 (7)
536 (10)	442 (39)	539 (9)	464 (13)
653 (32)	652 (7)	608 (20)	538 (72)
703 (16)	663 (6)	645 (8)	679 (8)
711 (25)	717 (41)	679 (18)	701 (32)
748 (17)	736 (16)	733 (30)	739 (25)
814 (17)	812 (6)	810 (10)	775 (54)
825 (21)	837 (2)	841 (0)	824 (9)
842 (7)	868 (15)	857 (7)	852 (3)
881 (19)	885 (1)	877 (8)	865 (5)
898 (4)	923 (8)	900 (0)	904 (3)
917 (9)	937 (1)	932 (6)	924 (1)
986 (7)	961 (2)	948 (3)	950 (2)
1018 (4)	992 (17)	1004 (0)	992 (5)
1032 (2)	1018 (1)	1034 (3)	1037 (1)
1052 (2)	1069 (3)	1058 (1)	1108 (3)
1090 (4)	1080 (3)	1109 (3)	1141 (4)
1131 (4)	1111 (1)	1141 (4)	1150 (7)
1226 (3)	1130 (10)	1214 (1)	1166 (2)
1247 (7)	1188 (6)	1226 (0)	1197 (5)
1265 (2)	1219 (9)	1239 (2)	1244 (1)
1350 (5)	1249 (3)	1256 (16)	1261 (17)
1467 (1)	1355 (9)	1335 (3)	1379 (23)
1510 (5)	1420 (1)	1392 (2)	1518 (10)
1565 (5)	1598 (7)	1586 (6)	1569 (1)
2959 (22)	2934 (37)	2950 (33)	2950 (54)
3102 (17)	2986 (8)	2969 (47)	2969 (24)
3126 (1)	3066 (19)	3097 (17)	3084 (19)
3126 (38)	3091 (47)	3115 (10)	3094 (42)
3134 (23)	3117 (12)	3129 (43)	3104 (19)
3154 (22)	3156 (21)	3132 (15)	3140 (27)

[a] BLYP/6-31G*, unscaled.[32]

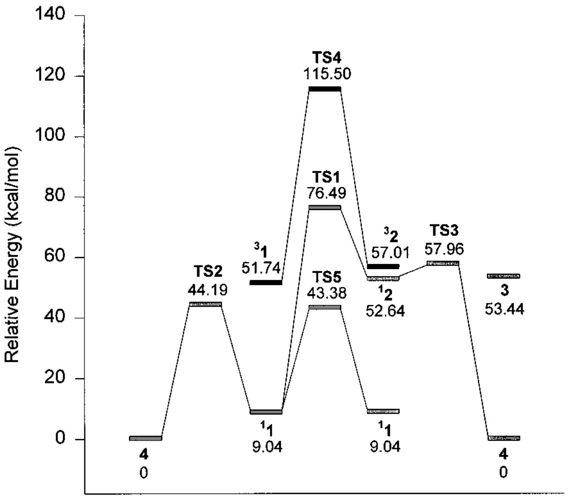

Figure 3. Potential energy surface for the C_7H_6 isomers considered in the present study. Energies shown are at the CCSD(T)/TZ (estim)//BLYP/6-31G* + ZPVE level.

displays a triplet ground state. High-level ab inito calculations place the singlet−triplet gap of vinylcarbene at 12 kcal/mol, using a multireference configuration interaction method.[57] Conversely, alkyl substituents stabilize the singlet state by hyperconjugation. Using multireference configuration interaction, Matzinger and Fülscher showed that the effect of methyl substitution is approximately additive for the series methylene (singlet−triplet gap of 9.5 kcal/mol), methylcarbene (3.8 kcal/mol), dimethylcarbene (−0.9 kcal/mol).[48] Indeed, recent studies establish that several dialkyl-substituted carbenes possess singlet ground states.[58−60] The effect of ring size plays an important role in influencing ground state multiplicity. In a constrained ring, the small bond angle may cause the singlet state to drop below the triplet in energy. The three-membered ring carbenes cyclopropylidene and cyclopropenylidene both exhibit singlet ground states.[56,57] Nevertheless, various five-membered ring carbenes (cyclopentadienylidene, benzannelated cyclopentadienylidenes,[61] α-keto carbenes[62−64]) display triplet ESR signals, indicating that the triplet is either the ground state or very close in energy to the ground state. Cyclopentadienylidene, which can be considered a divinylcarbene, possesses a triplet ground state,[56] with a singlet−triplet gap computed to be 6.3 kcal/mol at the CISD+Q level of theory.[65] It is difficult to draw a direct analogy between these systems and bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**2**); however we anticipate that the singlet−triplet gap for **2** should be smaller than that for cyclopentadienylidene. This is borne out by our calculations.

Bicyclo[3.2.0]hepta-2,3,6-triene (3). The geometry of **3** reflects that of a strained, cyclic allene.[66] The five-membered ring is significantly twisted (Figure 2). The dihedral angles that define the ring fusion are 127° (C7−C1−C5−C2) and 107° (C6−C1−C5−C4). The *cis* ring fusion destroys the inherent C_2 symmetry of the allene moiety. Consequently, the C−C bond lengths of the allene are slightly different (1.367 and 1.371 Å; Figure 1), and the twisting about the allene is slightly unsymmetrical (HCCC dihedral angles of 22.8° and 27.9°; Figure 2). Both of these observations are in good agreement with results obtained for cyclopenta-1,2-diene.[67] The infrared stretching frequency for the allene moiety is predicted to occur at remarkably low frequency (1518 cm^{-1}) when compared to other strained allenes (e.g. 1,2-cyclohexadiene, 1886 cm^{-1};[68] cyclohepta-1,2,4,6-tetraene (**4**), 1810 cm^{-1} [7,18]). Allene **3** lies significantly higher in energy (53.4 kcal/mol) than cycloheptatetraene (**4**), but only 0.8 kcal/mol higher in energy than singlet bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (^{1}**2**) at the CCSD(T)/TZ(est.)//BLYP/6-31G* + ZPVE level.

Cyclohepta-1,2,4,6-tetraene (4). This species has been treated previously,[18−20] and is included here for the purposes of comparison. Cycloheptatetraene adopts a

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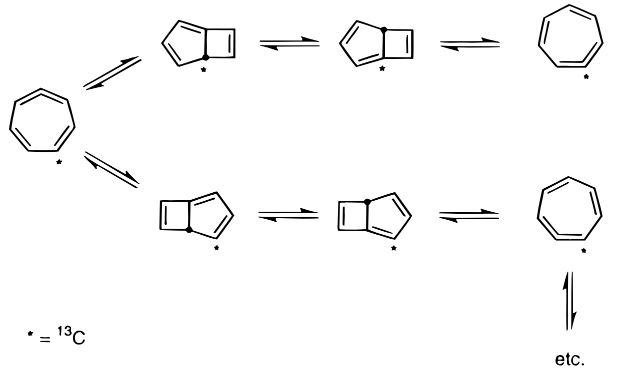
Scheme 4



chiral, C_2 structure and is the lowest energy isomer of those considered in this study.[69]

The Potential Energy Surface

Figure 3 presents our computational results for this portion of the C_7H_6 energy surface. These results provide a framework for interpreting earlier experimental observations. The energy barrier between cycloheptatetraene (**4**) and bicyclo[3.2.0]hepta-1,3,6-triene (**1**) separates the rearrangement pathways of C_7H_6 isomers into a low temperature manifold and a high-temperature manifold.[1−4] In the low-temperature manifold, phenylcarbene and cycloheptatetraene (**4**) equilibrate via reversible C−C bond migration reactions. Isotopic labeling experiments establish that H-migration reactions do not occur. The "unique" C-atom in phenylcarbene and in cycloheptatetraene (i.e. the single carbon atom that does not bear hydrogen) remains unique while all other positions undergo label scrambling. In the high-temperature manifold, H-migration reactions afford further label scrambling. Our calculations predict a barrier height of 44 kcal/mol (**TS2**) for the electrocyclic closure of cycloheptatetraene (**4**) to bicyclo[3.2.0]hepta-1,3,6-triene (**1**) (Figure 3), in good agreement with the recent report by Wong and Wentrup.[19,70] Interestingly, the transition state for the degenerate 1,5-sigmatropic H-shift in triene ^{1}**1** (**TS5**, 43 kcal/mol) occurs at a very similar energy.[71−73] In an isotopically labeled system, the 1,5-sigmatropic H-shift in triene **1** provides a mechanism for equilibrating the unique C-atom of cycloheptatetraene (**4**) with all other positions (Scheme 4).[3] Given the similar energies for **TS2** and **TS5**, label scrambling into the unique position will inevitably occur once the system crosses into the high-temperature rearrangement manifold.

The relatively high barrier (35 kcal/mol) for the ring opening of triene **1** to cycloheptatetraene (**4**) is consistent with the fact that triene **1** dimerizes in the gas phase at relatively "low temperatures" (300 °C) or in solution.[24] The barrier for the ring opening of singlet bicyclo[3.2.0]hepta-3,6-dien-2-ylidene (^{1}**2**) (5 kcal/mol) is much lower than that for the opening of triene **1**. Interestingly, the barrier for the 1,2-hydrogen migration in singlet carbene ^{1}**2** to yield triene **1** is exceptionally high (24 kcal/mol) by comparison with 1,2-hydrogen migrations in other singlet carbenes.[74] Thus, our calculations predict that hydrogen migration will not compete with ring opening in singlet carbene ^{1}**2**. This interpretation is consistent with the observations of Chapman and Abelt,[10] namely, that photolysis of 2-diazobicyclo[3.2.0]hepta-3,6-diene (**5**) yields exclusively cycloheptatetraene (**4**). Of course, our calculations do not bear on the possibility of a direct photochemical rearrangement of the excited state of **5** to **4** without intervention of carbene **2**.[75]

Given the low triplet energy of bicyclo[3.2.0]hepta-1,3,6-triene (**1**), we investigated the possibility that the 1,2-hydrogen shift might occur from the triplet state of carbene **2** to yield the triplet state of triene **1**. The transition structure (**TS4**) interconnecting ^{3}**2** and ^{3}**1** is quite similar to its counterpart on the singlet surface (**TS1**) in terms of geometry, but dramatically different in terms of energy. The barrier for the rearrangement of **2** to **1** is 58.5 kcal/mol on the triplet surface and 23.9 kcal/mol on the singlet surface.

Comments on Different Computational Methods

Our results demonstrate that density functional methods, and BLYP in particular, can provide reliable insight into the structures and relative energies of carbene systems. In terms of computational efficiency, DFT calculations are comparable to UMP2 methods; in terms of accuracy, DFT calculations are vastly superior. A small drawback of the DFT methods employed in this study concerns the erroneous overstabilization of allenic structures.[76] A quick scan of the total energies computed for cycloheptatetraene (**4**) and of the relative energies of triene **1** (Table 1 and Table S1 of Supporting Information) reveals that the BLYP/6-31G* energy for cycloheptatetraene (**4**) is anomalously low. Applying a correction of 6 kcal/mol to the BLYP/6-31G* energy for cycloheptatetraene (**4**) brings the BLYP/6-31G* relative energies for ^{1}**1**, ^{1}**2**, and ^{3}**2** into very good agreement with the relative energies obtained for these species at the CCSD(T)/TZ (estim) level.[70]

For the transition states, the BLYP and CCSD(T) relative energies show poorer agreement. The BLYP

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[69] We note some differences between the structure and energy for cycloheptatetraene (**4**) reported here and in our earlier report due to the fact that the latter was optimized using Gausian 92/DFT. The default grid used for density functional methods in Gaussian 94 is finer than the grid used in Gaussian 92/DFT. Using the defaults in both packages will result in minor differences in optimized geometries and energies.

[70] In Wong and Wentrup's recent study, BLYP calculations provided consistently higher energies for numerous C_7H_6 isomers, relative to cycloheptatetraene, than G2 calculations. We speculate that this situation may arise because the BLYP energy of cycloheptatetraene is anomalously low.

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functional performs particularly poorly for **TS3**.[77] Here, the BLYP/6-31G* + ZPVE energies put **TS3** *below* **^{1}2** by 1 kcal/mol. This result highlights the importance of performing high-level single-point calculations, whenever possible, to produce a reliable picture of the potential energy surface.

The appropriateness of a single-reference treatment vs a multireference treatment is not completely clear for the molecules in this study. All T_1 diagnostics obtained from the CCSD(T) calculations (Table 1) are within acceptable limits,[43] suggesting that the single-reference CCSD(T) results are reliable. On the other hand, several of the species show contributions from low-lying excited configurations to the CASSCF wave function in the range of 2−5% (Table 1), indicating that these species may benefit from a multireference treatment. The reference weight of the CASSCF wave function in the CASPT2N calculation is 77% in every case (Table 1). Ideally, the reference weighting should be as large as possible. Examination of the CASPT2N diagnostic output reveals several important configurations which are not explicitly treated in the active space for all isomers. This situation is potentially remedied by enlarging the active space.[78] These two facts establish that the CASPT2N results are not converged with respect to the CASSCF active space. Given the fact that the T_1 diagnostics of the CCSD(T) calculations are acceptable and that the CASSCF calculations are not converged with respect to the size of the active space, we consider the CCSD(T) results to be the more reliable.

Not surprisingly, singlet bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**^{1}2**) represents the most difficult computational challenge. Single-reference and multireference relative energies for **^{1}2** differ by 7 kcal/mol (Table 1). Moreover, single-reference and multireference treatments for **^{1}2** and **^{3}2** provide different predictions for the ground state multiplicity of the carbene. A clear-cut resolution of these issues will require further investigation at very sophisticated levels of ab initio theory.

Summary

The computed barrier for ring opening of singlet bicyclo[3.2.0]hepta-1,3,6-triene (**^{1}1**) to cycloheptatetraene (**4**) (35 kcal/mol) is significantly higher than the barrier for ring opening of singlet bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**^{1}2**) to cycloheptatetraene (**4**) (5 kcal/mol). The barrier separating carbene **^{1}2** and triene **^{1}1** is also rather high (24 kcal/mol). These results suggest that the rearrangement of carbene **^{1}2** to cycloheptatetraene (**4**) occurs without intervention of triene **^{1}1**. The transition state for the electrocyclic ring closure of cycloheptatetraene (**4**) to triene **^{1}1** (44 kcal/mol) is very close in energy to the transition state for the degenerate 1,5-sigmatropic H-shift in triene **^{1}1** (43 kcal/mol). This result provides a possible explanation for the ^{13}C-label scrambling that is observed upon high-temperature pyrolysis of C_7H_6 isomers. Singlet bicyclo[3.2.0]hepta-1,3,6-triene (**^{1}1**) lies 9 kcal/mol higher in energy than cycloheptatetraene (**4**), while triplet bicyclo[3.2.0]hepta-1,3,6-triene (**^{3}1**), bicyclo[3.2.0]hepta-3,6-diene-2-ylidene (**^{1}2** and **^{3}2**), and bicyclo[3.2.0]hepta-2,3,6-triene (**3**) lie ca. 52−57 kcal/mol above **4**. The singlet−triplet gap of carbene **2** is 4 kcal/mol in favor of the *singlet* at CCSD(T), yet 5 kcal/mol in favor of the *triplet* at CASPT2N. At best, we can note that the gap is sensitive to the level of theory.

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Supporting Information Available: Table of relative energies for all species computed by various methods at BLYP/6-31G* geometries. Tables of cartesian coordinates for all species computed using BLYP/6-31G* (5 pages). 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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(77) For examples that illustrate the limitations of DFT methods in computing transition states, see: (a) Gronert, S.; Merrill G. L.; Kass, S. R. *J. Org. Chem.* **1995**, *60*, 488. (b) Johnson, B. G. *Chem. Phys. Lett.* **1994**, *221*, 100.

(78) Roos, B. O.; Andersson, K. *Chem. Phys. Lett.* **1995**, *245*, 215−223.